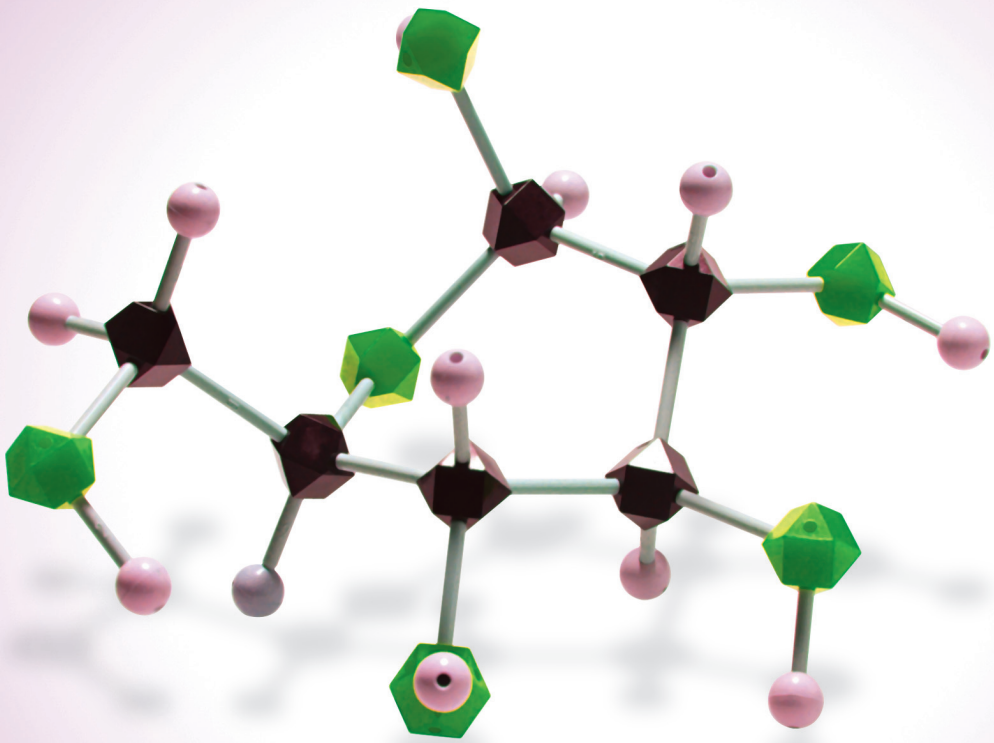
Basic Concepts of ORGANIC CHEMISTRY

For Competitive Examinations



D. N. Singh

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PEARSON

BASIC CONCEPTS OF ORGANIC CHEMISTRY

D. N. Singh
(M.Sc., Ph.D)
Formerly, Reader in Chemistry
P.G.M.S. College, Motihari.
(B.R. Ambedkar Bihar University Muzaffarpur)

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Preface

This book is based on lectures prepared for students appearing in engineering and medical entrance examinations. It is also useful for those who have opted for the Chemistry (Honours) course. Although it is by no means a comprehensive text, it covers the principles of the subject in a lucid manner to enable students to understand easily.

Purpose of the Book

There are excellent books on organic chemistry easily available in the market. Prominent among these are by Morrison and Boyd, Jerry March, Roberts and Caserio, Cram-Hammond, Finar and Pine. However, most of the students do not find these text-books easy to use during the short period of their preparations. Keeping this in mind, the lectures were delivered to provide students with relevant standard materials of organic chemistry.

Organization of the Book

The book has 22 chapters. Chapters 1–5 deal with the basic principles needed to understand organic chemistry. Chapter 6 is on name reactions. Chapter 7 is devoted to benzene, aromaticity and chemistry of benzene derivatives. A separate chapter is given on ring formation. Chapters 9–16 discuss chemistry of different functional groups. Chapter 17 is on carbohydrates, Chapter 18 is on amino acids, proteins and nucleic acids and Chapter 19 is on organic polymers.

Problems are categorized into medium and complex levels, and these are given at the end of the book with their solutions.

I thank the following people during the writing of this book:

- Several of my colleagues for their suggestions and feedback on the manuscript.
- My family members for providing encouragement.
- Mr Lalit Kumar Gupta for typing the entire manuscript.

I have tried my best to ensure that there are no errors in this book. However, suggestions for improving the text are welcome.

Finally, I hope that those who read this book will utilize their knowledge carefully, honestly and responsibly for the benefit of all who come after.

D. N. Singh

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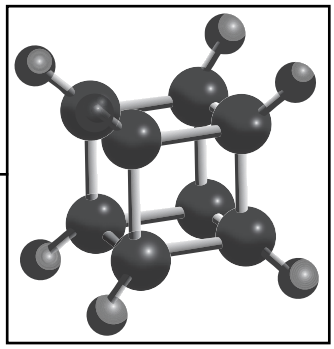
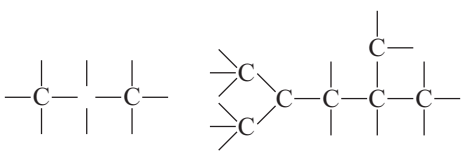
CHAPTER 1



Organic Chemistry

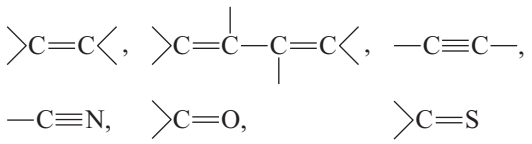
The chemistry of carbon and hydrogen compounds, except CO_2, CO, carbonates (CO_3^{-2}) and bicarbonates (HCO_3^-), is called 'Organic Chemistry'. In addition to C and H, other elements, such as N, O, P, S and As, and metals may also be present in an organic compound. The organic compounds containing metals are called 'Organometallic Compounds'. They have M–C bond. For example, MeLi, Bu_4Sn, RMgX and Et_4Pb. Many organometallic compounds have become important industrially, medicinally, etc. The number of organic compounds far exceeds the total number of compounds formed by elements other than carbon. The vast number of organic compounds is due to some special properties associated with carbon. They are

1. High catenation: The property of self-linking is called 'Catenation'. It depends on the bond energy. The C–C bond energy is high (~83kcal/mole); hence, carbon has high catenation property.
2. The ability of carbon to form variety of chains, i.e., straight and branched chains.



3. Carbon can also form ring compounds.

4. Carbon can form multiple bonds with itself as well as with the heteroatoms (N, O, P, S, etc.).



The nature of bonds in the organic compounds is mainly covalent and the carbon in them is always tetravalent. It can achieve tetravalency in different ways. We will return to this topic later.

The produces of chemical technology (pesticides, herbicides, plastics, synthetic drugs, etc.) serve human welfare to a large extent. However, it is now realized that our environment cannot accommodate all the products that are being added to it without decomposition. The grave consequences of a polluted environment can only be avoided by wise application of the chemical knowledge.

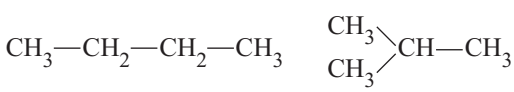
CLASSIFICATION OF ORGANIC COMPOUNDS

The chemistry of organic compounds is most systematic and depends on the class of the compound. So, classification of the organic compounds is the first step towards their study.

Carbon forms the basic skeleton of every organic compound. On this basis, the compounds are broadly divided into two groups:

1. Aliphatic or open-chain compounds: In aliphatic compounds, carbon may form either straight or branched chains. The word 'Aliphatic' is derived from the Greek word 'Aliphos' meaning fat. Some of the compounds of this class were initially obtained from fat and so they were called aliphatic.

(Straight Chain) (Branched Chain)

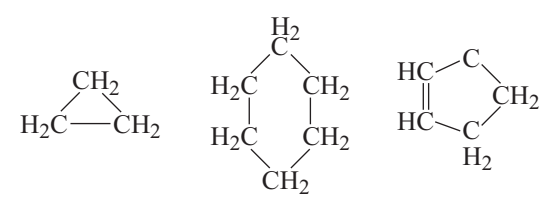


(*n*-Butane) (*iso*-Butane)

2. Cyclic or closed-chain compounds: In such compounds, carbon forms a ring. This class is further divided into two groups:

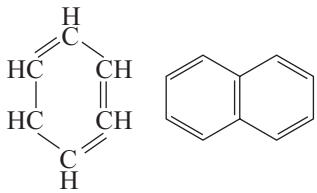
(a) Carbocyclic or homocyclic: The compounds of this class contain only carbon atoms in the ring. Carbocyclic compounds are further divided into two groups:

(i) Alicyclic compounds: Compounds of this class have properties similar to the aliphatic compounds.



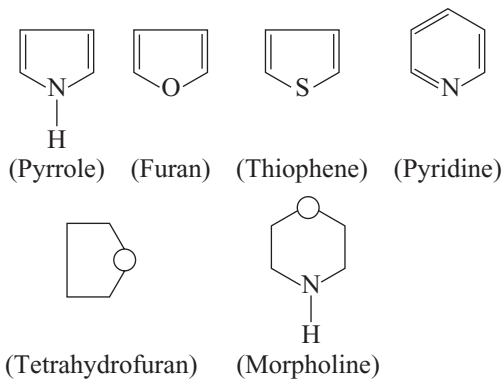
(Cyclopropane) (Cyclohexane) (Cyclopentene)

(ii) Aromatic compounds: The word 'Aromatic' is derived from the Greek word 'Aroma' meaning 'Fragrant Smell'. Compounds of this class possess specific odour and so they are called aromatic. The name is still in use. Aromatic compounds contain alternate single and double bonds in their structure. It imparts special stability to such compounds that is termed as 'Aromaticity'. We will return to this with some more details later.



(Benzene) (Napthalene)

(b) Heterocyclic: The word 'Hetero' means different. Therefore, organic cyclic compounds containing other polyvalent atoms (N, O, S, etc.) in the ring are called 'Heterocyclic' compounds.



(Pyrrole) (Furan) (Thiophene) (Pyridine)

(Tetrahydrofuran) (Morpholine)

HYDROCARBONS

Organic compounds which contain only carbon and hydrogen are called 'Hydrocarbons'. They are found in nature in abundance in the form of petroleum, natural gas and coal. Hydrocarbons can be divided into three main groups: open chain or aliphatic or acyclic hydrocarbons, alicyclic hydrocarbons and aromatic hydrocarbons.

Acyclic Hydrocarbons

Acyclic hydrocarbons contain carbon atoms bonded together in the form of linear or branched chains. They are of three types: alkanes, alkenes and alkynes.

Alkanes

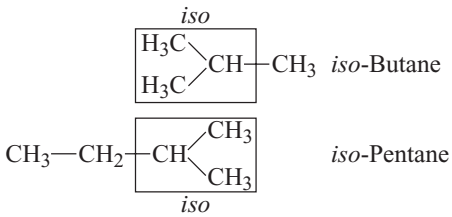
The general formula of alkanes is C_nH_{2n+2} where $n = 1, 2, 3$, etc. They are also called saturated hydrocarbons or paraffins (paraffins from the word parum that means less and affins that means affinity). Alkanes contain only single bond (or σ bond) between carbon and carbon. Carbon atoms may be present in the form of a linear or a branched chain in alkanes.

Types of chains The different types of chains are as follows:

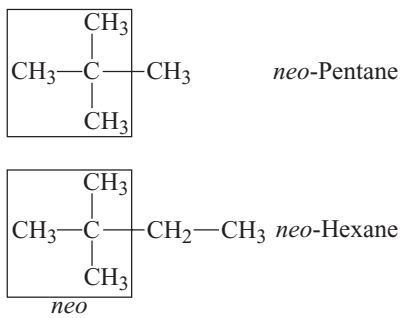
1. Normal chain (*n*-chain): Alkanes in which carbon atoms are joined linearly are called normal-chain hydrocarbons. In such alkanes, none of the carbon contains less than two hydrogen atoms or is joined with more than two carbon atoms.

$$CH_3–CH_2–CH_2–CH_3 \quad (n\text{-butane})$$
$$CH_3–CH_2–CH_2–CH_2–CH_3 \quad (n\text{-pentane})$$

2. *Iso*-chain: In *iso*-chain, carbon atom is joined with two methyl groups at either of the terminals.

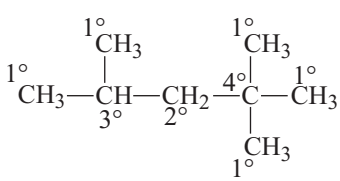


3. *Neo*-chain: A hydrocarbon chain in which one C atom is joined to three methyl groups is called a *neo*-chain.



Nature of carbon atoms Four types of carbon atoms may be present in a chain.

1. Primary carbon (1°): The carbon that is joined with one carbon and three hydrogen atoms is called a primary carbon.
2. Secondary carbon (2°): The carbon that is joined to two carbon atoms (and two hydrogen atoms) is called a secondary carbon.
3. Tertiary carbon (3°): The carbon that is joined with three carbon atoms and one hydrogen atom is called a tertiary carbon.
4. Quaternary carbon (4°): The carbon that is joined to four carbon atoms only is called a quaternary carbon.



Alkyl groups When an H atom is removed from an alkane, an alkyl group is formed.

$$\text{Alkane-H} = \text{alkyl group}$$

Alkyl groups are named by replacing 'ane' of the hydrocarbon by 'yl'.

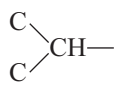
$$\underset{\text{Methane}}{CH_4—H} \longrightarrow \underset{\text{Methyl}}{CH_3—}$$

$$\underset{\text{Ethane}}{CH_3—CH_3—H} \longrightarrow \underset{\text{Ethyl}}{CH_3—CH_2—}$$

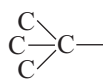
Thus, methane and ethane can form only one alkyl group each but propane (CH_3–CH_2–CH_3) can produce more than one alkyl group as hydrogen atoms are not all equivalent. Removing one of the six terminal H-atoms forms *n*-propyl group, CH_3–CH_2–CH_2– but removal of one of the two central hydrogrn atoms produces the isopropyl group $CH_3—\underset{|}{CH}—CH_3$.

Alkyl groups are classified as

1. Primary alkyl group (1°), if a C, having a free valency, is joined to only one C atom (and two H atoms) C–CH_2–.
2. Secondary alkyl group (2°), if a C, having a free valency, is joined to two C atoms (and one H atom)



3. Tertiary alkyl group (3°) if a C, having a free valency, is joined to three C atoms (and no H atom).



The methyl group is a special case and is taken as a primary alkyl group. Alkyl groups are denoted by R–.

Alkenes

Alkenes are hydrocarbons, which have at least one C–C double bond. They have the general formula C_nH_{2n}. They are also called olefins.

Table 1.1

Name	Molecular formula	Structure
Ethylene (ethene)	C_2H_4	$H_2C=CH_2$
Propylene (propene)	C_3H_6	CH_3–$CH=CH_2$
1-Butylene (1-butene)	C_4H_8	CH_3–CH_2–$CH=CH_2$
2-Butylene (2-butene)	C_4H_8	CH_3–$CH=CH$–CH_3

Alkenes having more than one double bonds are also known. They are:

1. Two double bonds – diene
2. Three double bonds – triene
3. Multiple double bonds – polyene

The location of each double bond is denoted by numbers.

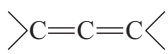
Table 1.2

Name	Molecular formula	Structure
Propadiene (allene)	C_3H_4	$H_2C{=}C{=}CH_2$
1,3-Butadiene	C_4H_6	$CH_2{=}CH{-}CH{=}CH_2$
2-Methyl-1,3-butadiene (isoprene)	C_4H_8	$H_2C{=}C(CH_3){-}CH{=}CH_2$
1,2,3-Butatriene	C_4H_4	$CH_2{=}C{=}C{=}CH_3$

The polyenes that have alternate single and double bonds are called conjugated polyenes (e.g. 1,3-butadiene). Small-chain polyenes are colourless but long-chain polyenes are coloured. Carrot and tomato contain long-chain polyenes that are coloured (yellowish) and are called 'Carotene'.

Polyenes are further classified according to the position of the double bonds, one to the other.

1. Cumulated double bond: In this type of bond, the double bonds are continuous between the carbon atoms.



For example, propadiene (allene),

$$CH_2{=}C{=}CH_2$$

2. Conjugated double bond: Substances having alternate single and double bonds are called conjugated systems. Example, 1,3-butadiene.

$$CH_2{=}CH{-}CH{=}CH_2$$

3. Isolated double bonds: Compounds with double bonds that are neither cumulated nor conjugated are said to have isolated double bond. Example, 1,4-pentadiene.

$$CH_2{=}CH{-}CH_2{-}CH{=}CH_2$$

Alkenyl group Alkenyl group is formed when one of the hydrogen atoms of an alkene is removed. The name of the alkenyl is obtained by replacing 'e' of alkene by 'yl'.

$$\text{Alkene} - \text{H} = \text{Alkenyl}$$

Numbering of the chain starts at C atom that has free bond.

Table 1.3

Alkenyl group	Structure
Ethenyl (vinyl)	CH_2=CH–
1-Propenyl	CH_3–CH=CH–
Allyl (2-propenyl)	CH_2=CH–CH_2–
Crotyl (2-butenyl)	CH_3–CH=CH–CH_2–
3-Butenyl	CH_2=CH–CH_2–CH_2
1-Methyl ethenyl (isopropenyl)	CH_2=C(–CH_3)–

Alkynes

Acyclic hydrocarbons that contain carbon–carbon triple bonds are called 'alkynes'. Their general formula is C_nH_{2n-2}. They are also called acetylenes.

Table 1.4

Alkyne	Molecular formula	Structure
Acetylene (ethyne)	C_2H_2	HC≡CH
Propyne (methyl acetylene)	C_3H_4	CH_3–C≡CH
2-Butyne	C_4H_6	CH_3–C≡C–CH_3
1,3 Butadiyne	C_4H_2	HC≡C–C≡CH

Many of the polyynes are found in plants. A few of them have been isolated.

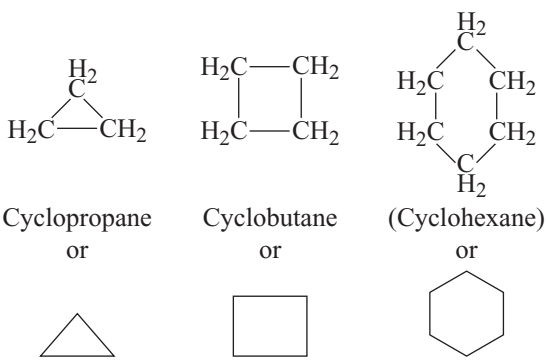
Alkynyl group When a hydrogen atom is removed from an alkyne, the group formed is called an 'alkynyl' group. Here 'e' of alkyne is replaced by 'yl'.

Ethynyl H–C≡C–

2-Propynyl (propargyl) H–C≡C–CH_2–

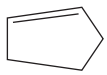
Alicyclic Hydrocarbons

Alicyclic hydrocarbons (or cycloalkanes) contain ring of C atoms linked together by single bonds. They have the general formula C_nH_{2n}. For example,



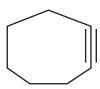
Cyclopropane or Cyclobutane or (Cyclohexane) or

Cyclic hydrocarbons that contain carbon–carbon double and triple bonds are called cycloalkenes and cycloalkynes, respectively.

Cyclopentene 

Cyclohexadiene

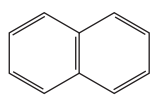
Cycloalkynes having less than seven C atoms are not known.

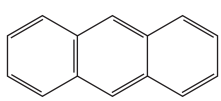
 Cycloheptyne

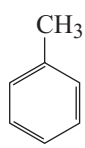
Aromatic Hydrocarbons

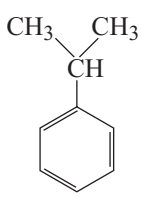
Cyclic unsaturated hydrocarbons having conjugated double bonds are called aromatic hydrocarbons. They are also called 'arenes'. Benzene (C_6H_6) is the parent member (discovered by M. Faraday). Compounds of this class possess characteristic smell. Thus, they were, and are, collectively called 'aromatic' (in Greek, *Aroma* means fragrant smell).

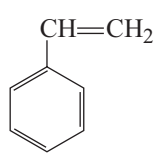
Benzene


Naphthalene

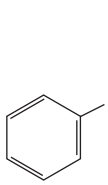

Anthracene

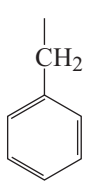

Toluene

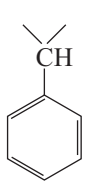

Isopropylbenzene
(Cumene)

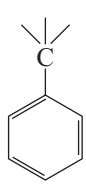

Vinyl benzene
(Styrene)

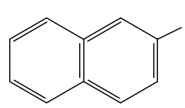
The common aryl groups are

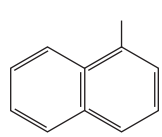

Phenyl


Benzyle


Benzal


Benzo

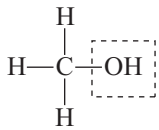

β-Naphthyl


α-Naphthyl

(Details of the above are given in the chapter "Benzene.")

Functional group and classification

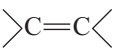
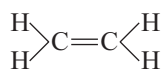
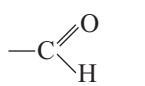
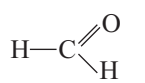
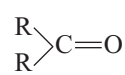
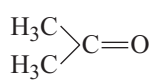
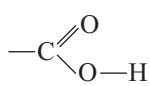
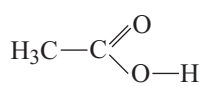
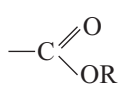
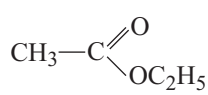
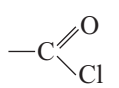
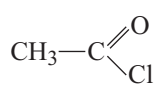
Many organic compounds contain two components. One component is the hydrocarbon, which mainly controls the physical properties and the other called the 'Functional Group', mainly controls the chemical properties.



Functional group

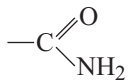
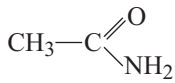
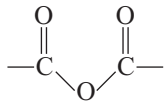
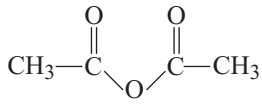
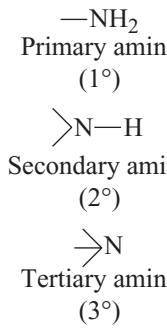
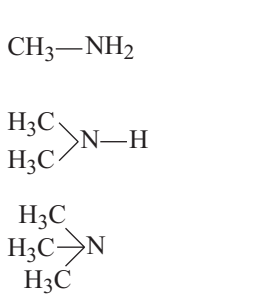
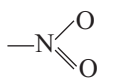
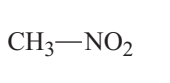
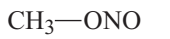
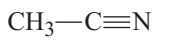
In the above compound, $-CH_3$ (methyl group) is the hydrocarbon and the –OH (hydroxyl group) is the functional group. It controls the chemical properties and is called the 'Alcoholic Functional Group'. Thus, various combinations of atoms that control chemical properties of an organic compound are called 'Functional Groups'. Such groups are generated from heteroatoms (N, O, P, S, etc.). Compounds of a given class have the same functional group and, hence, are chemically similar. The carbon–carbon double and triple bonds (C=C, C≡C) are also taken as functional groups.

Table 1.5

Class	Name of the functional group	Formula of the functional group	Example
Alkene	Double bond		
Alkyne	Triple bond	—C≡C—	H—C≡C—H
Alkyl halide	Halide	—X (X=F, Cl, Br, I)	CH_3—Cl
Alcohol	Hydroxyl group	—O—H	CH_3—OH
Ether	Ether group	R—O—R	CH_3—O—CH_3
Aldehyde	Aldehyde group or formyl group		
Ketone	Ketone group		
Carboxylic acid	Carboxyl group		
Ester	Carbalkoxy		
Acid chloride	Acid chloride		

(Continued)

Table 1.5 (Continued)

Class	Name of the functional group	Formula of the functional group	Example
Amide	Acid amide		
Acid anhydride	Anhydride		
Amine	Amino group		
Nitro	Nitro		
Nitrito	Nitrito		
Cyanide or nitrile	Cyano group or nitrile group		

NOMENCLATURE

Trivial System

In this system, compounds were named on the basis of their origin. The trivial names are also called 'Common names'. Some examples of common names include:

1. Methyl alcohol [CH_3–OH]: It was obtained by destructive distillation of wood and was called 'Wood Spirit'. From this, the name methyl alcohol was derived. (In Greek, Methu means wine and hule means wood.)
2. Acetic acid: The chief constituent of vinegar derived its name from the Latin word *Acetum* meaning vinegar.
3. Formic acid: It was obtained by the distillation of red ants (in Greek, *Formicus* means red ants).

Many more may also be included but the great problem was that different names were given to a single compound. For example, CH_4 was variously known as methane or marsh gas or fire-damp.

IUPAC system

Aliphatic compounds

The term IUPAC is the abbreviation of *International Union of Pure and Applied Chemistry*. This method of naming considers saturated hydrocarbon as the parent compound. The other classes of organic compounds

are taken as derivatives of the saturated hydrocarbons. Naming, according to this method, is a four-step process:

1. Specification of root name.
2. Specification of primary suffix.
3. Specification of secondary suffix.
4. Specification of prefix (if there is a substituent).

Root name The longest C chain in the compound determines the root name. They are given in the table below.

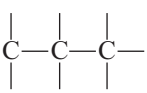
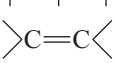
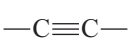
Table 1.6

C chain	Root name	C chain	Root name
C	Meth	C_6	Hex
C_2	Eth	C_7	Hept
C_3	Prop	C_8	Oct
C_4	But	C_9	Non
C_5	Pent	C_{10}	Dec

In general, the root name is 'alk'.

Primary suffix The term suffix means 'a group of letters added to the end of a word to make another word'. Thus, primary suffix is the term which is added to the root name (alk) to show the saturated or unsaturated nature of the C chain.

Table 1.7

Name of C chain	Primary suffix	Name
Saturated 	ane	Alkane
	ene	Alkene
Unsaturated 	yne	Alkyne

Note:

1. If there is more than one double and triple bonds, then

two	C=C	diene
three	C=C	triene
three	C≡C	triyne, etc.

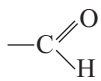
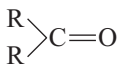
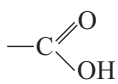
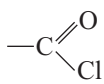
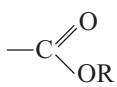
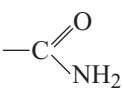
2. Hydrocarbon radicals are named as

Table 1.8

Hydrocarbon	Primary suffix	Name
Alkane–H	yl	Alkyl
Alkene–H	enyl	Alkenyl
Alkyne–H	ynyl	Alkynyl

Secondary suffix It represents the specific functional group. It is added after the primary suffix. It is the class of the compound.

Table 1.9

Functional group	Secondary suffix
Hydroxyl group	–ol
Saturated or unsaturated (C=C)	–ol
Unsaturated (C=C)	–ol
Formyl or aldehyde group 	–al
Ketonic group 	–one
Carboxyl group (saturated or unsaturated chain) 	oic acid
Acid chloride (saturated or unsaturated chain) 	oyl chloride
Ester group 	oate
Amide group 	amide
Cyanide group (–C≡N)	nitrile
Ether group (–OR)	alkoxy
Nitro group (NH_2)	nitro
Amino group (–NH_2)	Primary amine

Class of the organic compound When root name, primary suffix and secondary suffix are added together, class of the organic compound is obtained. The terminal 'e' of the primary suffix is generally removed before adding secondary suffix.

Table 1.10

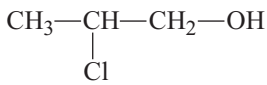
Trivial name	Root name	Primary suffix	Secondary suffix	IUPAC name
Alcohol	Alk	ane	ol	Alkanol
Unsaturated (C=C)	Alk	ene	ol	Alkenol
Unsaturated (C≡C)	Alk	yne	ol	Alkynol
Aldehyde	Alk	ane	al	Alkanal

(Continued)

Table 1.10 (Continued)

Trivial name	Root name	Primary suffix	Secondary suffix	IUPAC name
Ketone	Alk	ane	one	Alkanone
Carboxlic acid	Alk	ane	oic acid	Alkanoic acid
(C=C)	Alk	ene	oic acid	Alkenoic acid
(C≡C)	Alk	yne	oic acid	Alkynoic acid
Ester	Alk	ane	oate	Alkyl alkanoate
Acid chloride	Alk	ane	oyl chloride	Akanoyl chloride
Acid amide	Alk	ane	amide	Alkanamide

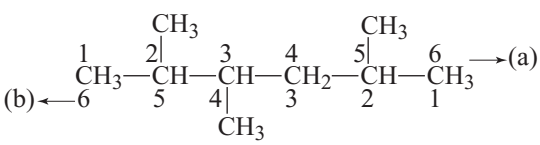
Prefix In many organic compounds, H atom (or atoms) of the parent C chain are replaced by other groups. Example, by –R or –Cl or –OH or –CN. They are called 'Substituents' (i.e., group of letters added to the beginning of a word). For example, in



Root name = prop (as there are three C atoms)
Primary suffix = ane (as the compound is a derivative of a saturated C chain)
Secondary suffix = ol (as it has hydroxyl,
–OH group)
Prefix= chloro (as Cl has replaced H, i.e., Cl is a substituent)
Thus, the above compound is
2-chloropropan-1-ol

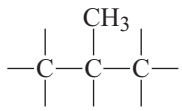
Steps to name simple compounds

1. The longest C chain is selected. If the compound contains a functional group, the longest chain must include it (functional group).
2. The C chain is numbered.
3. Numbering starts from the end (left or right), which puts substituent or the functional group at the lowest number.
4. If a functional group containscarbon, numbering starts from that C atom.
5. When many substituents are present, numbering starts from the end so that the sum of the locants (the number which locates a substituent) is minimum.

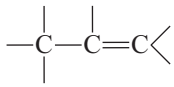


   (a) Sum of the locants = 2 + 3 + 5 = 10 (Correct)
   (b) Sum of the locants = 2 + 4 + 5 = 11 (Wrong)

6. Each substituent (or a functional group) is denoted by putting a hyphen between the number and the name of the substituent (or the functional group).



2-Methyl (substituent)

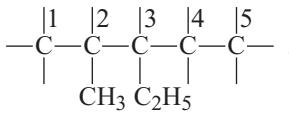


1-ene (functional group)

7. Presence of more than one identical group is denoted by the Greek numeral.

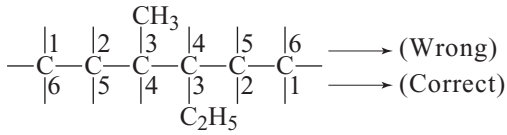
two	di
three	tri
four	tetra
five	penta
six	hexa, etc.

8. When there are different substituents, their names are written in the alphabetical order.

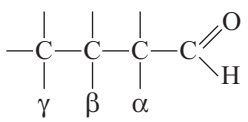


3-Ethyl-2-methyl

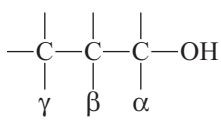
9. When different alkyl substituents are present at equivalent positions, numbering of the chain is done in such a way that puts the alkyl group, which comes first in the alphabetical order, at the lower number.



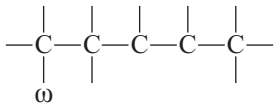
Note:
Greek letters (α, β, γ, etc.) are also used to denote the position of a substituent. When the functional group itself has carbon, the C atom adjacent to the functional group is α.

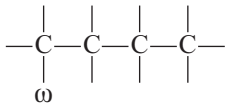


When the functional group has no carbon, the functional group bearing the C atom is α.



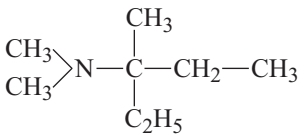
The letter ω (omega) always represents the last C atom of a chain irrespective of its length.


(Functional group)


(Functional group)

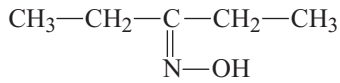
Examples

1.



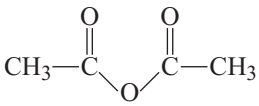
3-Methyl-3-N,N-dimethyl pentane

2.



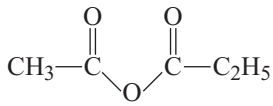
Pent-3-one oxime

3.



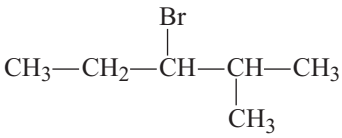
Ethanoic anhydride

4.



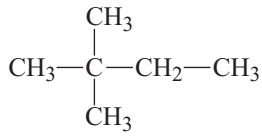
Ethanoic propanoic anhydride

5.



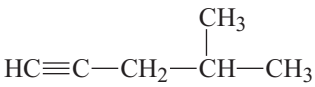
3-Bromo-2-methyl pentane

6.



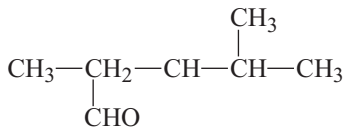
2,2-Dimethyl butane (neohexane)

7.



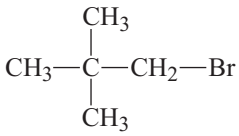
4-Methylpent-1-yne

8.



2-Ethyl-3-methyl butanal

9.



2,2-Dimethylbromopropane
(neopentyl bromide)

Naming of compounds having many functional groups

An organic compound may contain many functional groups. In such compounds, one functional group is the principal functional group that decides the class of the compound (secondary suffix). The other functional

groups are taken as substituents and are called prefixes. In selecting the principal functional group, an order of preference is established (Table 1.11). It is

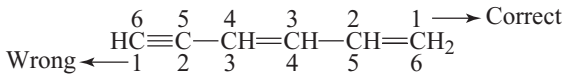
$$-SO_3H > -COOH > \text{acid anhydride} > -COOR > -COCl > -CONH_2 > -CHO > -CN > -\overset{|}{C}O \text{ (ketone)} > -OH > -OR > C{=}C > C{\equiv}C > -NO_2 > -X \text{ (halogens)}$$

Table 1.11

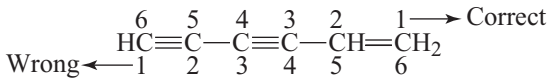
Functional group	Prefix name (substitutent)	Suffix name (class)
$-SO_3H$	–	Sulphonic acid
–COOH	Carboxy	oic acid
–COOR	Carbalkoxy or alkoxy carbonyl	Alkyl oate
–COCl	Chloro formyl or chloro carbonyl	oyl chloride
$-CONH_2$	Carbamoyl	Amide
–CHO	Formyl or aldo	al
–CN	Cyano	Nitrile
–NC	Isocyano	Carbylamine
>C=O	Oxo or keto	one
–OH	Hydroxy	ol
$-NH_2$	Amino	Amine
–OR	Alkoxy	–
>C=C<	–	ene
–C≡C–	–	yne
$-NO_2$	Nitro	–
–NO	Nitroso	–
–X	Halo	Halo (chloro, bromo, etc.)

Steps in Naming

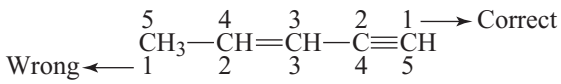
1. Principal functional group is decided using the preference table. It is the class of the compound.
2. The parent chain is selected in such a way that it includes the maximum number of substituents (here the functional group is other than the principal functional group) and also the principal functional group.
3. The chain is numbered so that the principal functional group falls at the lowest number.
4. Substituents are named in the alphabetical order.
5. Hydrocarbons with both double and triple bonds are called alkenynes (alkadienynes, alkenedynes, etc.), i.e., the order ‘enyne’ is used. Numbering starts to put double bonds at the lower number.



Hexa-1, 3-dien-5-yne



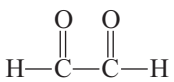
Hex-1-en-3,5-diyne



Pent-3-en-1-yne

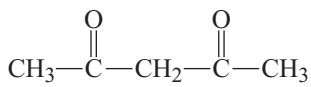
Examples

1.



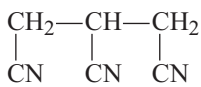
Ethanedial (glyoxal)

2.



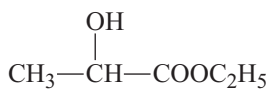
Pentane-2, 4-dione
(acetyl acetone)
β-diketone

3.



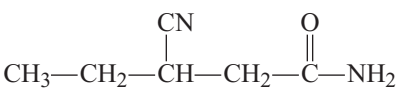
3-Cyanopentanonitrile

4.



Ethyl-2-hydroxypropanoate

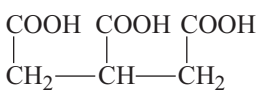
5.



3-Cyanopentanamide

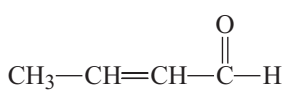
6. HOOC . CH(OH) . CH(OH) . COOH
2,3-Dihydroxybutanedioc
acid (tartaric acid)

7.



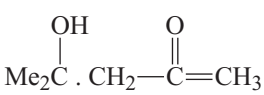
Propane-1,2,3-tricarboxylic acid

8.



But-2-enal

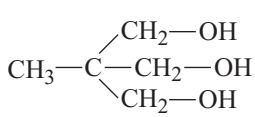
9.



4-Hydroxy-4-methylpentanone-2

10. CH≡C—COOH
Propynoic acid

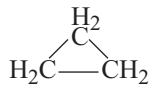
11.

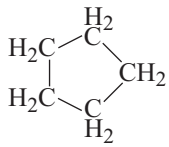


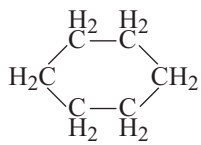
2-Methyl-2-hydroxymethyl
propan-1, 3-diol

Naming of cycloalkanes (alicyclic compounds)

Cycloalkanes are hydrocarbons, which contain rings of C atoms linked together with single bonds. The simple unsubstituted cycloalkanes have many CH_2 groups, i.e., they are polymethylenes, $(CH_2)_n$. The general formula of cycloalkanes with one ring is C_nH_{2n}. For example,

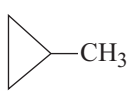
Cyclopropane 

Cyclopentane 

Cyclohexane 

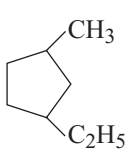
IUPAC Naming

1. Cycloalkanes are named by adding the prefix 'cyclo' to the name of the corresponding alkane (i.e., saturated hydrocarbon) Some examples are cyclopropane (C_3H_6), cyclobutane (C_4H_8), cyclopentane (C_5H_{10}) and cyclohexane (C_6H_{12}). Alkyl-substituted cycloalkanes are called alkyl cycloalkanes.

 Methyl cyclopropane

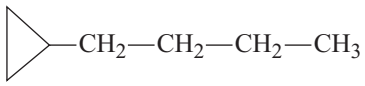
Ethyl cyclobutane

More than one substituents are given numbers consistent with their positions in such a way as to keep the sum of the numbers to a minimum.



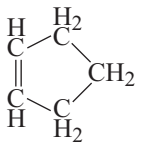
1-Ethyl-3-methylcyclopentane
(not 1-ethyl-4-methylcyclopentane)

If the number of C atoms in the side-chain are larger than the cycloalkane, the ring is taken as the substitutent.

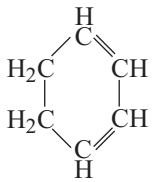


1-Cyclopropylbutane

2. If the hydrocarbon is unsaturated, the prefix 'cyclo' is added to the name of the alkene.



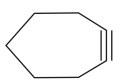
Cyclopentene



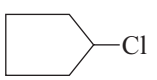
Cyclohexa-1, 3-diene
(not cyclohexa-1, 4-diene)

Cycloalkynes having less than seven C atoms are not yet known.

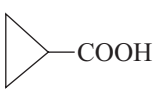
3. Functional groups containing cycloalkanes are named as aliphatic compounds.



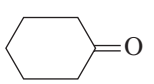
Cycloheptyne



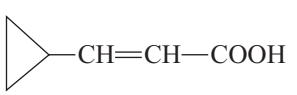
Chlorocyclopentane



Cyclopropane carboxylic acid



Cyclohexanone



3-Cyclopropyl prop-2-en-1-oic acid

Writing formula from the given name The IUPAC naming includes

1. *Root name*
It indicates the longest C chain.

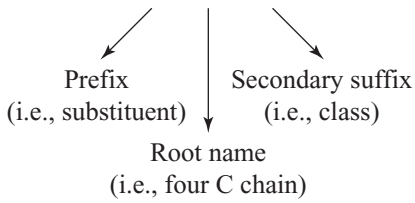
2. *Primary suffix*
It shows the nature of the chain, i.e., ane (saturated), ene (C=C) and yne (C≡C).

3. *Secondary suffix*
It indicates the principal functional group, i.e., class of the compound.

4. *Prefix*
It shows the substituents.

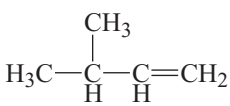
The above is explained by the following examples:

(a) 3-Methyl but-1-ene

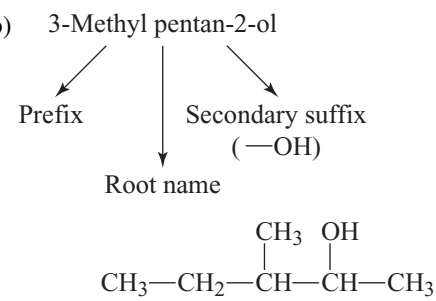


Steps in writing the formula

1. Since there is 'but', the parent compound has four C atoms in the chain.
2. Since there is 'ene' and it is 1-ene, the first and the second C atoms are joined by a double bond.
3. Since there is 3-methyl, the third carbon has the methyl group.
4. Since the compound is a hydrocarbon, the valencies of the H atoms satisfy the valencies of the C atoms.



(b) 3-Methyl pentan-2-ol



Different types of formulae

1. Molecular formula
2. Structural formula
3. Condensed formula
4. Line formula
5. Projection formula (it is explained in the Chapter 'Isomerism').

Molecular formula

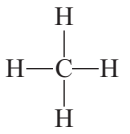
It gives the total number of each atom in the molecule. Example, C_2H_6O, but this formula can represent only two organic compounds, i.e.,

$CH_3–CH_2–OH$ (ethyl alcohol) and
$CH_3–O–CH_3$ (dimethyl ether).

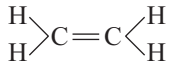
Thus, a molecular formula does not completely describe an organic compound.

Structural formula (suggested by Kekule)

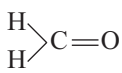
It shows the attachment of the atoms through bonds. Example,



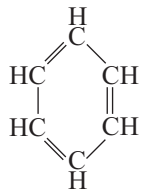
Methane



Ethylene



Formaldehyde

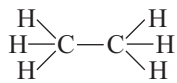


Benzene

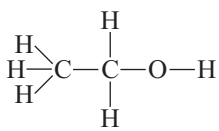
But for big molecules, it is a lengthy work, which is time-taking, and covers much more space. Therefore, it is generally not used unless it becomes essential.

Condensed formula

In this formulation, bonds are not drawn. The groups are linked by a line or a dot that shows the attachments of the atoms together. For example,

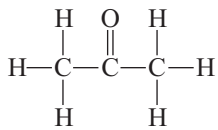


$\equiv$ $CH_3—CH_3$



$\equiv$ $CH_3—CH_2—OH$

or $CH_3.CH_2.OH$



$\equiv$ CH_3COCH_3

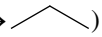
or $CH_3—\overset{\overset{O}{\|}}{C}—CH_3$

It is the most used way of representing the organic compounds.

Line formula

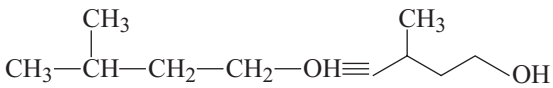
Formulation of long-chain or multi-ring compounds, even by condensed formula, is tedious. For such cases, line formula is used. It uses lines only to represent a molecule. Important points in writing the line formula are:

1. C and H are not shown except in the case of a functional group.
2. Methyl group (CH_3 or Me) is indicated by a single line (–) terminated at one end.

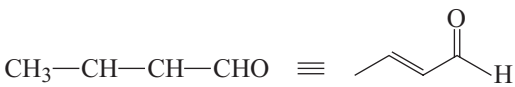
3. A double line (=) terminated at an end represents $=CH_2$ group.
4. A triple line (≡) terminated at an end represents (≡CH) group.
5. A $>CH_2$ group (methylene group) is denoted by the corner of a bent line ($>CH_2 \rightarrow$ )
6. The corner of the type ( ) represents a CH group.

Examples

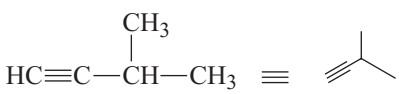
1. 3-Methyl butan-1-ol,



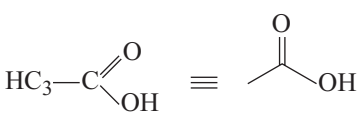
2. 2-Butenal



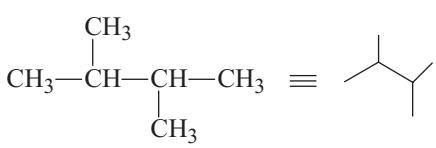
3. 3-Methyl-1-butyne



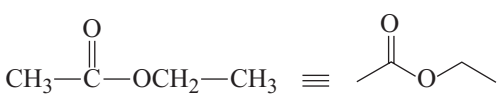
4. Acetic acid (ethanoic acid)



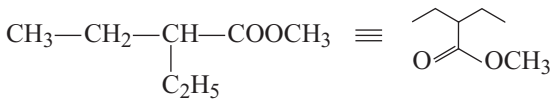
5. 2,3-Dimethyl butane



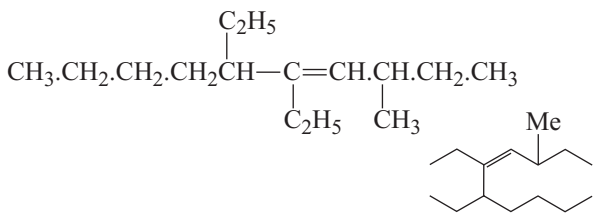
6. Ethyl acetate



7. 2-Ethyl methyl butanoate



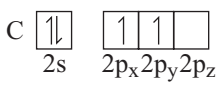
8. 5,6-Diethyl-3-methyl-dec-4-ene



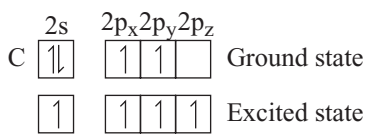
TETRAVALENCY OF CARBON AND STRUCTURE OF ORGANIC COMPOUNDS

The nature of bonds in the organic compounds is mainly covalent and the carbon in those compounds is always tetracovalent. It can achieve tetravalency in different ways.

Let us consider carbon that has valence shell configuration.



This configuration has two unpaired electrons. So, carbon should be dicovalent. Although species such as CH_2 (carbene) is known, it is highly reactive reaction intermediate. In its stable compounds, carbon is always tetravalent. Tetravalency requires four unpaired electrons. Carbon achieves this by promotion of one of its two 2s electrons to a high-energy 2p orbital.



The excited state has four unpaired electrons. Thus, carbon can form four bonds. Now, a question may be asked. From where 2s electron gets the energy for promotion to the high energy 2p orbital? It is explained that in the excited state, carbon can form four bonds (instead of two) leading to greater energy lowering, which compensates need of energy for electron promotion. However, the four bonds of carbon should not be identical as electrons are in different orbitals, 2s and 2p. But the four bonds of C (in CH_4, CCl_4, etc.) are found quite similar and are tetrahedral. Promotion of the electron does not explain it. The similarity of four bonds is explained by the concept of hybridization.

Hybridization

The process of mixing of atomic orbitals in an atom to give equivalent (or non-equivalent) orbitals is called 'Hybridization'. The new orbitals are known as hybrid orbitals. The number of hybrid orbitals formed is equal to the no. of atomic orbitals mixed.

Hybrid Orbitals of Carbon

The valence orbitals of carbon are s and p orbitals. Therefore, carbon can form hybrid orbitals involving s and p orbitals only.

Table 1.12

Hybrid type	Atomic orbitals	Structure	Bond angle
sp^3	$s + p_x + p_y + p_z$	Tetrahedral	109°20′
sp^2	$s + p_x + p_y$	Triangular planar	120°
sp	$s + p_z$	Linear	180°

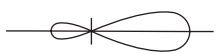
sp^3 hybridization (C–C single bonds only)

The carbon atom in saturated organic compounds (CH_4, CCl_4, C_2H_6, C_2H_5–OH, etc.) is sp^3 hybridized, i.e., when carbon forms four single bonds (or four σ bonds) it is sp^3 hybridized.

The mixing of s-orbital with all the three p-orbitals is called sp^3 hybridization. As four atomic orbitals are mixed, four equivalent sp^3 hybrid orbitals are formed.

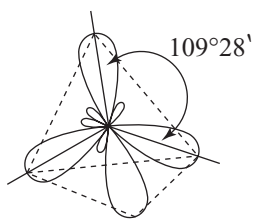
$$2s + 2p_x + 2p_y + 2p_z \rightarrow \text{four } sp^3 \text{ hybrids}$$

An sp^3 hybrid orbital may be denoted as

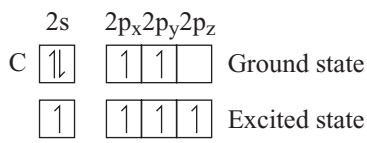


sp^3 hybrid orbital

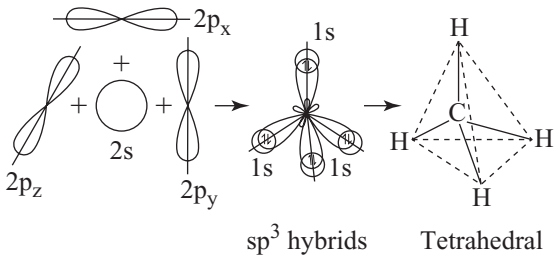
The hybrid orbitals are oriented along the corners of a regular tetrahedron. (A tetrahedron is a figure made by four equilateral triangles or six equal edges.) An sp^3 hybrid orbital has 25 per cent s-character and 75 per cent p-character.



The valence shell of carbon is



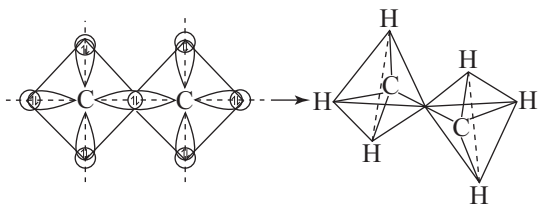
In the excited state, 2s and 2p orbitals hybridize to form four sp^3 hybrids. These hybrids are oriented along the four corners of a regular tetrahedron. The C–H σ bonds in CH_4 are formed by the linear overlap of sp^3 hybrid orbital of C with 1s of H. Methane, therefore, is a tetrahedral molecule.



In C_2H_6, both C atoms are sp^3 hybridized. There are C–C and C–H σ bonds.

1. C–C σ bond: It is formed by the linear overlapping of sp^3 hybrid of one carbon with that of the other.
2. C–H σ bond: It is formed by the linear overlap of sp^3 hybrids of carbon with 1s orbital of H.

Therefore, in C_2H_6 two tetrahedra are joined at a corner.



sp^2 Hybridization (C–C double bond)

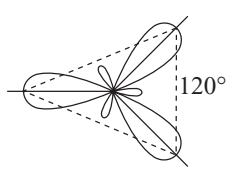
Only the C-atom that forms three σ bonds is sp^2 hybridized. Thus, the C atoms of >C=C<, >C=O, etc. are also sp^2 hybridized.

The mixing of s-orbital with two of the p-orbitals (say p_x and p_y) is called sp^2 hybridization. As three atomic orbitals are mixed, three equivalent sp^2 hybrid orbitals are formed.

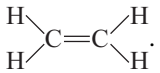
$$s + 2p_x + 2p_y \rightarrow 3sp^2 \text{ hybrids}$$

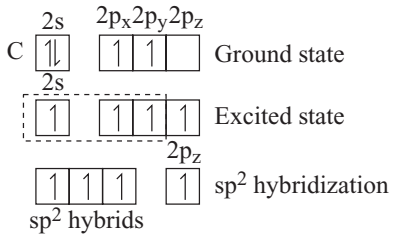
An sp^2 hybrid orbital may be denoted as

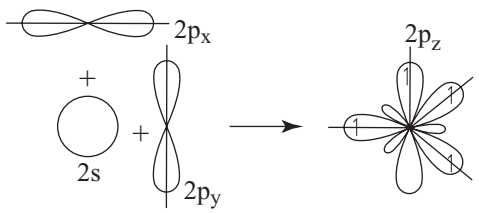
The hybrid orbitals are oriented along the corners of an equilateral triangle.



An sp^2 hybrid orbital has 33.3 per cent s-character and 66.6 per cent p-character.

Ethylene (C_2H_4) molecule Ethylene is  . In this structure C-atoms form three σ bonds. Therefore, C atoms are sp^2 hybridized. The structure is trigonal planar. It can be explained using sp^2 hybrid nature of C orbitals.

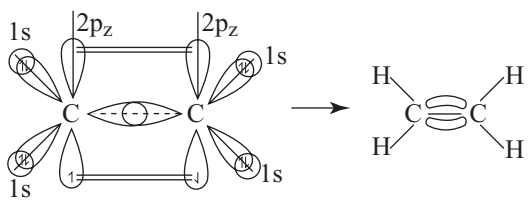




The sp^2 hybridized C atom has three sp^2 hybrids oriented along the corners of an equilateral triangle. The unhybridized $2p_z$ orbital is perpendicular at the plane of the carbon and the three hybrids.

In C_2H_4, the bonds present are formed as

1. C–H, σ bonds (four) are formed by the linear overlap of sp^2 of C with 1s of H.
2. C–C, σ bond is formed by the linear overlap of sp^2 of one C with that of the other.
3. C–C, π bond is formed by sidewise overlapping of $2p_z$ orbitals present at C atoms.

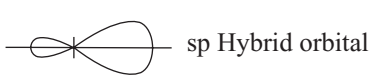


sp hybridization (C–C triple bond)

The C atom, which forms two σ bonds only is sp hybridized. Thus, the C atoms of –C≡C–, –C≡N, etc. are sp hybridized.

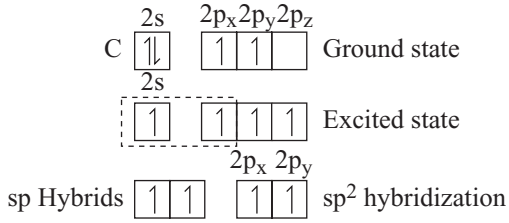
The mixing of s-orbital with only one p-orbital is called sp hybridization. As two atomic orbitals are mixed, two equivalent sp hybrid orbitals are formed.

$$s + 2p_z \rightarrow \text{Two sp hybrids.}$$



The hybrid orbitals are oriented in opposite directions on the same axis.

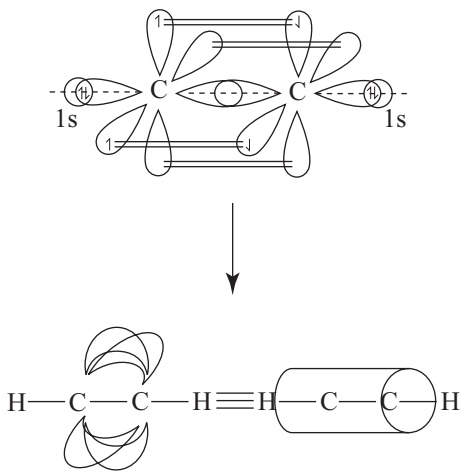
Acetylene (C_2H_2) Molecule Acetylene is H–C≡C–H. In this structure, each C atom forms two σ bonds only. Therefore, they are sp hybridized.This molecule is linear in structure. It is explained by using sp hybrid orbitals of carbon.



The sp hybridized C atom leaves two atomic p-orbitals ($2p_x$ and $2p_y$) which are mutually perpendicular.

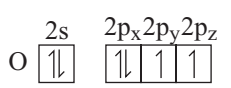
In C_2H_2, bonds are formed as

1. C–C, σ bond: It is formed by the linear overlap of sp hybrid orbital of one carbon with that of the other.
2. C–H, σ bonds (two): They are formed by the linear overlap of sp hybrid of C with 1s of H.
3. C–C, π bonds: The two π bonds are formed by sidewise overlapping of $2p_x$–$2p_x$ and $2p_y$–$2p_y$ orbitals.



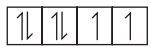
The p_x and p_y orbitals are perpendicular to each other. Therefore, the two π-bonds are in planes at right angles to each other. Thus, C_2H_2 molecule is sheathed in a cylinder of negative charge.

Carbon-oxygen bond The carbon–oxygen bonds are either C–O (single bond) or C=O (double bonds) in stable compounds. The O atom (atomic number 8) has the valence electron configuration.



The O atom, too, uses hybrid orbitals to form strong bonds. Two situations are found.

1. When O atom forms two single bonds (i.e., two σ-bonds) to achieve octet, it is sp^3 hybridized. Out of the four sp^3 hybrids, two accommodate two lone pairs and the rest two hybrids have one electron each.


sp^3 hybrid of O atom

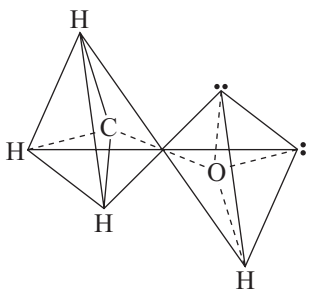
The above for O atom is found in alcohols (R—$\ddot{O}$—H) and ethers (R—$\ddot{O}$—R) or in $\ddot{O}$H group wherever it is present.

Methyl alcohol

In this molecule, C and O both are sp^3 hybridized. The details of bonds and lone pairs at O atom are as follows:

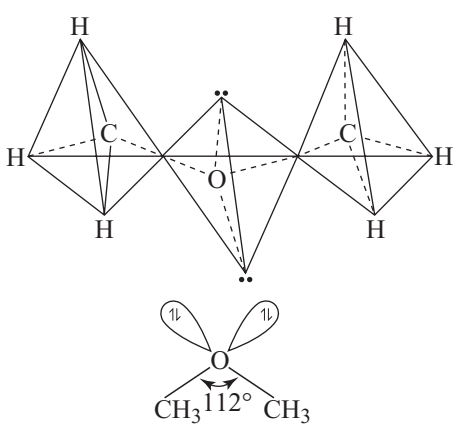
1. C–H σ bonds: They are formed by the linear overlapping of sp^3 of C with the 1s orbital of H.
2. C–O σ bond: It is formed by the linear overlapping of sp^3 of C with sp^3 of O atom.
3. O–H σ bond: It is formed by the linear overlapping of sp^3 of O with 1s of H.

The two lone pairs at O atom are housed in sp^3 hybrids.



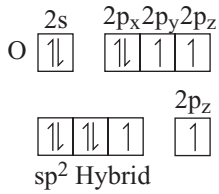
(Bond angle is greater than H_2O due to steric factor.)

In the same way, dimethyl ether (CH_3–O–CH_3) can be represented as follows:

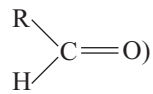
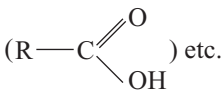


Bond angle is greater than tetrahedral angle partly due to large steric repulsion and partly due to more electronegative nature of O atom).

2. When O atom forms double bond with carbon (>C=O) to achieve octet, it is sp^2 hybridized.



Out of the three sp^2 hybrids, two contain lone pairs and one has a single electron. The unhybridized p-orbital ($2p_z$) has one electron. It is used for π bonding by O atom.

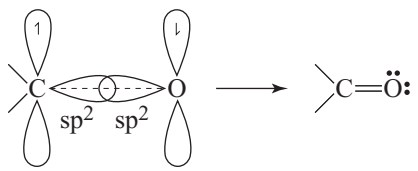
This situation is found in ketones ($R_2C=O$), aldehydes () carboxylic acids () etc.

Acetalaldehyde (CH_3–CHO) and acetone (CH_3COCH_3)

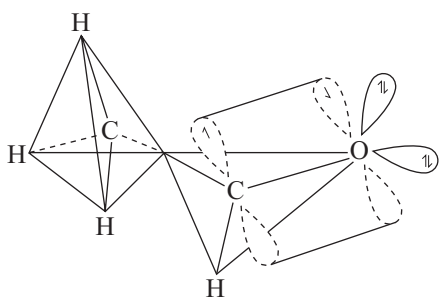
In acetaldehyde (CH_3–CHO), aldehydic C and O atom both are sp^2 hybridized. The bonds are formed as follows:

1. C–O σ bond: It is formed by the linear overlapping of sp^2-orbital of C with sp^2-orbital of O atom.

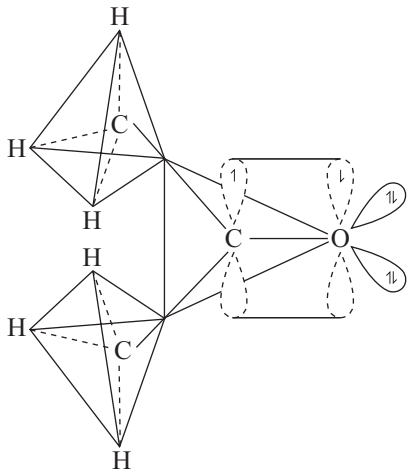
2. C–O π bond: It is formed by sidewise overlapping of p-orbitals at both C and O.



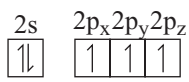
The lone pairs at O-atom are present in sp^2 hybrids.



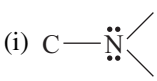
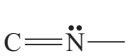
The structure of acetone (CH_3COCH_3) is also similar.



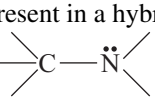
Carbon–nitrogen bond The N atom has following valence electron configuration.



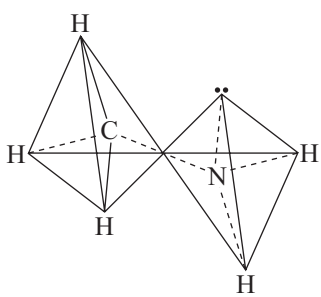
It can enter into bonding with carbon in the following way:

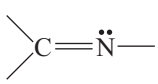
(i)  (ii)  (iii)

In each case, the lone pair is present in a hybrid orbital.

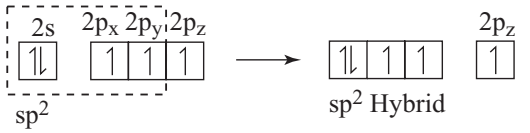
1. Single-bonded N atom, 

   In this case, N is sp^3 hybridized (C is also sp^3). Three sp^3-orbitals have single electron and the fourth sp^3 hybrid orbital has a lone pair. Example, amines CH_3NH_2 or $(CH_3)_2NH$ or $(CH_3)_3N$.

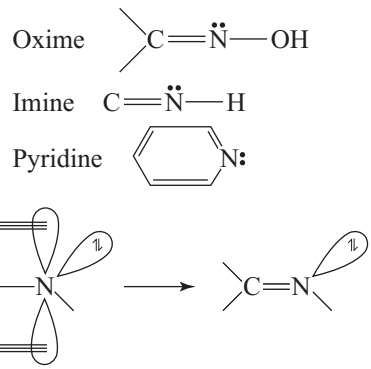


2. Double-bonded N atom, 

In such cases, N is sp^2 hybridized.

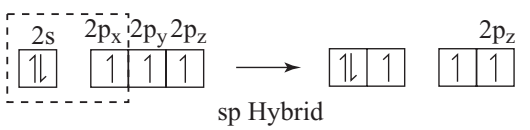


Two sp^2 hybrids contain single electron and they form two σ bonds. The lone pair is present in the third sp^2 hybrid. The unhybridized p-orbital ($2p_Z^1$)with one electron forms π bond. Example,

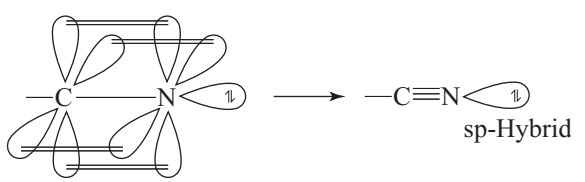


3. Triple-bonded N atom, –C≡N

In this case, N is sp–hybridized.



One sp hybrid has the lone pair and the other has a single electron. It forms σ bond. The two unhybridized p-orbitals ($2p_y^1$ & $2p_z^1$) form two π bonds, e.g. the cyanide ion (–C≡N).



Quick Reference Tables

1. Bond properties of C–N and C–O

Table 1.13

Bond	Bond length (Å)	Bond Energy (Kcal/mole)
C–N	1.47	73
C–O	1.42	86
C=N	1.29	147
C=O	1.22	179
C≡N	1.16	213

2. Characteristics of different hybrids

Table 1.14

Hybrid	Structure	Bond nature	Bond angle	s-character	p-character
sp^3	Tetrahedral	σ bond	109°28'	25	75
sp^2	Trigonal planar	σ bond one π bond	120°	33.3	66.6
sp	Linear	σ bond two π bonds	180°	50	50

3. C hybrids and some molecular parameters

Table 1.15

Property	Ethane $H_3C–CH_3$	Ethylene $H_2C=CH_2$	Acetylene HC≡CH
C hybrid	sp^3	sp^2	sp
C–C length (Å)	1.54	1.33	1.20
C–H length (Å)	1.09	1.07	1.05
C–C bond energy (kcal/mole)	83	143	192

Note: The bond dissociation energy is total C and C-bond energy, not the C–C single bond energy.

4. Hybrid of C and some typical bond lengths (Å)

Table 1.16

Bond type	Bond length (Å)	Bond type	Bond length (Å)	Bond type	Bond length (Å)
C–C		C=C		C–H	
sp^3–sp^3	1.54	sp^2–sp^2	1.34		
sp^3–sp^2	1.50	sp^2–sp	1.31		
sp^3–sp	1.46	sp–sp	1.28[b]	sp^3–H	1.09
sp^2–sp^2	1.48			sp^2–H	1.08
sp^2–sp	1.43	C≡C		sp–H	1.06
sp–sp	1.38[a]	sp–sp	1.20[c]		

Notes: [a]The sp–sp bond length 1.38Å is present in butadiene and cyanoaectylene.
[b]The C–C bond length of 1.28 Å is found in butatriene and carbon suboxide (O=C=C=C=O).
[c]The C–C bond length of 1.2 Å is present in acetylene.

5. Hybrids of carbon and bond length in some common compounds

Table 1.17

Bond type		Bond length (Å)	Examples
[a]	**C–C**		
	sp^3–sp^3	1.54	Ethane
	sp^3–sp^2	1.50	CH_3–CHO, CH_3–CH=CH_2, Toluene
	sp^3–sp	1.46	CH_3–C≡CH

(Continued)

Table 1.17 (Continued)

Bond type	Bond length (Å)	Examples
sp^2–sp^2	1.48	1,3-Butandiene, glyoxal, biphenyl
sp^2–sp	1.43	Acrylonitrile, vinyl acetylene
sp–sp	1.38	Butadiyne, cyanoacetylene
[b] **C=C**		
sp^2–sp^2	1.34	Ethylene
sp^2–sp	1.31	Allenes, ketene
sp–sp	1.28	Butatriene
[c] **C≡C**		
sp–sp	1.20	Acetylene
[d] **C–H**		
sp^3–H	1.11	Methane
sp^2–H	1.10	Benzene, ethylene
sp–H	1.08	Acetylene

PROBLEMS

Structure and Nomenclature

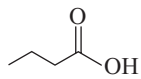
1. Write the structures of the following compounds.
(a) Butyric acid (b) Acrylic acid
(c) Propiolic acid (d) Sec-butyl bromide
(e) Neopentyl bromide (f) Methyl vinyl either
(g) Allyl alcohol (h) N,N-dimethyl formamide
(i) Maleic acid (j) Fumaric acid
(k) Tetracyano ethylene (l) Allene
(m) Acetyl chloride (n) *Cis*-syn-di-t-butyl ethylene

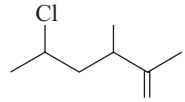
2. What are the functional groups of the following class of compounds?
(a) Ester (b) Acid anhydride
(c) Primary alcohol (d) Secondary alcohol
(e) Tertiary alcohol (f) Primary amine
(g) Aldehyde (h) Carboxylic acid

3. Write the structure of the following compounds (IUPAC names are given).
(a) 2,2-Dimethyl-1-bromopropane
(b) 2,3-Pentane dione
(c) 1,2,3-Propantriol
(d) 1,3-Butadiene
(e) Propadiene
(f) Ethanoyl chloride
(g) Butanal
(h) 3-Chlorobutanol-2
(i) Butenedioic acid
(j) 2,3-Dihydroxy butandioic acid
(k) 4-Amino-butan-2-one
(l) 4-Methyl-pent-2-en-1-ol
(m) 2-Methylbut-1,3-diene
(n) 2-Oxopropanoic acid
(o) Prop-2-en-1-ol
(p) 3-Chloro propane
(q) 2-Oxopropanal
(r) 2-Ethyl-3-methyl but-1-ene

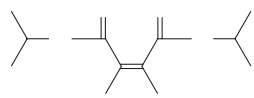
4. Sketch line formulae from (a) to (r) of question number [3].

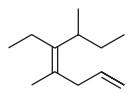
5. Write IUPAC names of the following compounds represented by the line formula.

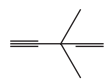
(a) 

(b) 

(c)

(d) 

(e) 

(f) 

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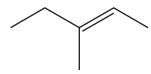
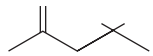
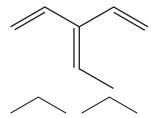
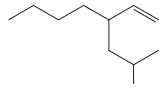
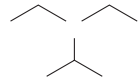
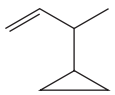
(h) 

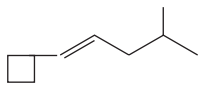
(i) 

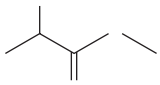
(j) 

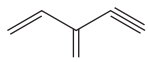
(k) 

(l) 

(m) 

(n) 

(o) 

(p) 

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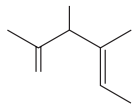
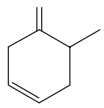
(r) 

(s) 

6. Draw the shape of the following species.
(a) CH_3^- (b) CH_3^+
(c) CH_3NH_2 (d) CH_3–CHO
(e) CH_3–$CONH_2$ (f) CH_3–$COCH_2$–CH_3
(g) CH_2=CH–CN

7. Predict hybridization of each C atom in
(a) propadiene (b) butatriene
(c) 1,3-butadiene (d) ethandioic acid
(e) but-2-en-dioic acid

OBJECTIVE-TYPE QUESTIONS

1. The alkane in which all H atoms are equivalent is
(a) Pentane (b) Isopentane
(c) Isohexane (d) Neopentane

2. The correct decreasing order of C–H bond length is represented by
(a) $C_2H_6 > C_2H_2 > C_2H_4$
(b) $C_2H_6 > C_2H_4 > C_2H_2$
(c) $C_2H_2 > C_2H_4 > C_2H_6$
(d) $C_2H_4 > C_2H_2 > C_2H_6$

3. Total number of σ and π bonds in tetracyano ethene is
(a) 2 and 9 (b) 9 and 9
(c) 9 and 4 (d) 9 and 6

4. The hybridization of C atoms in C–C single bond of $HC\equiv C–CH=CH_2$ is
(a) sp-sp^2 (b) sp^2-sp^2
(c) sp-sp^3 (d) sp^2-sp^3

5. The number of σ and π bonds in but-1-en-3-yne, respectively, are
(a) 5 and 2 (b) 7 and 3
(c) 6 and 4 (d) 8 and 2

6. The IUPAC name of CH_2=CH–$CH(CH_3)_2$ is
(a) 1-isopropyl ethylene
(b) 3-methyl-1-butene
(c) 2-vinyl propane
(d) 1,1-dimethyl-2-propene

7. The IUPAC name of isooctane is
(a) 6-methyl heptane (b) 3-methyl octane
(c) 2-methyl heptane (d) 2-methyl octane

8. *Neo*-hexane has
(a) no tertiary C atom
(b) three tertiary C atoms
(c) two tertiary C atoms
(d) only one tertiary C atom

9. The compound 1,2-butadiene has
(a) only sp hybridized C atom
(b) only sp^2 hybridized C atoms
(c) both sp- and sp^2 hybridized C atoms
(d) sp-, sp^2- and sp^3 hybridized C atoms

10. The bond between C atom (1) and C atom (2) in compound $N\equiv\overset{1}{C}–\overset{2}{C}H=CH_2$ involves, respectively, the hybrid orbitals
(a) sp^2 and sp^2 (b) sp^3 and sp
(c) sp and sp^2 (d) sp and sp

11. The compound in which C uses its sp^3 hybrid orbitals for bond formation is
(a) HCOOH (b) $(H_2N)_2CO$
(c) $(CH_3)_3COH$ (d) CH_3CHO

12. The compound which has only one isopropyl group is
(a) 2,2,3,3-tetramethylpentane
(b) 2,2-dimethylpentane
(c) 2,2,3-trimethylpentane
(d) 2-methylpentane

13. The number of σ and π bond in 1-butene-3-yne are
(a) 5 sigma and 5 pi
(b) 7 sigma and 3 pi
(c) 8 sigma and 2 pi
(d) 6 sigma and 4 pi

14. Which of the following statements regarding the molecule $CH_2=C=CH_2$ is not correct?

(a) Both the two π bonds are present in the same plane.

(b) The central C atom is sp hybridized while the terminal atoms are sp^2 hybridized.

(c) The molecule is linear.

(d) The molecule contains six σ bonds and two π bonds.

15. Arrange the following compounds in order of the increasing dipole moment.

(I) Toluene (II) *m*-Dichlorobenzene

(III) *o*-Dichlorobenzene (IV) *p*-Dichlorobenzene

(a) I < IV < II < III (b) IV < I < II < III

(c) IV < I < III < II (d) IV < II < I < III

16. In the compound $CH_2=CH–CH_2–CH_2–C\equiv CH$, the $C_2–C_3$ bond is of the type

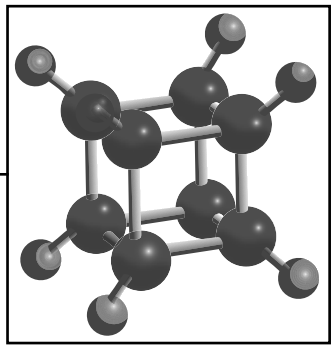
(a) $sp\text{-}sp^2$ (b) $sp^3\text{-}sp^3$

(c) $sp\text{-}sp^3$ (d) $sp^2\text{-}sp^3$

Answers

1. (d)	2. (b)	3. (b)	4. (a)	5. (b)
6. (b)	7. (c)	8. (a)	9. (d)	10. (c)
11. (c)	12. (d)	13. (b)	14. (a)	15. (d)
16. (d)				

CHAPTER 2



Isomerism

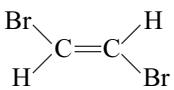
Substances having the same molecular formula but different physical and chemical properties are called 'Isomers' and this phenomenon is called isomerism. Some examples are given below.

1. C_2H_6O represents both dimethyl ether and ethyl alcohol.

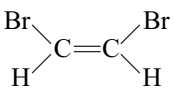
$CH_3—O—CH_3$	$CH_3—CH_2—OH$
MP =142°C, BP = 25°C	MP =114°C, BP = 78°

   The above mentioned two compounds also differ in their chemical properties as their functional groups are different.

2. The two geometrical isomers of BrCH=CHBr are given below.



trans-Isomer
Dipole moment, $\mu = 0$
MP = 6.5°C, BP = 108°C



cis-Isomer
Dipole moment, $\mu = 1.3D$
MP = 53°C, BP = 110°C

Isomerism is a characteristic of complex covalent molecules. It can be broadly classified into two groups: (i) structural isomerism and (ii) stereoisomerism.

STRUCTURAL ISOMERISM

Structural isomers have different arrangement of atoms, i.e., they have different structural formulae. Structural isomerism may be of the following types:

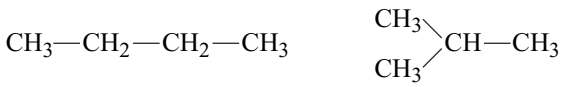
1. Chain isomerism
2. Ring–Chain isomerism

3. Position isomerism
4. Functional group isomerism
5. Metamerism
6. Tautomerism

Chain isomerism

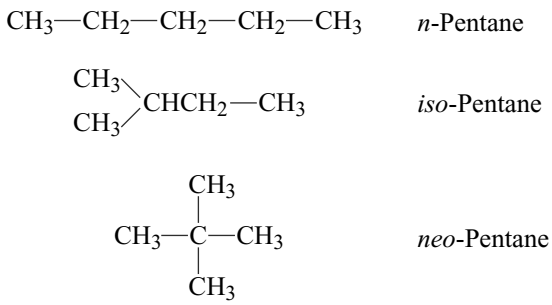
Chain isomers are formed due to the difference in the nature of the carbon skeleton, i.e., the 'back bone' of the molecule. For example,

1. The two butane isomers



n-Butane *iso*-Butane

2. The three pentane isomers



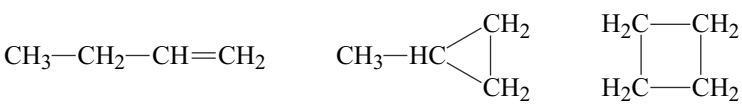
n-Pentane

iso-Pentane

neo-Pentane

Ring–chain Isomerism

This type of isomerism arises due to the open-chain or closed-chain structures. For example, C_4H_8, which represents three isomeric structures.



1-Butene
BP = 6.3°C

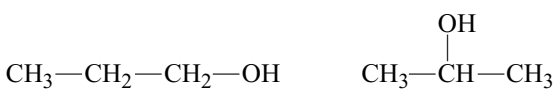
Methyl cyclopropane
BP = 4°C

Cyclobutane
BP = 11°C

Position Isomerism

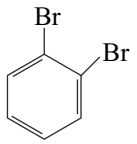
The isomers that have similar carbon skeleton but differ in the position of the attached atom or group are called position isomers. Some examples are

1. The two propanols

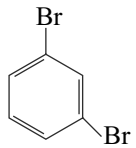


1-Propanol 2-Propanol

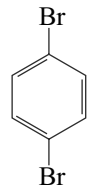
2. The three dibromobenzenes



o-Dibromobenzene



m-Dibromobenzene



p-Dibromobenzene

3. The two butenes

$CH_3—CH_2—CH=CH_2$ 1-Butene

$CH_3—CH=CH—CH_3$ 2-Butene

Functional group isomerism

The isomers that have the same number of atoms arranged to form molecules but differ in their functional groups are called functional group isomers and, thus, show functional group isomerism. It is generally found when the general formulae of the compounds are the same. Some examples are as follows:

1. Alcohol and ether (having the general formula $C_nH_{2n+2}O$)

C_2H_6O $CH_3—O—CH_3$ Dimethyl ether $CH_3—CH_2—OH$ Ethyl alcohol

2. Cyanides and isocyanides

$CH_3—CN$ Methyl cyanide $CH_3—NC$ Methyl isocyanide

3. Aldehydes, ketones and unsaturated alcohols (having the general formula $C_nH_{2n}O$)

C_3H_6O $CH_3—CH_2—CHO$ Propanal $CH_3—\overset{\overset{O}{\|}}{C}—CH_3$ Acetone $CH_2=CH—CH_2—OH$ Allyl alcohol

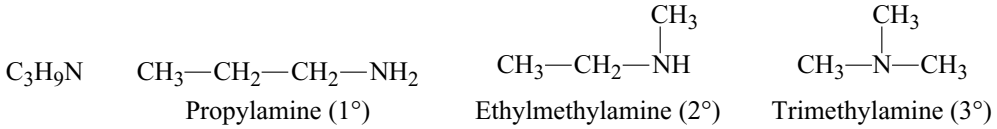
4. Acid and ester (having the general formula $C_nH_{2n}O_2$)

$C_2H_4O_2$ $CH_3—COOH$ Acetic acid $H—COOCH_3$ Methyl formate

5. Oxime and amide

C_2H_5NO $CH_3—CH=NOH$ Acetaldoxime $CH_3—\overset{\overset{O}{\|}}{C}=NH_2$ Acetamide

6. Amines (1°, 2° and 3°)



Metamerism

Isomers that have the same functional group but different alkyl groups attached to it are called metamers. For example,

1. $C_4H_{10}O$

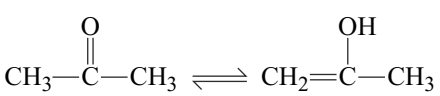
2. $C_4H_{11}N$

3.

Tautomerism

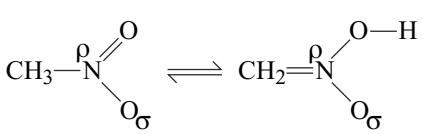
Tautomers are also functional group isomers that can easily interconvert into one another and can also exist in rapid equilibrium. The common examples are

1. Keto–enol tautomers

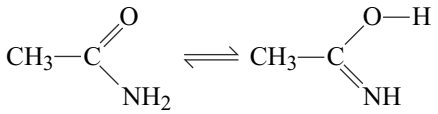


The form I has keto group as the functional group whereas form II has ene (=) and ol (–OH) as the functional groups. The two when taken together form ene + ol ⟶ enol ('e' of ene is replaced by ol).

2. Nitro–acinitro tautomers



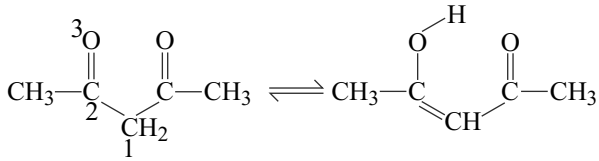
3. Amide–imidol system



Amide Imidol

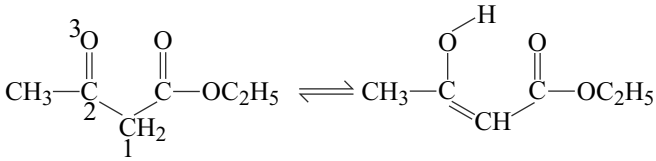
Keto–enol tautomerism

Tautomerism that is most common in carbonyl (>C=O) compounds is termed as keto–enol tautomerism. For example,



Keto form Enol

(Pentane 2,4-dione)

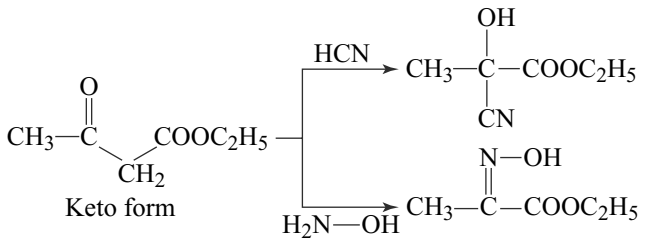


Keto form Enol form

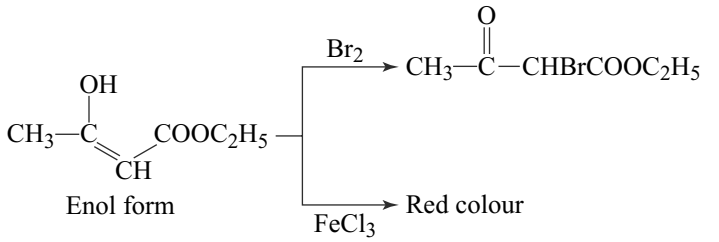
(Ethyl acetoacetate)

Keto–enol tautomerization involves shifting of a proton (1,3-shift or α,γ-shift). This shifting of proton is termed as prototropy. Thus, a keto–enol change is a prototropic change.

The most studied example of keto–enol tautomerism is ethyl acetoacetate (ethyl-2-ketobutanoate). It behaves both as a keto compound, adds HCN and condenses with H_2N–OH, and as an unsaturated hydroxy ester that decolourizes Br_2 and forms a coloured derivative with $FeCl_3$.

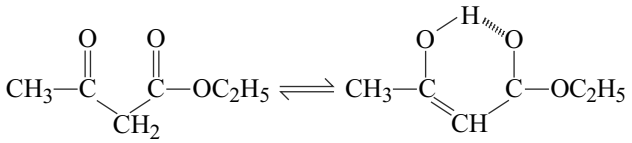


Keto form

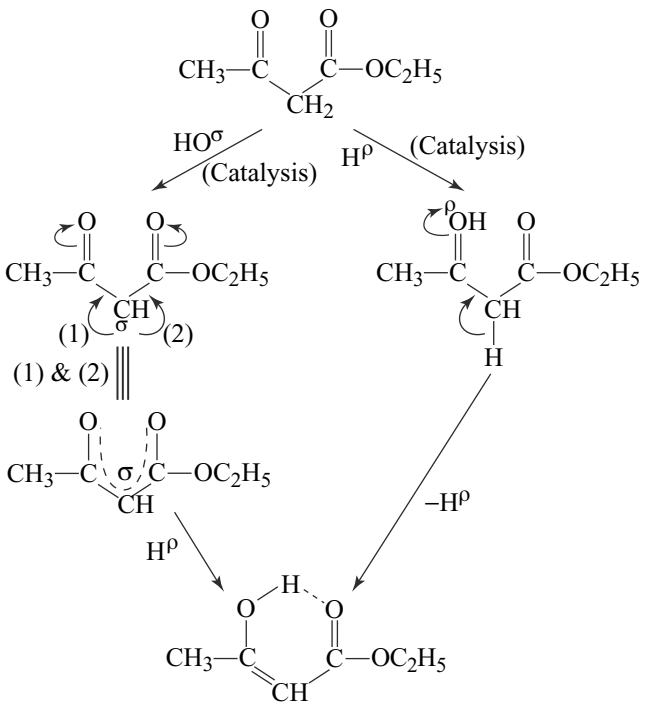


Enol form

Thus, ethyl acetoacetate exists as an equilibrium mixture of keto and enol forms in the ratio of 92.5 : 7.5 at room temperature.



This interconversion is powerfully catalysed by bases and to some extent by acids.



Because of the rapid interconversion, tautomers are not isolable in ordinary conditions but can be separated and preserved in special conditions. Tautomers of ethyl acetoacetate have been separated using quartz vessel at –80ºC (glass surface is slightly alkaline).

Keto–enol content (or percentage) Many factors such as solvent, H-bonding and conformation affect keto–enol content. They are discussed separately below.

1. Solvent and keto–enol (percentage): The amount of enol in keto–enol equilibrium varies with the nature of the solvent. The keto form of a diketone or keto ester is more polar than the enol form. The intramolecular H-bonding in the enol results into a more compact, folded structure making it less polar. Therefore, the percentage of enol increases as the polarity of the solvent decreases (Table 2.1).

Table 2.1 Percentage of enol of ethyl acetoacetate

Solvent	Enol (in %)	Solvent	Enol (in %)
Water	0.4	Chloroform	8.2
Acetic acid	5.7	Benzene	16.2
Methanol	6.9	Hexane	46.4

2. π-Orbital system and percentage of enol: A π-orbital system, such as a phenyl group, can conjugate with C = C in the enol form. It results into higher percentage of enol (Table 2.2).

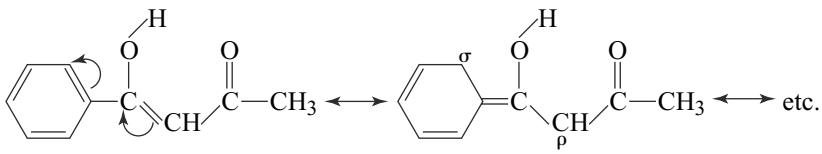
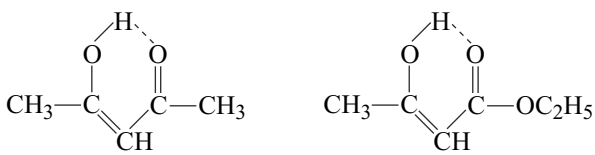


Table 2.2 Percentage of enol

Compounds	Enol (in %)
$CH_3COCH_2COOC_2H_5$	8
$CH_3COCH(Ph)COOC_2H_5$	30
$CH_3COCH_2COCH_3$	76.4
$PhCOCH_2COCH_3$	89.2

3. Intramolecular H-bonding and percentage of enol: Intramolecular H-bonding is an important structural feature that stabilizes the enol over keto form.



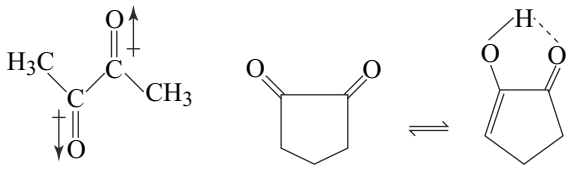
This H-bonding lowers the boiling point of enol as compared to the keto form. The carbonyl group (>C=O) of a ketone is more effective electron-attracting group than the carbonyl group of an ester. Thus, a diketone (Example, acetylacetone) has more enol content than an ester (ethyl acetoacetate) (Table 2.3).

Table 2.3 Percentage of enol in some compounds

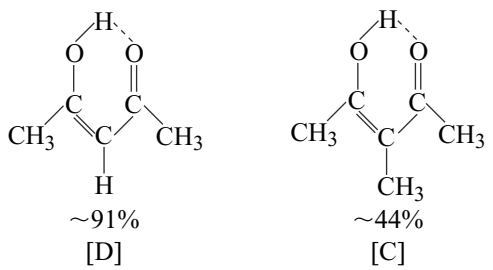
Compounds	Enol (in %)
CH_3–CO.CH_3	0.00025
CH_3–CO.CH_2–$COCH_3$	80.4
CH_3COCH_2–$COOC_2H_5$	7.5

Note: The enol content of acetone is very small as it has no possibility of intramolecular H-bonding.

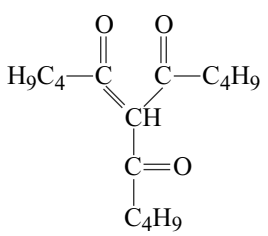
4. Conformation and percentage of enol: Conformation is also an important factor in deciding the percentage of enol form. For example, biacetyl [A] has very little enol content (0.0056%) whereas 1,2-cyclopentane dione [B] exists mostly in the enol form (99.0%). The carbonyl groups of biacetyl are oriented in an anti-conformation that reduces the dipole–dipole repulsion. In keto [B], the >C=O groups are locked in the syn-conformation (because of the ring structure rotation around C–C σ bond that is not possible). Therefore, the enol form has strong intramolecular H-bonding resulting into increased enol content.



5. Steric factor and percentage of enol: Steric factor also determines the enol content. For example, α-methyl acetylacetone [C] has lesser enol content than acetylacetone [D].



The best example of the steric factor is triacyl methane [e.g., $(BuCO)_3CH$], which is found to exist completely in the keto form.



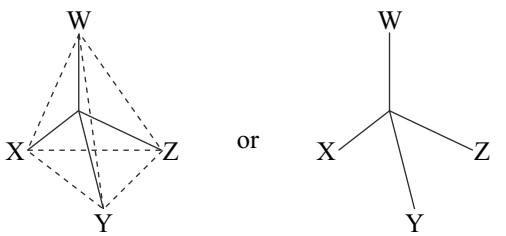
PROJECTION FORMULAE

Organic compounds containing sp^3-hybridized C atoms are tetrahedral in structure, i.e., they have 3D structure. Example, CH_4, CCl_4 and C_2H_6. The paper on which such structures are being written is 2D (i.e., planar). Therefore, the physical reality of a 3D structure becomes difficult to represent on a 2D paper. For this purpose, some devices have been developed. They are called 'Projection Formulae'. Three types of projection formulae that are in use are (i) perspective projection formulae, (ii) Newman projection formulae and (iii) Fisher projection formulae.

Perspective and Newman projection formulae are generally used to describe the conformational isomers and Fisher projection formulae are used to describe the optical isomers.

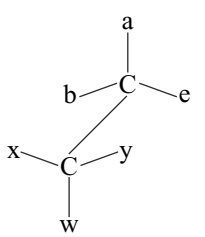
Perspective Projection Formulae

The word 'Perspective' means the art of creating an effect by drawing. Perspective formulation is, thus, a device to represent a 3D covalent molecule by drawing, in which relative projection of groups, their size and distance between them is denoted. For this purpose, a tetrahedral carbon is represented as (I).



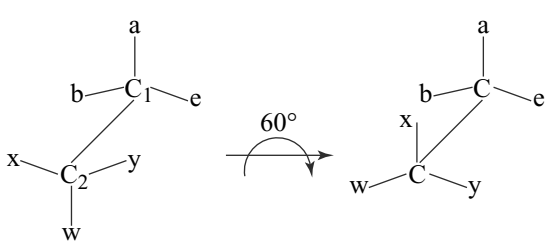
(I)

In such a representation, C atom is thought to be present at the centre of a regular tetrahedron and the solid lines, which join the four corners emanating from C, represent the four bonds. Two sp^3-hybridized C atoms, which are joined, are represented as (II).



(II)

This representation of the molecule clearly indicates the changes in the relative position of the groups when rotation around C–C axis is made (C_2 is rotated).



(II) (III)

Thus, a rotation through 60° around C–C σ bond changes the structure of (II) to (III). This projection formulation is also called 'Sawhorse projection'.

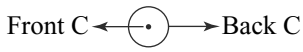
Newman Projection

The following points are considered to represent a molecule by Newman projection.

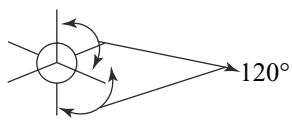
1. The molecule is viewed at C–C axis. Thus, one carbon completely eclipses the other.

- - - C–C - - - - eye

2. C atoms are denoted by circles.
3. To differentiate two C atoms, the front carbon is denoted by the centre dot and the back carbon by the circle.



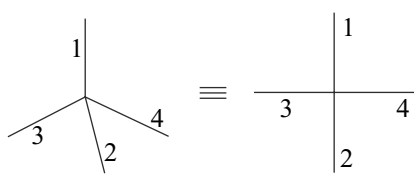
4. Bonds of the front carbon appear to extend from the centre and the bonds of the back carbon appear to extend from the circumference (or edge of the circle).
5. The groups attached to C atoms appear at 120°.



Fisher Projection Formula

According to this formulation, an sp^3 carbon on paper is represented on the basis of the following points.

1. C atom is thought to be present in the plane of the paper.
2. Top and bottom bonds (1 and 2) are projected below the plane of the paper. The bonds extended towards left and right (3 and 4) are projected above the plane of the paper. Thus, the structure appears as a cross on the paper.



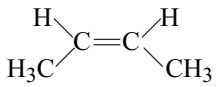
STEREOISOMERISM

Isomers, which differ only in the spatial arrangement of constituent atoms are called 'Stereoisomers' (in German *Stereos* means solid, i.e., a 3D projection). Stereoisomerism can be of the following types:

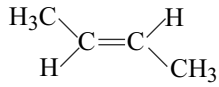
1. Geometrical isomerism
2. Optical isomerism
3. Conformational isomerism

Geometrical and optical isomers are separable in ordinary condition. It is because they have configurations that require large amount of energy for interconversion (i.e., bond breaking is actually required). The term

'Configuration' is defined as the arrangement of atoms which represents a particular stereoisomer, e.g., *cis*- and *trans*-2-butenes.



cis-2-Butene



trans-2-Butene

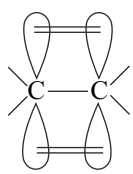
Conformational isomers are formed due to the rotation around C–C σ bond axis and so can easily interconvert into one another at room temperature. Thus, they can be separated only in special conditions.

Geometrical Isomerism

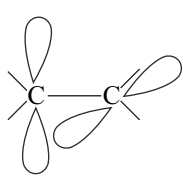
The basic reasons for geometrical isomerism are as follows:

1. The rigidity of a molecule, which may develop due to the presence of (a) C=C in the molecule and (b) alicyclic ring.
2. Proper substitution

A C=C has one σ and one π bond. The π bond is formed by the sidewise overlap of p orbitals. For proper overlap, the p orbitals must be present at parallel axes (say each at $2p_z$), which lie above and below the plane of the sp^2 orbitals of carbon.

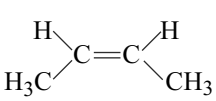


The rotation of any of the carbon atoms around C – C σ bond will lead to a situation where there will be no overlap.

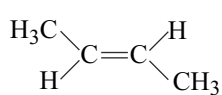


It shows that when there is a C=C bond, rotation around C–C σ bond axis is not possible. This restricted rotation sets rigidity in the structure, which may be responsible for geometrical isomerism.

Geometrical isomerism is also known as *cis–trans* isomerism (in Latin, *–cis* means on the same side and trans means across). For example, 2-butene has two geometrical isomers, the *cis*-2-butene and the *trans*-2-butene.



cis-2-Butene

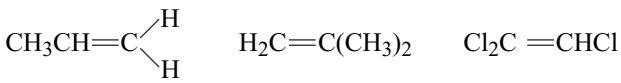


trans-2-Butene

These two compounds are quite stable, as interconversion requires a large amount of energy.

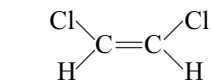
Which Compound Can Form Geometrical Isomers?

Alkenes (or dienes, trienes, etc.) are expected to form geometrical isomers due to restricted rotation (i.e. rigidity) around C=C, but geometrical isomers are not formed when one of the unsaturated carbon atoms is bonded to two similar groups (not proper substitution). For example,

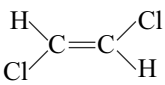


All other forms of the molecule will form geometrical isomers, example,

1.

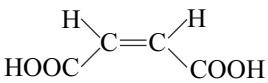


cis-1,2-Dichloroethene

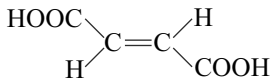


trans-1,2-Dichloroethene

2.

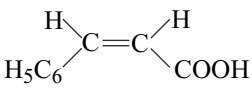


Maleic acid
MP = 130°C

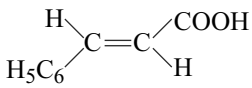


Fumaric acid
MP = 302°C

3.

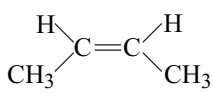


cis-Cinnamic acid
MP = 68°C

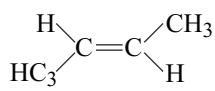


trans-Cinnamic acid
MP = 133°C

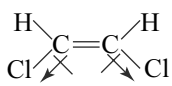
Geometrical (or *cis–trans*) isomers differ in physical and chemical properties.



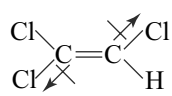
cis
BP = 4°C
μ = 0.4D



trans
BP = 1°C
μ = 0

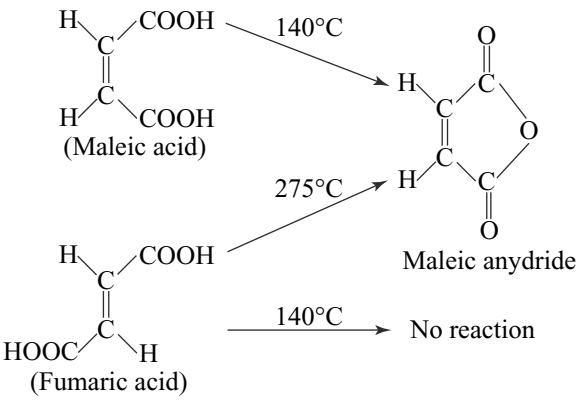


μ = 1.85D

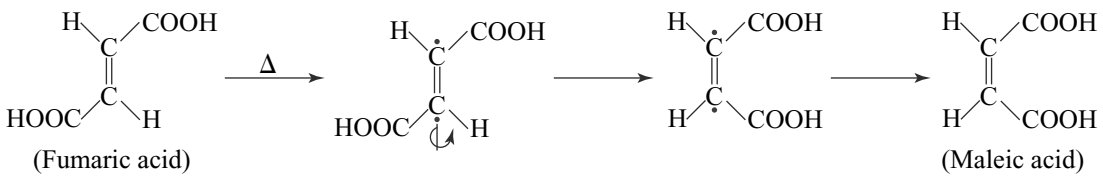


μ = 0

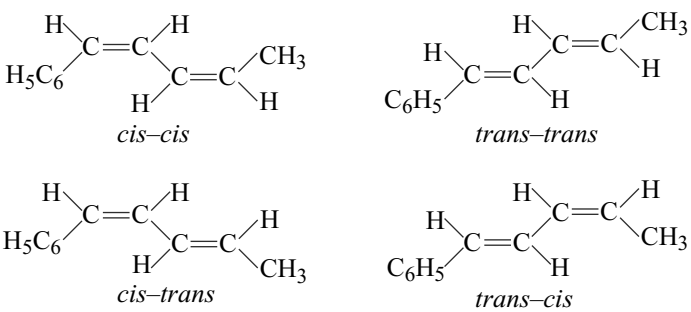
An obvious difference in maleic acid (*cis*) and fumaric acid (*trans*) is their behaviour towards heat.



Maleic acid (*cis* acid) loses water to form cyclic anhydride at low temperature, as two carboxyl groups are close enough to interact. Fumaric acid fails to form anhydride at 140°C as two –COOH groups are not close (they are *trans*). However, the *cis–trans* interconversion can take place at high temperatures (or by irradiation with light). It involves breaking of C–C π bond, rotation about C–C σ -bond axis and then formation of a new π bond. Therefore, the trans acid forms anhydride at higher temperature.

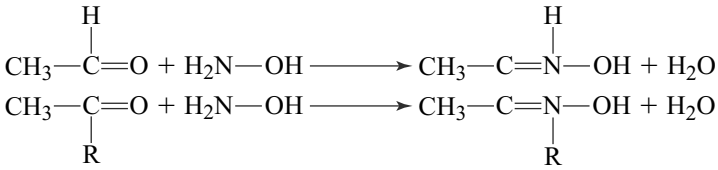


***Cis–trans* Isomerism in Dienes** In dienes, the number of *cis–trans* isomers is 2^n, where n is the number of double bonds. Thus, a diene can form four geometrical isomers if properly substituted, e.g., 1-phenyl-1,3-pentadiene forms four *cis–trans* isomers.

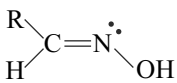


Geometrical Isomers of C=N and N=N Compounds Compounds containing C=N and N=N also form geomertrical isomers if properly substituted. The C=N has one σ and one π bond, both C and N are sp^2 hybridized and this portion of the molecule is planar. The presence of π bond restricts rotation around C–N σ bond axis. This rigidity makes the formation of *cis* and *trans* isomers in compounds having C=N possible. Hence, oximes form geometrical isomers. But in this case, *cis* and *trans* are called 'syn' and 'anti', respectively.

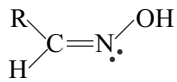
Aldehydes and ketones when react with hydroxylamine, $H_2N–OH$, form oximes.



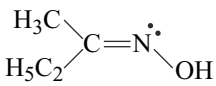
In aldoximes, H and OH are compared.



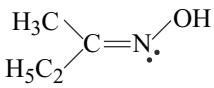
syn-Aldoxime
(H and OH *cis*)



anti-Aldoxime
(H and OH *trans*)

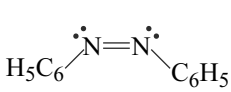


syn-Ethyl methyl ketoxime

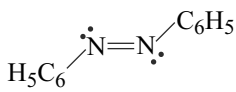


anti-Ethyl methyl ketoxime

The N=N bond has one σ and one π bond. Both N atoms are sp^2 hybridized and this portion of the molecule is planar. The presence of a π bond restricts rotation around N–N σ-bond axis. This rigidity makes the formation of *cis* and *trans* isomers in compounds containing N=N possible, e.g. azobenenes (the –N=N– group is called the azo group).

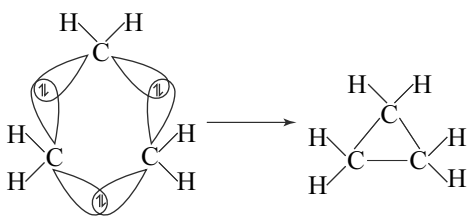


cis-Azobenzene

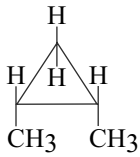


trans-Azobenzene

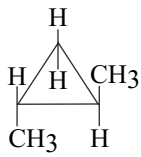
Geometrical Isomerism in Cycloalkanes Cycloalkanes have C–C and C–H σ bonds and C is sp^3 hybridized. The C–C σ bond is a bent bond.



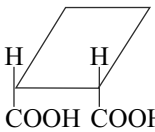
The bonding mode shows that there is a restricted rotation about a C–C bond. This rigidity makes the formation of *cis–trans* isomers in di-substituted cycloalkanes possible, e.g., 1,2-dimethyl cyclopropane exists in *cis* and *trans* forms. In the *cis*-isomer, both CH_3 groups are on the same side (either above or below the plane of the ring) and in the *trans*-isomers, they are on the opposite sides.



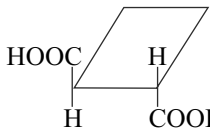
cis-1,2-Dimethyl cyclopropane



trans-1,2-Dimethyl cyclopropane



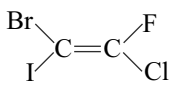
cis-Cyclobutane-1,2-dicarboxylic acid



trans-Cyclobutane-1,2-dicarboxylic acid

E–Z Nomenclature of Geometrical isomers

When C=C contain three or four different groups, it is difficult to assign *cis* or *trans* configuration to the geometrical isomers. Example,



In the above molecule, Br and Cl are *trans* and Cl and I are *cis*. But the problem is how to distinguish them as *cis* or *trans*? To deal with such problems, E–Z nomenclature is used. It is based on the priority rule (first developed to assign configuration to optically active compounds by Cahn, Ingold and Prelog).

Points to Consider for E–Z Nomenclature

1. Priority first ① and second ② is assigned to the groups.
2. Priorities are then compared at the two C atoms (C=C).
3. If the higher priority groups are on the same side of the double bond, the isomer (or the configuration) is Z (Zusammen). (In German, Zusammen means together.) If the higher priority groups are on the opposite side of the double bond, the isomer (or the configuration) is E (Entgegen). (In German, Entgegen means across.)

Rules to Decide Priority

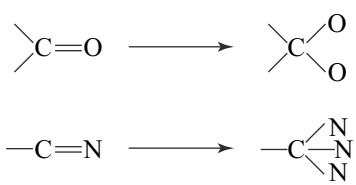
1. Highest priority is given to the atom with the highest atomic number.

$$I > Cl \text{ and } Br > Cl$$

2. Isotopes having higher atomic mass get the higher priority.

$$CD_3 > CH_3$$

3. Double- and triple-bonded atoms are considered to be joined twice and thrice.



Decreasing order of priority for common groups is as follows:

I, Br, Cl, S, F, O, N, C, N

$-C(CH_3)_3$, $-CH(CH_3)_2$, $-CH_2-CH_3$, $-CH_3$

$-COOCH_3$, $-COOH$, $-CONH_2$, $-COCH_3$, $-CHO$

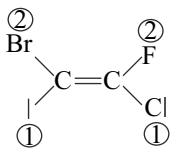
Examples

1. BrIC=CFCl

In this case, I has higher priority over Br.

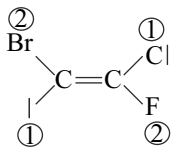
Thus, I ⟶ ① and Br ⟶ ②.

On the other carbon, Cl ⟶ ① and F ⟶ ②.



Z (higher priority groups on the same side)

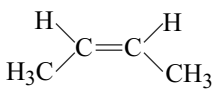
Z-1-bromo-2-chloro-2-fluoro-1-iodoethene



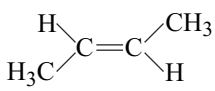
E (higher priority groups on the opposite side)

E-1-bromo-2-chloro-2-fluoro-1-iodoethene

2.

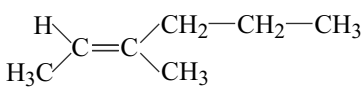


Z-2-butene

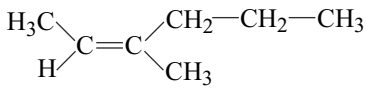


E-2-butene

3.

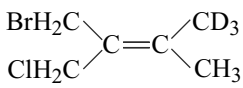


E-isomer

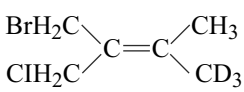


Z-isomer

4.



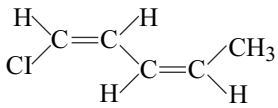
Z-isomer



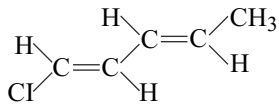
E-isomer

5. 1-Chloro-1,3-pentadiene

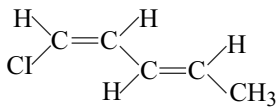
It has four geometrical isomers which are (Z, Z), (E, E), (Z, E) and (E, Z).



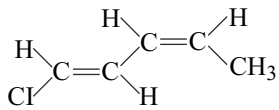
(Z, Z)



(E, E)

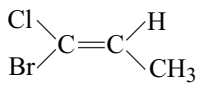


(Z, E)

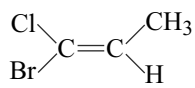


(E, Z)

6. $BrClC{=}CH(CH_3)$ (1-bromo-1-chloropropene)



Z



E

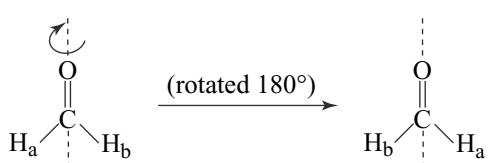
Optical Isomerism

Stereoisomers that are not superimposable on one another are known as 'Optical Isomers' and the phenomenon is called 'Optical isomerism'. Optical isomers have the ability to rotate the plane of polarized light (some may not have this ability). This property of a molecule is called the optical activity, i.e., the ability of a molecule (in liquid or solution) to rotate the plane of polarized light.

If a molecule is superimposable on its mirror image, it is optically inactive. The property of optical activity and optical isomerism is related to a molecular property called 'Symmetry'.

Symmetry

The spatial arrangement of atoms (or groups) in a molecule may impart some amount of symmetry to it. For example, let us consider formaldehyde ($H_2C{=}O$). If this molecule is rotated around C=O axis, a different configuration is not achieved.



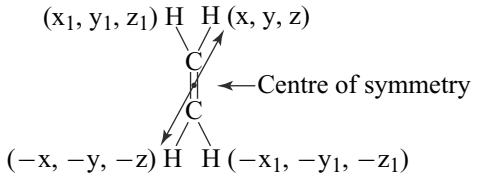
(I) Original (II)

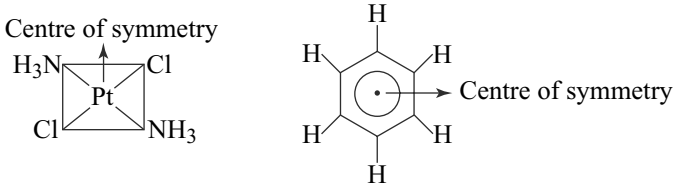
As H atoms (H_a and H_b) are not distinguishable, the new configuration (II) is not different from the original (I). Therefore, it is said that formaldehyde has a rotational symmetry. The following types of symmetry elements are considered here.

1. Centre of symmetry

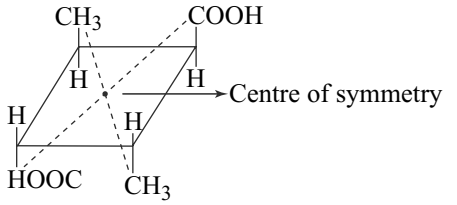
2. Plane of symmetry

Centre of Symmetry It is a point in a molecule such that when a line is drawn from any atom (or group) to this point and is extended on the other side to the same distance, it meets a similar atom. Molecules in which atoms (or groups) are geometrically arranged in this way are said to have a centre of symmetry. Some examples are,

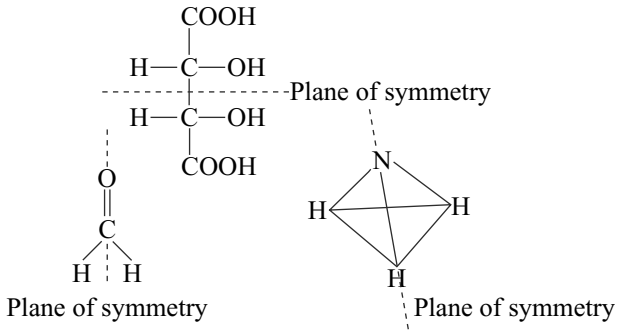




The molecule 2,4-dimethylcycobutane-1,3,-dicarboxylic acid also has a centre of symmetry.



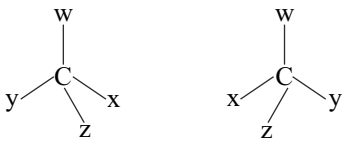
Plane of Symmetry A plane of symmetry bisects a molecule into two parts in such a way so that one part is exactly the mirror image of the other.



The molecules such as C_2H_4 and $[Pt(NH_3)_4]^{2+}$ also have the plane of symmetry. It is the molecular plane.

Plane-Polarized Light Light is an electromagnetic radiation. It has electric and magnetic fields perpendicular to each other, which vibrate in all directions perpendicular to the axis of propagation. But in plane-polarized light, electric field is restricted to a single plane. When ordinary light is passed through a Nicol prism, a plane-polarized light is produced. (Nicol prism is a double prism system made up of calcite, a form of natural $CaCO_3$.)

Chiral Centre and Chirality When a C atom is joined to four different atoms (or groups), e.g., C_{xywz}, it (the C atom) is said chiral centre and denoted as C^*. Such molecules can have two configurations which are not superimposable on each other, e.g., A and B.



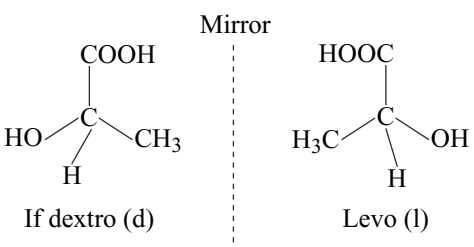
[A] [B]

The property of non-superimposability of a molecule on its mirror image is called chirality (or dissymmetry) and the molecule is called chiral. Chirality is an essential and sufficient condition for optical activity (i.e., optical isomerism). (It was used to deduce tetrahedral nature of carbon.) If a molecule is superimposable on its mirror image, it is called 'Achiral'. Such molecules are optically inactive.

Optical rotation Optical activity is the ability to rotate the plane-polarized light. The optically active isomers are of two types.

1. Dextrorotatory: The isomer that rotates the plane-polarized light to the right (clockwise) is called 'Dextrorotatory'. It is denoted as 'd' or (+).
2. Laevorotatory: The isomer that rotates the plane-polarized light to the left (anticlockwise) is called 'Laevorotatory'. It is denoted as 'l' or (–).

Thus, dextro- and laevo-isomers rotate the plane-polarized light in opposite directions (but in equal amounts), e.g., lactic acid (CH_3C^*H (OH) COOH).



If dextro (d) Levo (l)

Optical rotation is denoted in terms of the specific rotation [α]. It depends on many factors and is given as mentioned below:

for solutions

$$[\alpha]_{\lambda}^{t^{\circ}c} = \frac{\alpha \cdot 100}{l\,c} \text{ and}$$

for pure liquids

$$[\alpha]_{\lambda}^{t^{\circ}c} = \frac{\alpha}{l\,d}$$

where α = observed rotation,
l = length in decimetre of the light path through the solution,
c = concentration, grams of sample per 100 ml of solution,
d = density of the liquid, g/ml,

t°C = temperature of the experiment (i.e., room temperature) and
λ = wavelength of the light used.

The optical rotation is generally measured with sodium D light, λ = 5,893Å.

For example, when a compound is found to have $[\alpha]_D^{t°c} = -100$ (c = 2.5, chloroform), it means that it has a specific laevorotation of 100 degree when c = 2.5 g/100 ml $CHCl_3$, t = 25°C, cell = 1d long and D = 5,893Å.

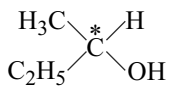
Often molecular rotation [μ] is used in preference to specific rotation. It is given as

$$[M]_\lambda^{t°c} = \frac{[\alpha]_\lambda^{t°c} \cdot M}{100}$$

where M = molecular weight of the optically active compound.

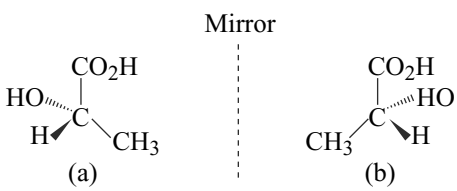
Optical Isomers of Compounds Having Only One Chiral Centre (C*) When a C atom is joined to four different groups, it is called asymmetric carbon or chiral centre, e.g., 2-butanol and 2-hydroxy propanoic acid (lactic acid). Such molecules are not superimposable on their mirror images, i.e., they are dissymmetric and so optically active (dextro and laevo). Therefore, a molecule having only one chiral centre has only two optical isomers (dextro and laevo).

The C-2 in 2-butanol is a chiral centre as it carries four different groups, H, OH, CH_3 and C_2H_5.



In lactic acid, $CH_3\overset{*}{C}H(OH)COOH$, the central C atom is joined to four different groups, H, OH, CH_3 and COOH. Therefore, it is the chiral centre.

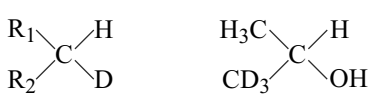
The structure of the molecule is shown below.



Dextrorotatory isomer (+) Laevorotatory isomer (−

If the molecule (a) is reflected through a mirror, the image (b) is not superimposable on the original molecule. Lactic acid, therefore, is a dissymmetric molecule and is optically active. The molecules (a) and (b) are optical isomers. If the molecule (a) is dextro (d) the molecule (*b*) is laevo (*l*), they rotate the plane-polarized light equally but in opposite directions. Such optical isomers are called enantiomers.

Compounds of the type R_1CHDR_2, $CH_3CHOHCD_3$, etc., are also found to be optically active.



It means that isotopic levelling makes the groups different from each other (e.g. CH_3 is not CD_3 and H is not D).

Enantiomers Optical isomers that are mirror images of each other are called enantiomers. They rotate the plane-polarized light equally but in opposite directions. Thus, the dextro and laevo lactic acids are enantiomers. Enantiomers are also called enantiomorphs or optical antipodes.

Properties of enantiomers:

1. They have similar physical properties, except optical rotation.

Table 2.4

Molecule	Enantiomer	Sp. rotation	M.P. (°C)
Lactic acid	+	+3.3	26
	–	–3.3	26
Tartaric acid	+	+11.98	170
	–	–11.98	170

2. Enantiomers are chemically similar, but their rates of reaction with other optically active molecules are different.
3. They differ physiologically, e.g. laevonicotine is more poisonous than dextronicotin and l(+) ascorbic acid (Vitamin C) is more active than d(–).

Racemic Mixture and Resolution An equimolar mixture of enantiomers (i.e., dextro- and laevoisomers) is called 'Racemic Mixture' or *d*, *l*-mixture or racemate. This mixture is optically inactive. It is because equal and opposite rotations of '*d*' and '*l*' isomers cancel each other, i.e., optical rotations are externally compensated.

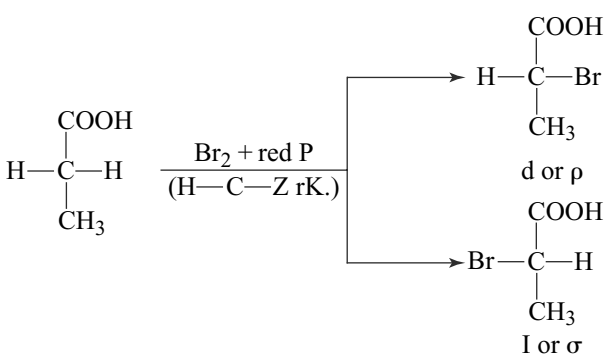
A *d*, *l*-mixture differs in MP, solubility, etc., from the enantiomers.

Table 2.5

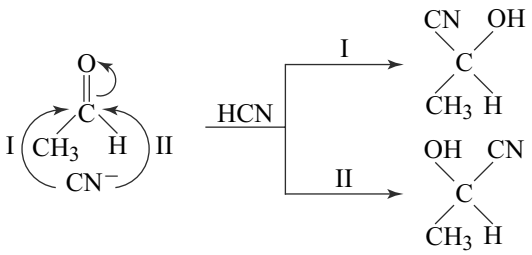
Tartaric acid	M.P. (°C)	Solubility
+ (or *d*)	170	1,390 g/L
– (or *l*)	170	
± (*d*, *l*-mixture)	204–206	206 g/L

The conversion of *d* (or *l*) isomer into a racemic mixture is known as 'Racemization' (see SN^1 reaction). Racemic mixtures (or modifications) can also be produced by synthesis. Example,

1. By conversion of propanoic acid into ρ and σ α-bromopropanoic acid by Hell–Volhard–Zelinsky method (H–V–Z method). It is because each of the two α-hydrogen is equivalent to the rest of the molecule.



2. Addition of HCN to acetaldehyde gives racemic cyanohydrine. It is because approach of CN^{σ} to the planar carbonyl carbon from either side is equally facile.

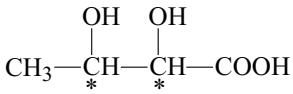


Resolution: The process of separating a racemate into dextro- and laevoisomers is called 'Resolution'. There are many methods of resolution including physical as well as chemical.

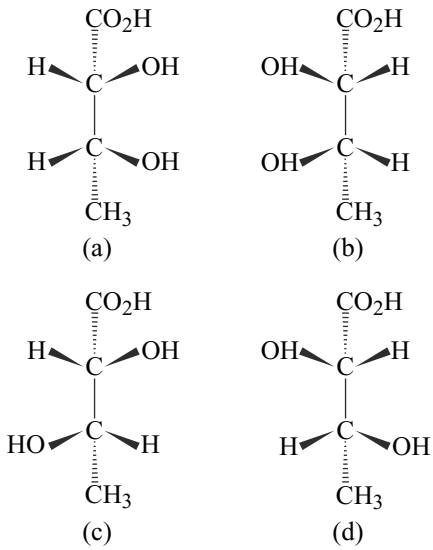
The chemical method of resolution is most common. Small-scale separation is carried out by chromatographic method.

Optical Isomers of Compounds Having Two Dissimilar Chiral Centres When the number of chiral centres in a molecule increases, the number of optical isomers also increases. In general, the number of optical isomers for a compound with n different chiral centres is 2^n.

Thus 2,3-dihydroxybutanoic acid has four optical isomers as it has two distinct chiral centres.



All the four isomers are known. They are shown in Fisher projection below.

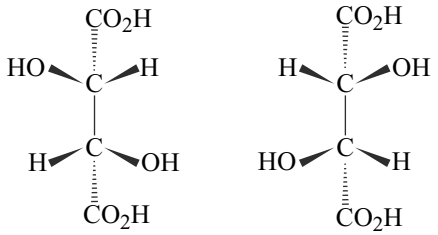


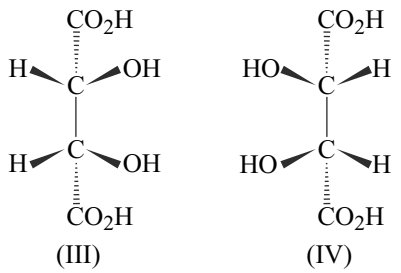
The isomer 'a' is mirror image of 'b', i.e., they are enantiomers. Similarly, 'c' and 'd' is another enantiomeric pair of isomers. However, 'a' and 'c' or 'b' and 'd' are optical isomers but not mirror images of each other (i.e., are not enatiomers). Such optical isomers are called *diastereomers*. Thus, optical isomers, which are not mirror images of each other, are called 'Diastereomers'. They differ both in physical and chemical properties.

Optical Isomers of Compounds Having Two Similar Chiral Centres The most common example of this type is tartaric acid.

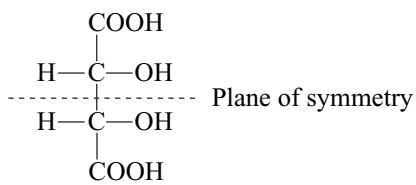
$$HOOC—\overset{*}{C}H(OH)—\overset{*}{C}H(OH)—COOH$$

It has two structurally similar chiral centres. It exists only in three isomeric forms, two of which are optically active dextro- and laevo forms (i.e., enantiomers) and a third form, which is optically inactive, the mesoform. The structures of these forms are shown below.





The structures I and II are mirror images of each other. Thus, they (I and II) represent enantiomeric pair of tartaric acid. The structure III has a plane of symmetry.

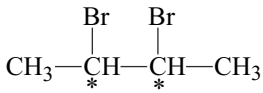


This plane divides the structure in two identical halves. One half is a mirror image of the other. Hence, optical rotation produced by one half is cancelled by the other half. As the optical rotations are equal in degree but opposite in sign, III is optically inactive. It is called the 'meso' tartaric acid. The prefix 'meso' denotes an optically inactive isomer of a compound that can exist in other optically active forms. Optical inactivity in this case is due to the internal compensation. Thus, the three isomers of tartaric acid are *d*, *l* and meso-tartaric acids. The meso-tartaric acid and either of the two '*d*' or '*l*' are diastereomers. Diastereomers have different physical properties.

Table 2.6

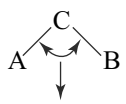
Tartaric acid	M.P. (°C)	Solubility (g/100 g at 25°C) in H_2O
Meso	140	120
+	170	147
–	170	147

The molecule 2,3-dibromobutane is another example of this class.



CONFORMATIONAL ISOMERISM

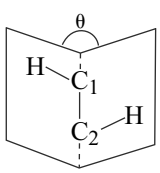
Bond angle: The angle made by two atoms covalently linked to a third atom is called 'Bond Angle' (A and B are linked to C).



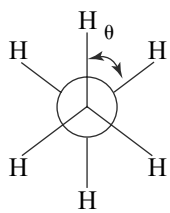
Bond angle

I

Dihedral angle (θ): The angle between two planes containing H–C_1–C_2 and C_1–C_2–H in a molecule H–C_1–C_2–H is called a dihedral angle.



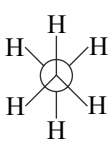
II



III

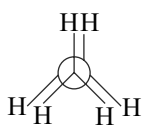
Stagged C_2H_6

Rotation around single bonds: The single bond is a σ bond and the σ molecular orbital is symmetrical around the bond axis (or internuclear axis). Therefore, previously it was thought that rotation around single bond is free. It meant that the potential energy of the molecule is independent of the dihedral angle. But calculations show that potential energy depends upon dihedral angle. For example, an energy barrier of about 12 KJ/mole exists for two arrangements A and B for ethane.



[A]

(Dihedral angle, θ = 60°)



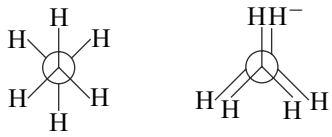
[B]

(Dihedral angle, θ = 0°)

The main reason for energy barrier is thought to be due to the repulsion between filled molecular orbitals. The repulsion is maximum when C–H bonds overlap each other (B, θ = 0º) and is minimum when they are at maximum separation (A, θ = 60º).

Conformational Isomers

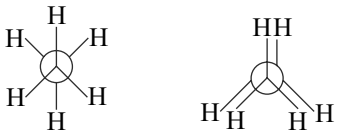
Different arrangements of the atoms of a molecule in the space that can be converted into one another by rotation around a bond are called 'Conformational isomers' or 'Rotamers'. The energy gap between rotamers is small enough to be isolated (for isolation of isomers, an energy gap of about 67 to 84 KJ is required). The rotamers differ in potential energy. The main reason of the energy barrier is the repulsion between filled molecular orbitals. For example, ethane has two rotamers, staggered and eclipsed, which differ in energy by about 12 KJ/mole.



Staggered Eclipsed

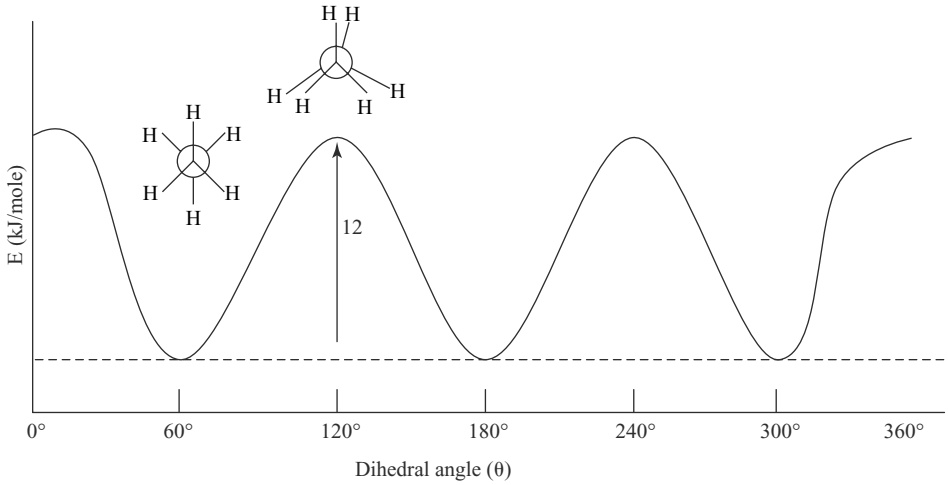
Conformation of Ethane and Propane

The infinite number of arrangements of the atoms in space of a molecule, which result from rotation about a single bond, are called 'Conformations'. Newman projection formula (or Sawhorse formula) is generally used to specify the conformations. The 109.5° angle of a tetrahedral carbon appears as 120° when projected on a plane. When one carbon of ethane is rotated around C–C bond axis, only two extreme situations exist: they correspond to (i) $\theta = 60°$ and (ii) $\theta = 0°$.



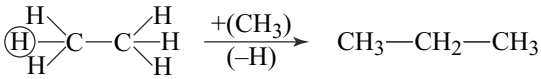
(i) $\theta = 60^{\circ}$ (ii) $\theta = 0°$

The structure (i) is called staggered and (ii) is called eclipsed. The staggered conformation is more stable by about 12 KJ/mole than the (ii). It is because in staggered conformation, H atoms of each C atom are at maximum separation ($\theta = 60°$), whereas in eclipsed conformation they overlap each other ($\theta = 0°$).The energy change with the change in dihedral angle is shown below.

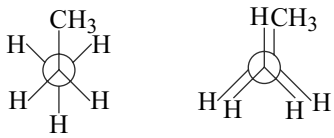


Every point on the curve represents a conformation of ethane, of which I and II are the extremes.

The staggered conformation has lower energy (~12 kJ/mole), and it is the ground state of ethane. As the energy barrier is small, the conformers are not isolable. The case of propane is a bit different. If one H atom of ethane is replaced by CH_3, propane is obtained.



The eclipsed and staggered conformations of propane are shown below.



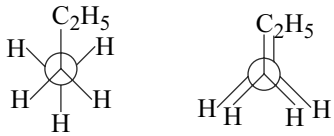
III
Staggered

IV
Eclipsed

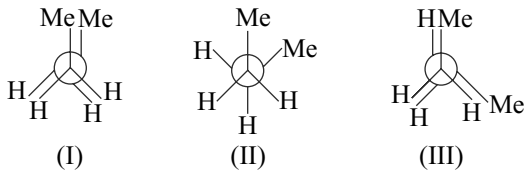
The difference in energies between III and IV is about 14 kJ/mole, which is higher than ethane (12 kJ/mole). This is due to eclipsing of CH_3 and H (CH_3, being larger in size and causes greater repulsion).

Conformation of n-Butane

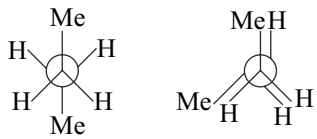
The molecule *n*-butane is represented by CH_3–CH_2–CH_2–CH_3. Rotation around C_1–C_2 or C_3–C_4 bond gives conformers as in propane, with the only difference that CH_3 is replaced by C_2H_5.



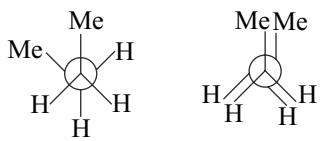
These are of no importance, but rotation around C_2–C_3 bond can give many conformations. They are shown below by Newman projection formulae.



(I) (II) (III)



(IV) (V)

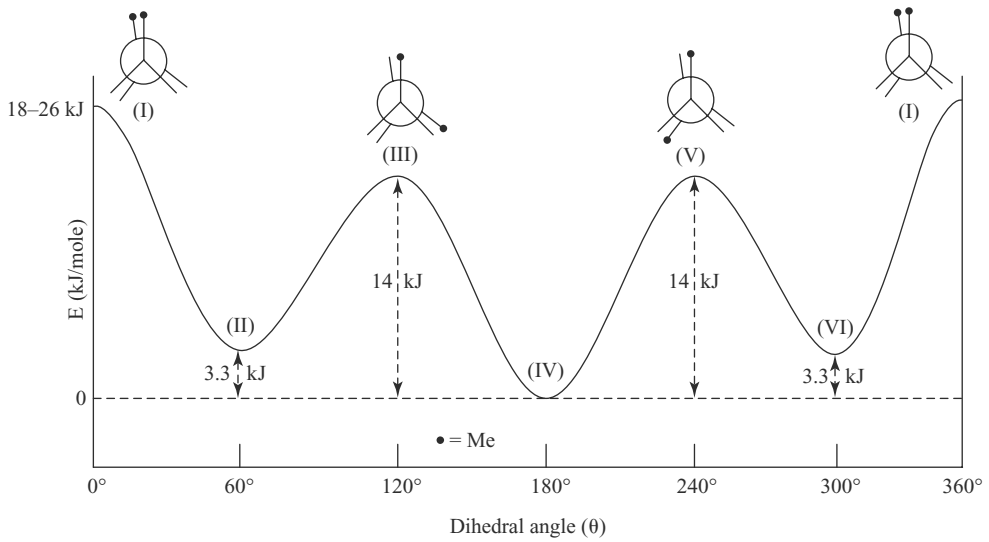


(VI) (I)

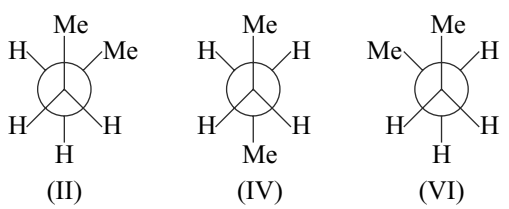
Out of these conformations, there are four extremes.

1. Fully eclipsed (Me and Me eclipsed) called syn-periplanar (I).
2. Partially eclipsed (Me and H eclipsed) called anticlinal (III).
3. Fully staggered (Me and Me looks at 180º) called anti or anti-periplanar (IV).
4. Conformational (Me and Me looks at 60º) called gauche or synclinal (II).

An energy diagram for the conformations of *n*-butane is given below.



The above diagram has three energy minima marked as II, IV and VI. They are actually the three conformers of *n*-butane as shown below



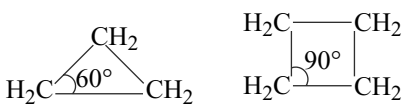
Features of the Conformers

1. The shape of the diagram: The variation of potential energy with torsion angle is approximately sinusoidal. Calculations show that the energy minima conformations (II, IV and VI) correspond to the staggered forms and the energy maxima to the eclipsed forms (I, III and V).
2. Energy barrier: The energy barrier is shown in the diagram.
   (a) (I) has the highest energy as two Me groups are fully eclipsed.
   (b) (III) and (V) have equal energies (~14 kJ). They contain a pair of Me–H and one H–H-eclipsed interactions.
   (c) (IV) has lowest energy and is the most stable.
   (d) (II) and (VI) have equal energies (3.3 kJ).

3. Conformers: The potential energy diagram has three energy minima conformations (II), (IV) and (VI). The following are the three conformers of *n*-butane.
   (a) The conformer marked (IV) with two Me groups oppositely placed ($\theta = 180^\circ$) is the most stable and is called *anti*.
   (b) The conformers (II) and (VI) ($\theta = +60^\circ$ and -60°) are equi-energetic. They have a potential energy of 3.3 kJ/mole above that of (IV).
4. Population of conformers: At low temperature, the stable *anti*-conformer (IV) is present to a large extent. But with the rise in temperature, the population of the less-stable conformer increases and eventually becomes equal to (IV).

Conformation of Monocyclic Compounds

1. Shape of rings: According to Baeyer's strain theory (1885), all ring compounds were supposed to be planar. But to adopt a planar geometry, a molecule must suffer from angle strain due to deviation from the natural tetrahedral angle of 109°28' (Table 2.4). It is supported by the fact that three- and four-membered rings, e.g., cyclopropane and cyclobutane, are most unstable.



The angle strain is defined as,

$$\text{Angle strain} = \frac{1}{2}(109^\circ 28', \text{actual bond angle})$$

Table 2.7 Angle strain in cycloalkanes

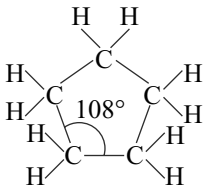
Ring size	Three	Four	Five	Six	Seven
The C–C angle for planar ring	60°	90°	108°	120°	128°34′
Strain	24°44′	9°44′	44′	–5°16′	–9°33′

Table 2.4 shows that five- and six-membered rings, in which angle strain is small, are stable and easily formed. But higher membered rings (greater than seven) in which angle strain is again high are difficult to form. The angle strain sets in the molecule by compressing (or expanding) C–C–C angle from the tetrahedral angle of 109°28′ to adopt planar structure. But the shape of cyclic compounds, e.g. cyclopentane and cyclohexane, are not planar (tetrahedral theory of Le Bel and van't Hoff). The rings actually have 'puckered' structure, to be relieved from the angle strain.

Cyclopentane is a stable molecule. But if it has a planar regular pentagonal configuration, it will have

1. a small angle strain (44) and
2. all 10 adjacent pairs of C–H bonds into the eclipsed arrangement.

These two factors distort cyclopentane from the planar to a slightly puckered configuration.



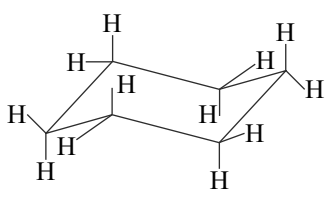
Cyclopentane
(C atoms planar)

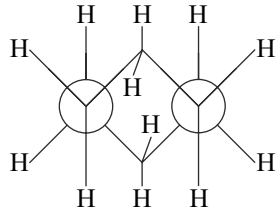
Cyclopentane
(Puckered)

Conformations of Cyclohexane If C atoms of cyclohexane were to remain coplanar, the C–C–C bond angles would be 120º. It sets appreciable angle strain in cyclohexane. The ring is, therefore, puckered and has two extreme conformations, the *boat* form and the *chair* form. These two forms are almost free of angle strain.

Chair form

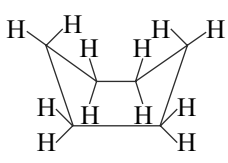
Angle strain is negligible and all H atoms are fully staggered.

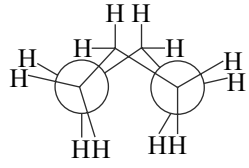




Boat form

1. Angle strain is negligible.
2. The H atoms at C_1 and C_4 are very close, (1.8Å). This separation is less than the sum of the Van der Waals radii of two H atoms (2.4Å). It causes enough nonbonded repulsion, which is called flag–pole interaction.
3. The C_2–C_3 and C_5–C_6 pairs of C–H bonds are eclipsed.



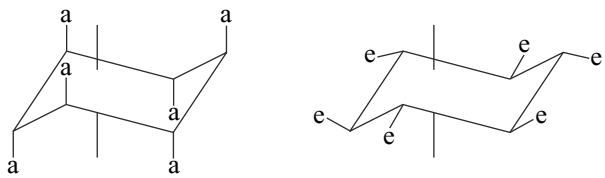


The above points show that total strain in the boat form is greater than that in the chair form. The chair form is, thus, more stable than the boat form. Therefore, cyclohexane exists mostly in the chair form at room temperature. The energy gap between the two forms is about 25 KJ/mole (the chair shape of cyclohexane has been confirmed by X-ray analysis and electron diffraction as well as by Raman and IR spectra).

Axial and equatorial bonds

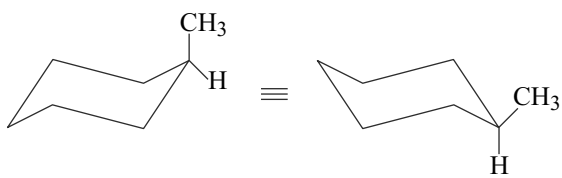
Two types of C–H bonds are present in the cyclohexane chair form.

1. Six C–H bonds lie in a plane around the cycle of the C atoms. These are called equatorial hydrogens (H_e).
2. The rest six C–H bonds lie above and below (shown alternately) the plane of the carbon ring. These are called axial hydrogens (H_a).



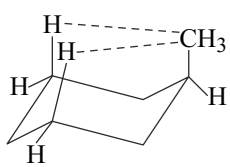
Conformation of Monosubstituted Cyclohexane The stable conformation of cyclohexane in normal condition is chair form. It has two types of C–H bonds, the axial (pointing up and down in the ring) and the equatorial (present in the plane of the C ring). Substituents attached to these bonds are called 'Axial and Equatorial Substituents'. Therefore, two isomeric monosubstituted cyclohexanes are possible, one with the substituent in the axial position (A) and the other with the substituent in the equatorial position (E), i.e., the two methylcyclohexanes.

It is not possible to isolate the two forms. It seems that they interconvert rapidly at room temperature causing a substituent in the axial position to go to the equatorial position and vice versa. Thus, methylcyclohexane is an equilibrium mixture of these two forms.



(A) (E)

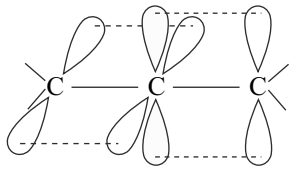
The above structure (A) shows that the axial H atoms at C_3 and C_5 are close to CH_3 group at C_1. On the other hand, no H atoms approach the equatorial CH_3 so closely. Thus, nonbonded steric repulsion is greater in the axial isomer and it is less stable than the equatorial one. The energy gap between the two isomers is about 7.5 KJ/mole.



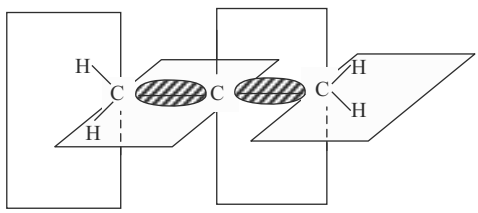
The interaction between CH_3 (at C_1) and axial hydrogens (at C_3 and C_5) is known as 1,3-diaxial interaction.

Optical Activity of Allenes, Spiranes

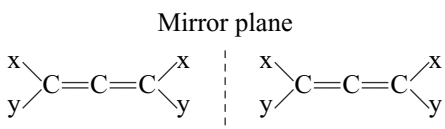
Allenes Allenes have the carbon skeleton $\diagdown C{=}C{=}C \diagup$. Here, the central carbon is sp hybridized, whereas terminal ones are sp^2 hybridized. The two p orbitals on the central C atom are perpendicular to each other and each overlap with the p orbitals of one adjacent C atom.



Thus, in a molecule of allene, the two planes that contain the terminal methylene (CH_2) groups are mutually perpendicular because of the rigidity and directional character of the two cumulated double bonds.

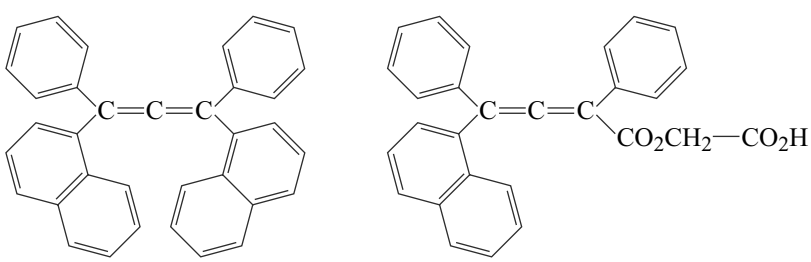


Consequently, an allene of the type *xy*C=C=C*xy*, in which x is not y, is asymmetric and can exist in two, non-superimposable, optically active forms.



The optical isomerism of allenes was predicted by van't Hoff about 60 years before and experiments now have proved him to be correct.

The first successful resolutions were achieved with the allenes I and II.

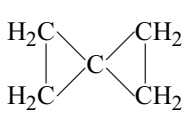


(I) (II)

Later on, many optically active allenes have been obtained.

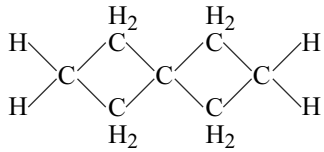
The antibiotic mycomycin is an allene derivative, which occurs in nature in the optically active form.

Spiranes A class of bicyclic compounds with one atom (and only one) common to both the rings are known as 'spiranes'. The simplest example is spiro [2,2] pentane.

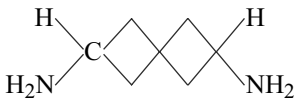


(I)

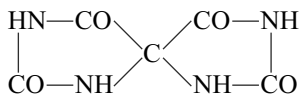
The two rings of I, or any spirane, cannot lie in a common plane, they are rather orthogonal and the group attached at the two ends define planes at right angles to the adjacent ring and to each other. Consequently, properly substituted spiranes may be resolvable.For example, spiro [3,3] heptane has a plane of symmetry and is not resolvable.



The plane of symmetry may be destroyed either by attaching two unequal groups at the sides of the ring or by introducing suitable groups within the ring, e.g.

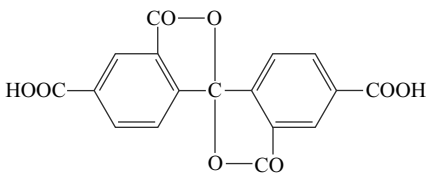


Active



Active
(5,5′spirobihydantoin)

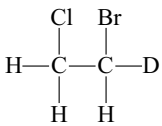
The first spirane, ever to be resolved, was of the type

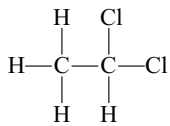


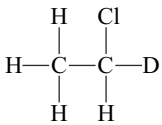
PROBLEMS

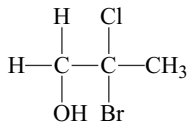
Objective-Type Questions

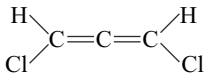
1. Which of the following have asymmetric C atoms?

(a) 

(b) 

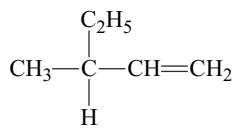
(c) 

(d) 

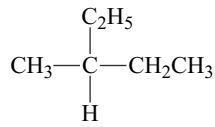
2. 1,3-Dichloroallene  shows

(a) geometrical isomerism (b) optical isomerism
(c) both (a) and (b) (d) none

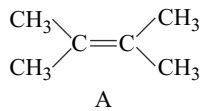
3. An optically active compound 'A' having molecular formula C_6H_{12} gives inactive compound 'B' upon hydrogenation. A and B are

(a) 

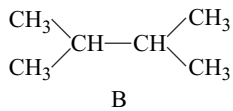
A

(b) 

B

(c) 

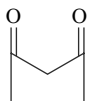
A

(d) 

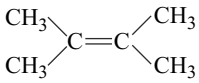
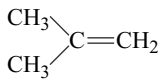
B

4. Which of the following has maximum enol content?

(a) Acetaldehyde (b)

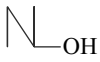
(c) Acetyl acetaldehyde (d) 

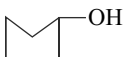
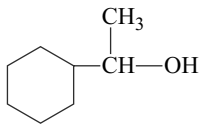
5. Which one of the following alkene, when reacted with HCl, produces racemic mixture?

(a)  (b) 

(c) $CH_3—CH_2—CH=CH$ (d) $CH_3CH=CH_2$

6. Which of the following can be resolved?

(a) (b) 

(c)  (d) 

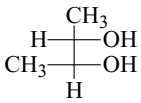
7. Correct configuration of the given structure is

(a) 1S, 2S

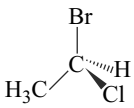
(b) 1S, 2R

(c) 1R, 2S

(d) 1R, 2R



8. The chirality of the compound

 is

(a) R (b) S (c) E (d) Z

9. In the following reaction

$$CH_3CHO + HCN \longrightarrow CH_3CH(OH)CN \xrightarrow{H\cdot OH} CH_3CH(OH)COOH$$

an asymmetric centre is generated. The acid obtained would be

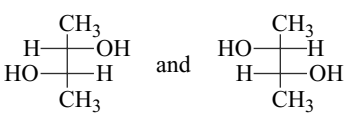
(a) *d*-isomer

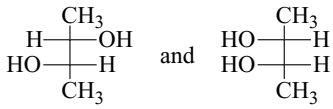
(b) *l*-isomer

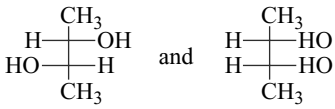
(c) 50% *d* + 50% *l*-isomer

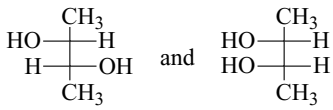
(d) 20% *d* + 80% *l*-isomer

10. Which of the following pairs of compounds are enantiomers?

(a) 

(b) 

(c) 

(d) 

11. A carbonyl compound reacts with hydrogen cyanide to form cyanohydrin which on hydrolysis forms a racemic mixture of α-hydroxy acid. The carbonyl compound is

(a) acetone (b) diethyl ketone

(c) formaldehyde (d) acetaldehyde

12. Which of the following is not chiral?

(a) 2,3-Dibromopentane

(b) 3-Bromopentane

(c) 2-Hydroxypropanoic acid

(d) 2-Butanol

13. Of the five isomeric hexanes, the isomer which can give two monochlorinated compounds is

(a) *n*-hexane

(b) 2,3-dimethylbutane

(c) 2,2-dimethylbutane

(d) 2-methylpentane

14. Which type of isomerism is shown by 2,3-dichlorobutane?

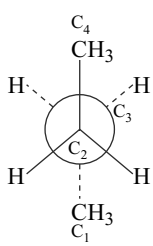
(a) Diastereo

(b) Optical

(c) Geometric

(d) Structural

15. In the given conformation, C_2 is rotated about C_2–C_3 bond anti-clockwise by an angle of 120°. The conformation then obtained is



(a) Fully eclipsed conformation

(b) Partially eclipsed conformation

(c) Gauche conformation

(d) Staggered conformation

16. On monochlorination of 2-methylbutane, the total number of chiral compounds is
(a) two (b) four (c) six (d) eight

17. Which of the following is used for the conversion of 2-hexyne into *trans*-2-hexane?
(a) $H_2/Pd/BaSO_4$ (b) H_2, PtO_2
(c) $NaBH_4$ (d) $Li–NH_3/C_2H_5OH$

18. The compound which is not isomeric with diethyl ether is
(a) *n*-propyl methyl ether (b) 1-butanol
(c) 2-methyl-2-propanol (d) butanone

19. The maximum number of isomers for an alkene with the molecular formula C_4H_8 is
(a) two (b) three (c) four (d) five

20. Which of the following compounds will exhibit *cis–trans* (geometrical) isomerism?
(a) 2-Butene (b) 2-Butyne
(c) 2-Butanol (d) Butanal

21. Only two isomeric monochloro derivatives are possible for
(a) *n*-butane (b) 2, 4-dimethyl pentane
(c) benzene (d) 2-methylpropane

22. The number of isomers of C_6H_{14} is
(a) four (b) five (c) six (d) seven

23. The number of structural and configurational isomers of a bromo compound C_5H_9Br, formed by the addition of HBr to 2-pentyne, respectively, are
(a) one and two (b) two and four
(c) four and two (d) two and one

24. Keto–enol tautomerism is observed in

(a) $H_5C_6—\overset{\overset{O}{\|}}{C}—H$

(b) $H_5C_6—\overset{\overset{O}{\|}}{C}—CH_3$

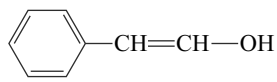
(c) $H_5C_6—\overset{\overset{O}{\|}}{C}—C_6H_5$

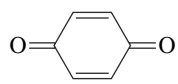
(d) $H_5C_6—\overset{\overset{O}{\|}}{C}—CH_2—\overset{\overset{O}{\|}}{C}—CH_3$

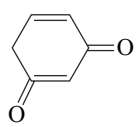
25. The enolic form of acetone contains
(a) 9 sigma bonds, 1 pi bond and 2 lone pairs
(b) 8 sigma bonds, 2 pi bonds and 2 lone pairs
(c) 10 sigma bonds, 1 pi bond and 1 lone pair
(d) 9 sigma bonds, 2 pi bonds and 1 lone pair

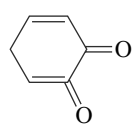
26. Which of the following compounds will show geometrical isomerism?
(a) 2-Butene (b) Propene
(c) 1-Phenylpropene (d) 2-Methyl-2-butene

27. Tautomerism is exhibited by

(a) 

(b) 

(c) 

(d) 

28. The enol form of acetone after treatment with D_2O gives

(a) $CH_3—\overset{\overset{OD}{\|}}{C}=CH_2$ (b) $CD_3—\overset{\overset{O}{\|}}{C}—CD_3$

(c) $CH_2=\overset{\overset{OH}{\|}}{C}—CH_2D$ (d) $CD_2=\overset{\overset{OD}{\|}}{C}—CD_2$

29. The optically active tartaric acid is named as D-(+)-tartaric acid because it has a positive
(a) optical rotation and is derived from *d*-glucose
(b) pH in organic solvent
(c) optical rotation and is derived from *d*-(+)-glyceraldehydes
(d) optical rotation only when substituted by deuterium

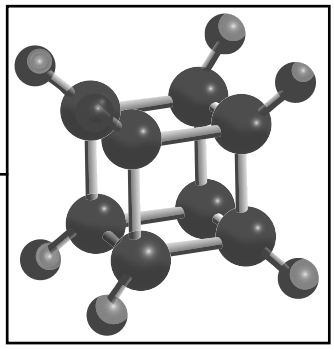
30. A solution of (+) 2-chloro-2-phenylethane in toluene racemizes slowly in the presence of small amount of $SbCl_5$ due to the formation of
(a) carbanion (b) carbine
(c) free radical (d) carbocation

31. Which of the following compounds will exhibit geometrical isomerism?
(a) 1-Phenyl-2-butene
(b) 2-Phenyl-1-butene
(c) 2-Phenyl-1-butene
(d) 1,1-Diphenyl-1-propene

Answers

1. a, c, d	2. b	3. a, b	4. c	5. c
6. b, c, d	7. d	8. a	9. c	10. a
11. d	12. b	13. b	14. b	15. c
16. b	17. d	18. d	19. a	20. a
21. a, d	22. b	23. b	24. d	25. a
26. a, c	27. a	28. b	29. c	30. d
31. a				

CHAPTER 3



Electron Shift

The distribution of bond-pair electrons between atoms in a molecule determines its behaviour. For example,

1. Between CH_4 and CH_3Cl, the latter is highly reactive whereas CH_4 is much less reactive (CH_4, a paraffin). It is all due to the fact that C–Cl bond in CH_3Cl is polarizable, making Cl partially negative and C partially positive (Cl is more electronegative than C).

$$H_3C\overset{\delta+}{\text{—}}\overset{\delta-}{Cl}$$

2. Unsaturated molecules such as C_2H_4 and HCHO are also highly reactive. Such species contain both σ and π bonds. The π electrons are loosely bonded and easily polarizable which makes these molecules reactive.

Thus, polarization of a bond-pair electron is closely related with the reactivity of the molecules. Polarization of a bond-pair electron may broadly be classified into two groups: (i) permanent polarization and (ii) temporary polarization.

PERMANENT POLARIZATION

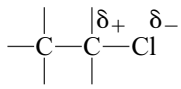
It is of different types: (i) inductive effect, (ii) resonance (or mesomeric effect) and (iii) hyperconjugation.

TEMPORARY POLARIZATION

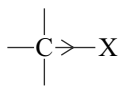
It is of two types: (i) electromeric effect and (ii) steric effect.

Inductive Effect

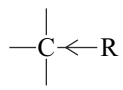
It is the polarization of σ-bond electrons. A σ bond between two unlike atoms is always polar. The negative end is towards the more electronegative atom. Thus, in an alkyl halide, halogen end is negative.



The chlorine atom being more electronegative attracts bond pair electrons. It, therefore, becomes partially negative. Such groups are called electron-attracting (or -withdrawing) groups. Other common electron-attracting groups are: $–NO_2$, –CN, >C=O, $–SO_3H$, etc. Many groups have reverse effect, i.e., they increase electron density at a C in a chain, e.g., alkyl groups.



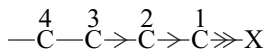
X = electron-attracting group (−I effect)



R = electron-donating group (+I effect)

Electron shift of such a type is called 'Inductive Effect'. Thus, it may be defined as 'the electron shift caused by the permanent polarization of a bond in the ground state of a molecule.

This effect may be transmitted in a chain.



However, the effect weakens with distance, being too small beyond C_2 and almost dies away at C_3 in a saturated chain.

Electronegativity of an atom changes with the state of its hybridization. A sp-hybridized C is more electronegative than sp^2, which in turn is more electronegative than sp^3. It is due to difference in the s character of the hybrids. Thus, electron-attracting power (i.e., –I effect) of C sharply decreases in the following order:

$$C—sp > C—sp^2 > C—sp^3$$

Order of inductive effect

The groups are either electron-attracting (–I effect) or electron-donating (+I effect) group. The following is the order of the decreasing inductive effect.

–I effect: R_3N^+, H_3N^+, NO_2, SO_3H, CN, COOH, F, Cl, Br, I, OR, OH

+I effect: O^-, CO^-_2, Me_3C, Me_2CH, $MeCH_2$, CH_3

Characteristics of inductive effect

1. It involves σ electrons.
2. It is a permanent effect.
3. It is a weak effect.
4. Valence shell of the bond pair is not changed.

5. It almost dies away at third C atom in a chain.
6. Hybrid state of C decides its I effect.

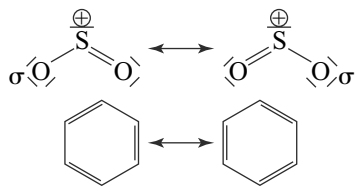
Applicability of inductive effect

1. To decide acid–base strength.
2. Stability of reaction intermediates.
3. Reactivity of a substrate.

Resonance

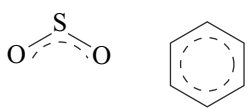
Many chemical species may have more than one perfect Lewis structure (or valence bond structure). This phenomenon is called resonance and the structures are known as resonating structures or canonical forms. The structures are written putting double-head arrow (↔) between them.

The concept of resonance was introduced in valence bond model by L. Pauling, to explain molecular properties like bond energy, bond length and bond angle, e.g., SO_2 and C_6H_6.



$$CH_2{=}CH{-}CH{=}CH_2 \longleftrightarrow \overset{\rho}{C}H_2{-}CH{=}CH{-}\overset{\sigma}{C}H_2$$

In SO_2, the S–O single and double bonds should not be equal. However, both the S–O bonds are equal. It is because the actual molecule is represented by neither of the structures. It is actually a resonance hybrid of both the structures and so both S–O bonds are equal. The resonance structures have no physical reality, i.e., they cannot be synthesized or isolated.



Resonance hybrids

Rules of resonance

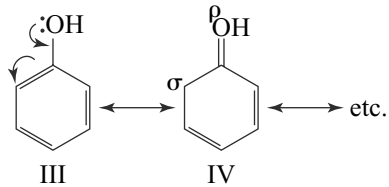
1. The position of nuclei should remain fixed in all the structures.
2. The molecule (or ion) should be planar (or nearly so).
3. Number of lone pairs should be equal in all the structures.
4. The structures should have comparable energy.
5. The energy of the actual molecule is lower than that of any form.
6. All the structures do not contribute equally to the true molecule.

Rules to decide stability of the resonance structure

1. Structures with more covalent bonds are more stable.

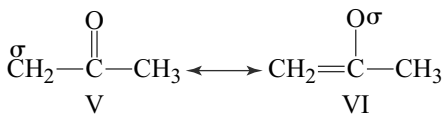
I is more stable as it has more bonds.

2. Charge-separated structures are less stable.



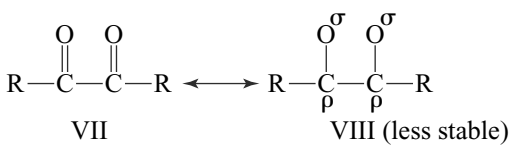
III is more stable, as it has no charge separation.

3. Structures' having negative charge on more electronegative atom is more stable.



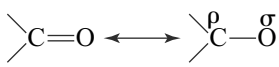
VI is more stable.

4. Structures having similar charge on adjacent atoms are less stable.

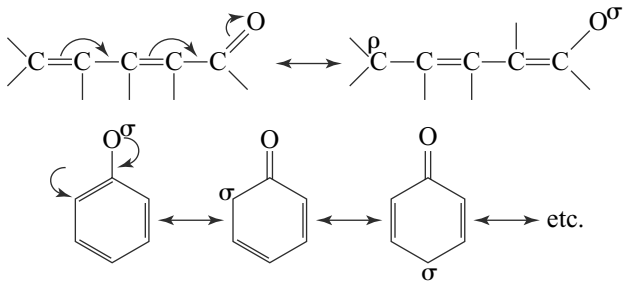


Resonance effect

Resonance always stabilizes a molecule or an ion or a reaction intermediate. The stabilization, which a chemical species achieve by resonance, is called 'Resonance Effect' or mesomeric effect. It is due to delocalization of π electrons. A carbonyl group, >C=O, is a resonance hybrid of the following structures.

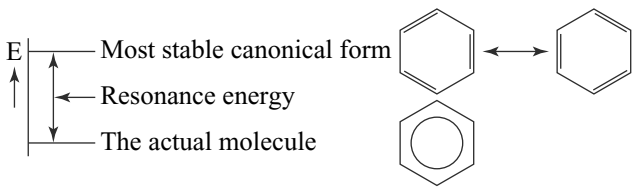


Thus, when C=O is conjugated with C=C the electron shift is transmitted in the chain even to a long distance.

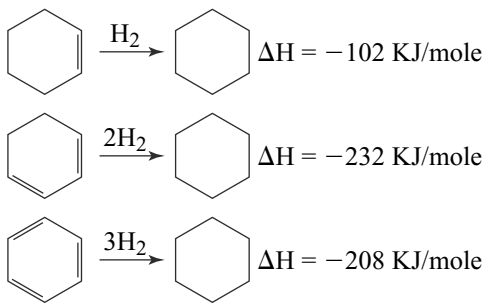


Resonance energy

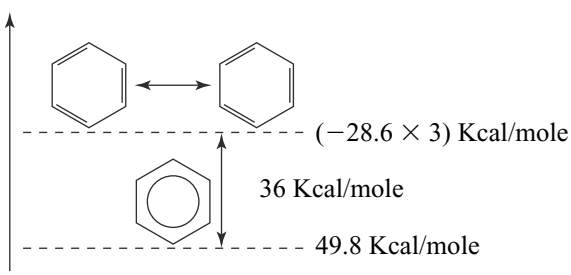
Resonance stabilizes a molecule, i.e., the resonance hybrid has lower energy compared even to the most stable resonating structure. The difference in the energies between the resonance hybrid and the most stable resonating structure is known as the resonance energy.



It is generally calculated from heat of hydrogenation and heat of combustion data. For C_6H_6, the resonance energy obtained by either method is close to about 36 Kcal/mole.



The heat of hydrogenation of cyclohexene is −28 Kcal/mole. For cyclohexadiene it is −55.6 Kcal/mole, i.e., very near to -28.6×2. Thus, for C_6H_6 it should be $-28.6 \times 3 = 85.8$ Kcal/mole. But for benzene it is only −49.8 Kcal/mole. The difference (85.8 − 49.8) 36 Kcal/mole is the resonance energy of the benzene. Thus, benzene is said to be stabilized by the resonance to the extent of 36 Kcal/mole. R. E. is also called the stabilization or the delocalization energy.



Resonance energies of fused systems increase as the number of principal canonical forms (Kekule structures) increase.

Table 3.1

Molecule	Forms	Resonance energy (Kcal/mole)
Benzene	2	36
Naphthalene	3	61
Arthracene	4	84
Phenanthrene	5	36

Resonance energy of Furan, Pyrole and Thiophene are 16, 21 and 29, respectively. This indicates the increasing effectiveness of delocalization of the lone pair of electrons at the heteroatom as the electronegativity of the heteroatom decreases in the order

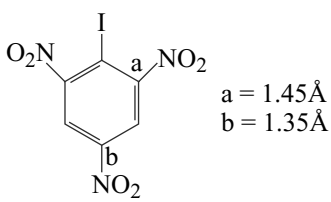
$$O > N > S.$$

Thus, Furan has more diene character and so it gives Diels–Alder reaction.

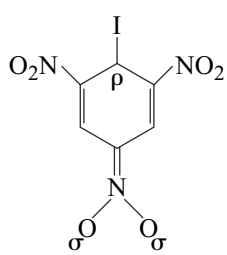
Steric inhibition of resonance

For resonance, planar structure is a precondition. But many times, steric interaction destroys planarity of structure that prevents (or reduce) resonance. It is called steric inhibition of the resonance. It has effect on bond length, acid–base strength, etc. (see base strength).

For example, C–N bond lengths for *o*- and *p*-nitro groups in picryl iodide are very different.



Here, *o*-nitro groups are forced out of the plane of the ring due to the steric interaction with large iodine atom. So, they cannot establish resonance. But the *p*-NO_2 group remains in the plane of the ring and enters into resonance. C–N bond has double bond nature. It is, therefore, shorter.



Characteristics of resonance

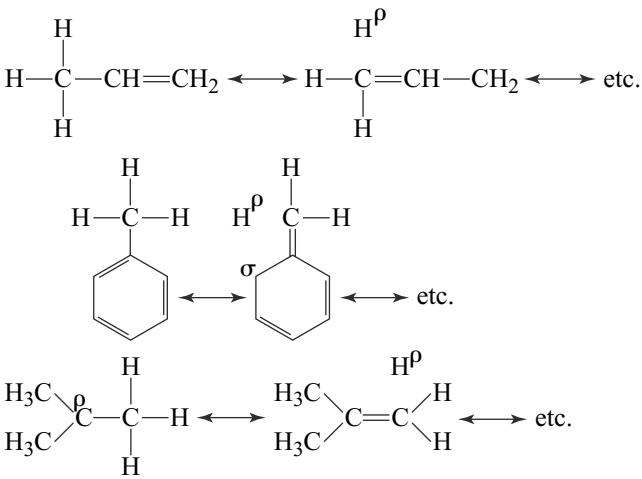
1. It is a permanent polarization.
2. It involves π electrons.
3. It occurs in unsaturated conjugated system.
4. It is transmitted over to a large distance provided that there is conjugation.
5. It imparts stability to a chemical species.
6. It is a much stronger effect than inductive effect and dominates when both operate together.

Hyperconjugation

The C–H σ-bond electrons can also take part in delocalization. It becomes possible when a C–H σ bond is adjacent to a

1. conjugated system,
2. positive centre and
3. free radical centre.

Thus, the delocalization caused due to the involvement of C–H σ electrons may be called hyperconjugation. The structures, which are produced, are called 'Hyperconjugative Structrues'.



As there is no bond between C and H in the hyperconjugative structures, it is also called no-bond resonance. The structures above show that the number of structures will depend on H attached to C atoms and α to the unsaturated centre. Thus, the number of structures will be maximum with CH_3 and will not operate at all with $(CH_3)_3C$. The order of decreasing hyperconjugative effect is thus,

$$CH_3 > CH_3CH_2 > (CH_3)_2CH > (CH_3)_3C$$

Hyperconjugation is important for excited state of molecules, e.g., for carbocations and for free radicals.

Applicability of hyperconjugation

1. To explain stability of alkenes

Heat of hydrogenation of an alkene is a measure of its stability. The lower is the heat of hydrogenation the greater is the stability of the alkene and vice-versa. Alkyl substitution at unsaturated C lowers the heat of hydrogenation and, therefore, increases stability. It is due to the hyperconjugative effect.

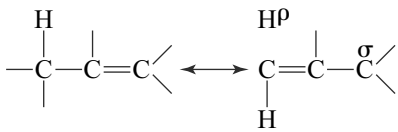
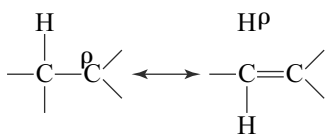


Table 3.2

Alkene	Hyperconjugative structures	Heat of hydrogenation Kcal/mole
$H_2C=CH_2$	0	31.0
$CH_3–CH=CH_2$	3	28.5
$CH_3–CH=CH–CH_3$ (*cis*)	6	27.0
$CH_3–CH=CH–CH_3$ (*trans*)	6	25.7

2. Stability of carbonium ions

Carbonium ions contain positive carbon atom. The hyperconjugative interaction spreads positive charge over alkyl groups and, thus, increases stability.



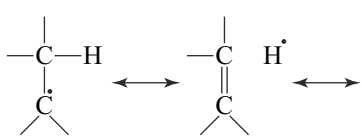
The stability order for different carbonium ions found is,

$$(CH_3)_3\overset{\rho}{C} > (CH_3)_2\overset{\rho}{C}H > CH_3\overset{\rho}{C}H_2 > \overset{\rho}{C}H_3$$

Strs (9) (6) (3) (0)

3. Stability of free radicals

A free radical has a half-filled orbital at C atom. The hyperconjugative effects fill this orbital and stabilize the radical.

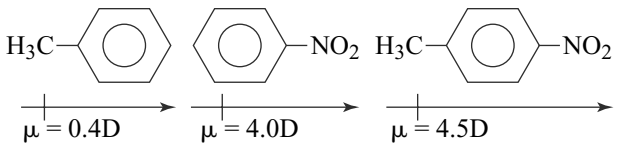


The stability order for different free radicals is

$$(CH_3)_3\dot{C} > (CH_3)_2\dot{C}H > CH_3\dot{C}H_2 > \dot{C}H_3$$

Strs (9) (6) (3) (0)

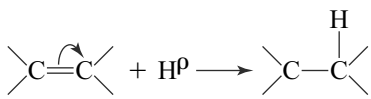
4. To account for dipole moment of compounds



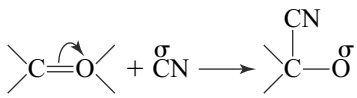
Electromeric Effect (E Effect)

It is temporary polarization of a π bond. It may be defined as the complete transfer of π electrons to one of the bonded atoms at the demand of a reagent. It is thus, a time-variable effect. Two types of such electron shifts are encountered.

1. +E effect: When the electron shift and the demand of the reagent are unidirectional, it is called +E effect.



2. –E effect: When the electron shift and the demand of the reagent take place in opposite directions it is called –E effect.



The CN^- joins with C and the π electrons shift over to O atom.

Characteristics of electromeric effect

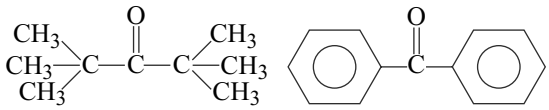
1. It is a temporary effect (time variable).
2. It involves π electrons.
3. It occurs at the demand of a reagent.
4. It is a strong effect.
5. Valence shell of the bond pair is changed.

Steric Effects

In addition to electronic effects, reactivity may also be influenced by sheer bulk of an atom or a group. It is called 'Steric Effect'. It may be defined as 'The non-bonded interaction between groups present in a molecule

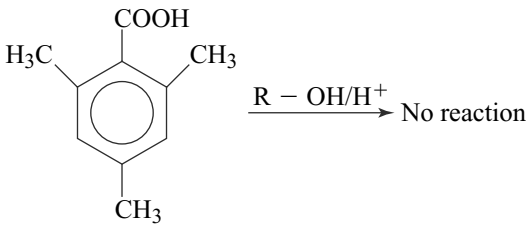
may be called 'Steric Effect'. At times, size of the reagent may also affect reactivity. It is also a steric effect. This effect can account various chemical changes. For example,

1. Cyanohydrins are not formed by the ketones of the type

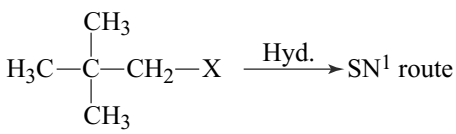


It is because >C=O groups are joined with large groups, which restricts approach of reagent to the carbonyl carbon.

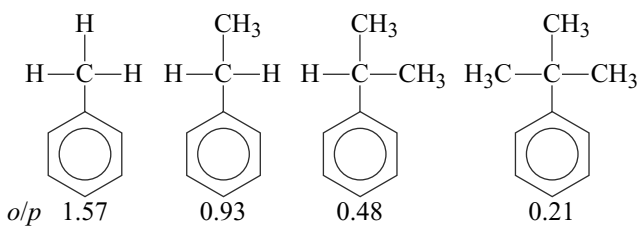
2. Mesotoic acid (2,4,6-trimethylbenzoic acid) is neither esterified under normal acid catalysis condition nor is hydrolyzed.



3. Neopentyl halides (a primary halide) are slow in SN^2 reactions. They rather react by SN^1 mechanism.



4. The steric effect is clearly seen in the *o/p* ratio of nitration of different alkyl benzenes.



5. Acid–base strength, bond length, elimination reaction, etc. are also influenced by steric effect.

PROBLEMS

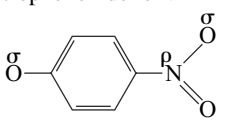
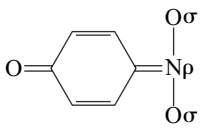
Objective-Type Questions

1. Which of the following carbonium ions is most stable?
(a) $Ph_3\overset{\oplus}{C}$ (b) $(CH_3)_2\overset{\oplus}{C}H$
(c) $CH_3\overset{\oplus}{C}H_2$ (d) $CH_2{=}CH{-}\overset{\oplus}{C}H_2$

2. Consider the following reaction:

$CH_3{-}CHD{-}CH(CH_3){-}CH_3 + Br \longrightarrow X + HBr$

The major product X is
(a) $CH_3 - CHDCH(CH_3)\dot{C}H_2$
(b) $CH_3 - CHD\,\dot{C}(CH_3)CH_3$
(c) $CH_3 - \dot{C}DCH(CH_3)CH_3$
(d) $CH_3 - \dot{C}HCH(CH_3)CH_3$

3. Which is the most unlikely resonance structure of *p*-nitrophenoxide ion?
(a)

(b)

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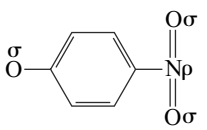
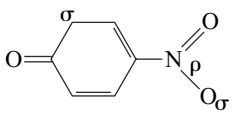
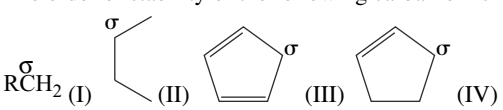
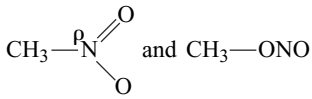
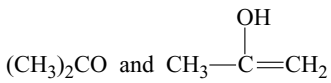
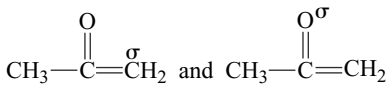
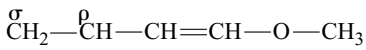
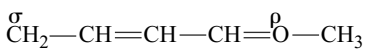
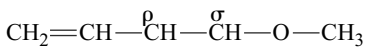
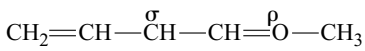

(d)


4. The order of stability of the following carbanion is

(a) I > II > III > IV (b) I > III > II > IV
(c) IV > III > II > I (d) III > IV > I > II

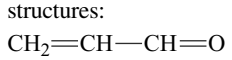
5. Hyperconjugation can explain stability of which of the following?
(a) Carbonium ion (b) Carbanion
(c) Carbenes (d) Free radicals

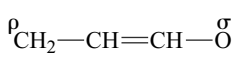
6. Which one is expected to be the most stable alkene?
(a) $(CH_3)_2CHCH{-}CHCH(CH_3)_2$
(b) $(C_2H_5)_2C{=}C(C_2H_5)_2$
(c) $(CH_3)_2C{=}C(CH_3)_2$
(d) $((CH_3)_2CH)_2C{=}C(CH(CH_3)_2)_2$

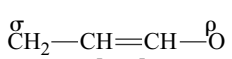
7. Which of the following pairs is a resonance structure?
(a)

(b)

(c)

(d) $CH_3{-}CH{=}CH{-}CH_3$

8. For 1-methoxy-1, 3-butadinene, which of the following resonating structure is least stable?
(a)

(b)

(c)

(d)


9. Acrolein (prop-2-en-1-al) has the following resonating structures:

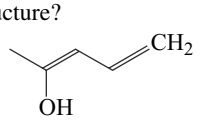
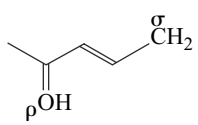
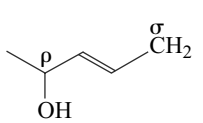
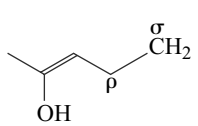

[I]


[II]


[III]

The decreasing order of the stability of the structures is represented by
(a) I > II > III (b) III > I > II
(c) II > III > I (d) III > II > I

10. Consider the carbocations $\overset{\oplus}{C}H_3$ (I), $\overset{\oplus}{C}F_3$ (II) and $CF_3\overset{\oplus}{C}H_2$ (III); mark the correct stability order.
(a) I > II > III (b) II > I > III
(c) III > II > I (d) III > I > II

11. Which of the following is the most stable resonance structure?
(a)

(b)

(c)

(d)


12. Diazomethane can be represented by the following resonance structures:

(a) $CH_2\overset{\rho}{=}N\overset{\sigma}{=}N:$ [I]

(b) $\overset{\rho}{C}H_2=N=\overset{\sigma}{N}:$ [II]

(c) $:\overset{\sigma}{C}H_2-\overset{\rho}{N}\equiv N:$ [III]

(d) $:\overset{\sigma}{C}H_2-N\equiv\overset{\rho}{N}:$ [IV]

The terminal N atom in most contributing structure is expected to be

(a) sp hybridized (b) sp^2 hybridized
(c) sp^3 hybridized (d) none of these

13. Which of the following is correct with respect to heat of hydrogenation?

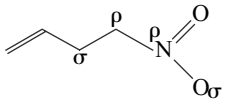
(a) 1,3-pentadiene > 1,4 pentadiene
(b) 1,5-hexadiene > 1,2-propadiene
(c) 1,4-pentadiene > 1,3-pentadiene
(d) 1,3-butadiene > 1,2-propadiene

14. Guanidine, a strong base, is protonated quickly. The cation forms

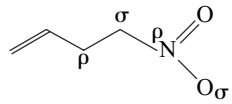
(a) three equivalent resonance structures
(b) two equivalent resonance structures
(c) five equivalent resonance structures
(d) four equivalent resonance structures

15. Among the following, the least-stable resonance structure is

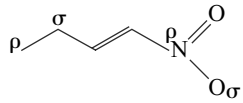
(a)



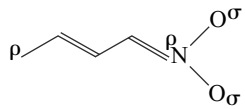
(b)



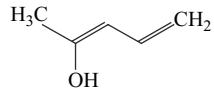
(c)



(d)



16. The number of resonance structures expected of

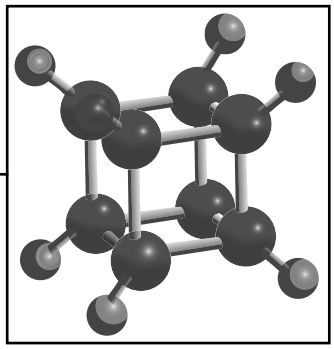


(a) two (b) three
(c) four (d) five

Answers

1. (a)	2. (b)	3. (c)	4. (d)	5. (a, d)
6. (c)	7. (c)	8. (c)	9. (a)	10. (b)
11. (a)	12. (b)	13. (c)	14. (a)	15. (a)
16. (b)				

CHAPTER 4



Organic Acids and Bases

BRONSTED–LOWRY THEORY (1923)

According to Bronsted–Lowry (B–L) theory, acids are proton (H^+) donors and bases are proton acceptors.

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

HCl donates a proton and H_2O accepts it. So, HCl is an acid and H_2O is a base.
Bare proton (i.e., H^+ only) does not exist in H_2O. It is associated with water molecules, i.e., it is solvated.

$$H^+ + xH_2O \longrightarrow [H(H_2O)x]^+$$

Solvated proton is simply denoted as H_3O^+, which is called 'Hydronium ion'. However, hydration number of a proton may be 1, 2, 3, 4, etc. which may be represented as H_3O^+, $H_5O_2^+$, $H_9O_4^+$, etc.

CONJUGATE ACID–BASE PAIR

When a substance donates a proton it is converted to a base, which is the conjugate base of the parent acid.

Acid		Conjugate base
CH_3COOH	$\xrightarrow[(-H^+)]{}$	CH_3COO^-
H_2SO_4	$\xrightarrow[(-H^+)]{}$	HSO_4^-

When a base accepts a proton, it is converted to an acid, i.e., the conjugate acid.

Base		Conjugate acid
$NH_3 + H^{\oplus}$	$\longrightarrow$	$NH_4^{\oplus}$
$HSO_4^- + H^+$	$\longrightarrow$	H_2SO_4

Thus, chemical species that differ in formula due to a proton are called 'A Conjugate Pair'.
B–L theory may, thus, be summarized as

$$\text{Acid}_1 + \text{Base}_2 \rightleftharpoons \text{Conjugate base}_1 + \text{Conjugate acid}_2$$

It is found that the conjugate base of a strong acid is a weak base and vice versa.

Thus, HSO_4^- is a weak base while H_2SO_4 is a strong acid and CH_3COO^- is a strong base while CH_3COOH is a weak acid. The conjugate acid of a weak base is a strong acid and vice versa. Thus, NH_4^+ is a strong acid while NH_3 is a weak base and CH_4 is a very weak acid while CH_3^- is a very strong base.

STRENGTH OF ACIDS

According to B–L theory, ionization equilibrium of an acid may be represented as

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

$$Keq = \frac{[H_3O^+]\,[A^-]}{[HA]\,[H_2O]}$$

The concentration of water, $[H_2O]$, is very large.
Therefore, constant

$$Keq = \frac{[H_3O^+]\,[A^-]}{[HA]}$$

In this case, Keq is called K_a, the dissociation constant of the acid HA. The numerical value of K_a decides the strength of an acid.
Another constant pK_a is often used instead of K_a to denote acid strength.

$$\text{Since } pK_a = -\log_{10}(K_a), \text{ for acetic acid, } K_a = 1.8 \times 10^{-5}.$$

$$pK_a = -\log(1.8 \times 10^{-5}) = -0.3 + 5 = 4.7$$

A stronger acid has a larger K_a but a smaller pK_a.

Table 4.1

Acid	K_a	pK_a
HCOOH	1.77×10^{-4}	3.7
CH_3COOH	1.8×10^{-5}	4.7

Thus, formic acid is stronger than acetic acid.

Polyprotic Acid

Acid that contain more than one ionizable hydrogen is called 'Polyprotic acid', e.g., $H_2C_2O_4$, tartaric acid, citric acid, maleic acid and fumaric acid. Such acids ionize in successive steps.

$$H_2C_2O_4 \overset{(K_a)_1}{\rightleftharpoons} H^+ + HC_2O_4^-$$
$$HC_2O_4^- \overset{(K_a)_2}{\rightleftharpoons} H^+ + C_2O_4^{-2}$$

The quantitites $(K_a)_1$ and $(K_a)_2$ are known as the first and second ionization constants, respectively. It is found that higher ionization constants are smaller than lower ionization constants. It is because of the loss of protons from the negative ions in the second and higher ionization constants.

Table 4.2

Acids	$(K_a)_1$	$(K_a)_2$	$(K_a)_3$
$H_2C_2O_4$	5.9×10^{-2}	6.4×10^{-5}	
Ascorbic acid	7.4×10^{-4}	1.6×10^{-12}	
Citric acid	7.4×10^{-4}	1.7×10^{-5}	4.0×10^{-7}

All H-containing organic compounds (XH) are potentially proton donors and may be taken as acids in the B–L sense. Even the H atom of a C–H bond becomes acidic when the C atom is linked to the electron-attracting groups, such as >C=O, –CN and $–NO_2$. Various other factors also have an effect on acid strength, such as

1. electronegativity of the atom to which H is linked,
2. factors that stabilize the conjugate base x^- over HX and
3. the solvents.

However, in many cases more than one effect operate together and affect acid strength.

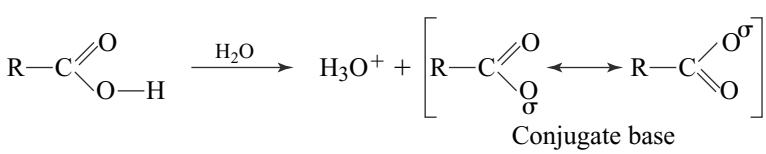
Electronegativity and Acid Strength

If electronegativtiy of the atom, to which H is linked, is high, the substance is more acidic. Thus, methanol, $H_3C–O–H$, is more acidic ($p^{K_a} \approx 16$) than methane $CH_3–H$ ($p^{K_a} \approx 43$).

It is because oxygen is more electronegative than carbon. Alcohols, in general, are slightly acidic but not the alkanes. The electronegativity of C, N and O is responsible for great difference in acidity between carboxylic acids, amides and ketones.

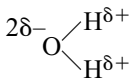
$$R–COOH > R–CONH_2 > R–COCH_3$$

In this case, the actual reason for acid strength is resonance stabilization of the conjugate base.

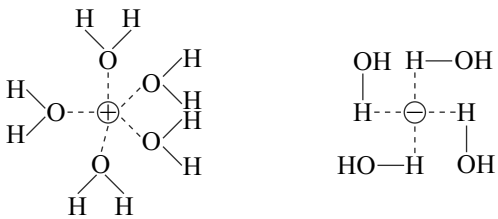


Solvent and Acid Strength

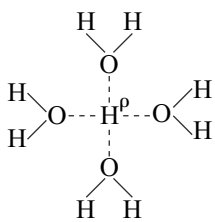
In addition to the structural features, solvent also has an effect on acid strength. Water is a dipolar molecule



that has the ability to solvate a cation as well as an anion.



The ions thus stabilize in water. In case of an acid, the proton is also solvated through H-bonding.



The degree of such stabilization has an effect on acid strength.

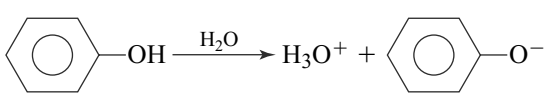
Structure and Acid Strength

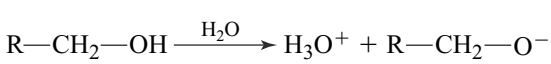
Various structural features also have an effect on acid strength.

Resonance and Acid Strength

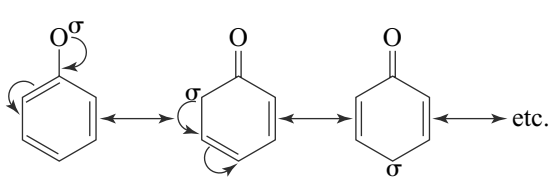
Resonance is the delocalization of π-electrons. It imparts stability to a chemical species. If the resonance stabilizes the conjugate base more as compared to the acid, the acid strength increases. For example,

1. Phenol is more acidic than primary alcohols.

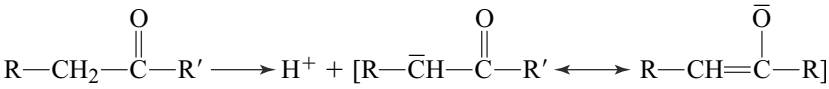




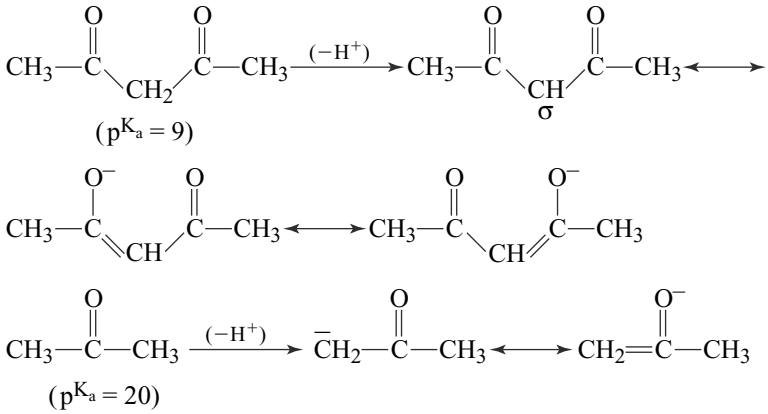
It is because phenoxide ion is resonance stabilized but the alkoxide ion is not.



2. Organic compounds containing C=O, C≡N, $-NO_2$, etc. groups also have some acidity due to the resonance effect. Thus, ketones, $R-CH_2-COR'$, are more acidic than alkanes, $R-CH_2-CH_2-R'$, amides, $R-CONH_2$, amines, $R-CH_2-NH_2$, etc.

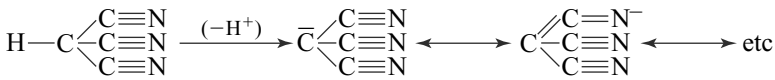


The effect is enhanced when two such groups are linked to the same carbon. Thus, β-diketones and β-ketoesters are more acidic than simple ketones.

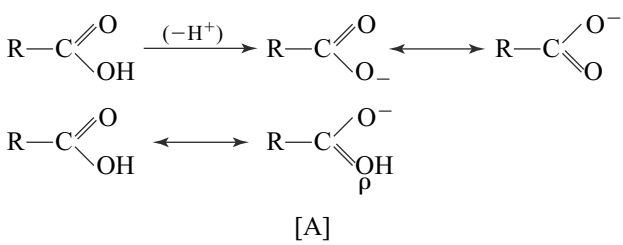


In the case of two C=O groups, spreading of the negative charge is more, i.e., a greater stabilizing effect.

The resonance effect is highly pronounced in tricyanomethane, $(NC)_3CH$, ($pK_a = -5$), which is a very strong acid.



The acidity of carboxyl group is also due to greater resonance stabilization of the carboxylate anion ($R-COO^-$) over the free acid.

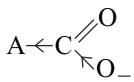


The resonance in $R-COO^-$ gives two equivalent structures but in the free acid the structure [A] involves charge separation. Thus, resonance in the acid is the stabilizing factor not as it is in the anion, $R-COO^-$. Proton loss is favoured and carboxylic compounds are acidic.

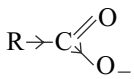
Inductive Effect and Acid Strength

Inductive effect is caused due to the shifting of σ-electrons. It has influence on the stability of the conjugate base of an acid. In general, *electron-attracting groups increase acidity, while electron-donating groups decrease acidity*. It is due to the fact that

1. electron-attracting groups disperse negative charge on the conjugate base, which is a stabilizing effect, and

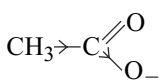


2. electron-donating groups increase negative charge on the conjugate base, which is a destabilizing effect.

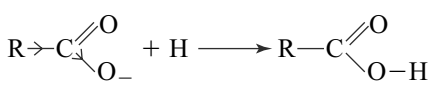


SIMPLE CARBOXYLIC ACIDS

Formic acid by organic standard is an acid of moderate strength ($p^{K_a} = 3.7$). When H atom (of C–H bond) of formic acid is replaced by CH_3 (i.e. by R), the product, acetic acid, is found to be a weak acid ($p^{K_a} = 4.7$). It is because CH_3 group is an electron-donating group that destabilizes the anion, CH_3COO^-.



Alternatively, the anions ($RCOO^-$) of such acids increase electron density on O atoms and recombination with proton is promoted.



However, further substitution of R groups in acetic acid has much less effect on acidity as is seen from the p^{K_a} values.

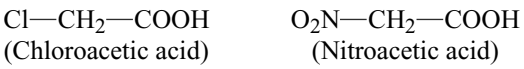
Table 4.3

Acid	p^{K_a}	Acid	p^{K_a}
CH_3COOH	4.76	$Me_2CHCOOH$	4.86
$CH_3–CH_2–COOH$	4.88	$Me_3C.COOH$	5.05
$CH_3(CH_2)_2COOH$	4.82		

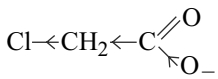
Notes: 1. Effect of different alkyl groups on acidity is not regular (see p^{K_a}).
2. Solvation and steric effect also play some role (the large Me_3CCOO^- is the least solvated).

SUBSTITUTED ACIDS

Chloroacetic acid, nitroacetic acid, 2-chlorobutanoic acid, etc. are all substituted aliphatic carboxylic acids.



These acids are stronger than acetic acid. It is because H (of C–H) is replaced by an electron-attracting group. Such groups attract electron from the negatively charged conjugate base, disperse it and then stabilize the anion.

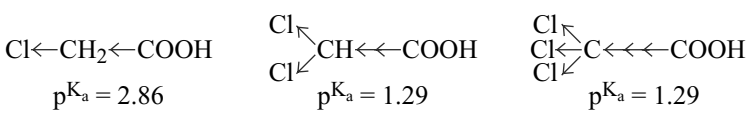


Thus, acid strength depends on the electron-attracting power of the substituent (i.e., –I effect). The group that is more electron attracting increases acidity and vice versa. It is shown in Table 4.4 below.

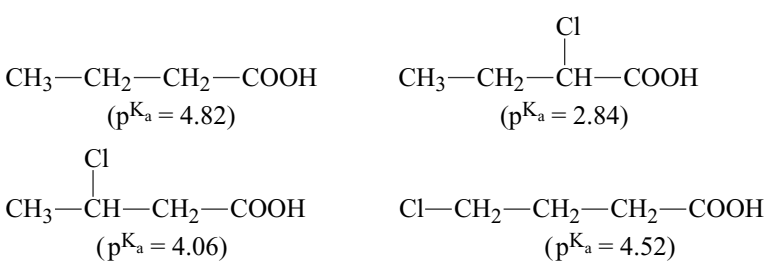
Table 4.4 pK_a values of some electron-attracting groups

Acid	pK_a	Acid	pK_a
FCH_2–COOH	2.66	O_2NCH_2–COOH	1.68
$ClCH_2$–COOH	2.89	$NCCH_2$–COOH	2.47
$BrCH_2$–COOH	2.90	HO–CH_2–COOH	3.83
ICH_2–COOH	3.16	$MeCOCH_2$–COOH	3.58

Introduction of more electron-attracting groups further increases the acid strength. Thus, trichloroacetic acid is a very strong acid.



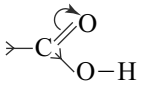
The introduction of an electron-attracting group, further away from the –COOH group, has very little effect on acidity. It is because of the inductive effect that decreases sharply in a saturated chain with distance. It is seen in the examples given below.



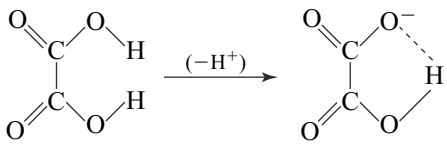
2-Chlorobutanoic acid is stronger than 3-chlorobutanoic acid which, in turn, is stronger than 4-chlorobutanoic acid. It is because of the electron-attracting group, –Cl, that is getting away and away from the –COOH group.

DICARBOXYLIC ACIDS

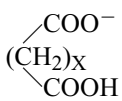
The carboxyl group has electron-attracting inductive effect (i.e., –I effect).



Therefore, one –COOH group enhances the acidity of the other COOH group. Oxalic acid is, thus, stronger than both formic acid and acetic acid in its first dissociation. The additional stabilization of the monoanion is by intramolecular H-bonding.



But intramolecular H-bonding is not effective when COOH groups are separated by $>CH_2$ groups.



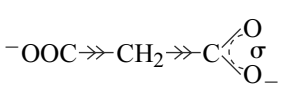
(X is more thatn one)

p^{K_a} of Some Dicarboxylic Acids

Table 4.5

Acid	p^{K_a}	Acid	p^{K_a}
CH_3COOH	4.76	HOOC–COOH	1.23
CH_3CH_2COOH	4.88	$HOOC.CH_2–COOH$	2.83
		$HOOC(CH_2)_2–COOH$	4.19
$C_6H_5–COOH$	4.17	$HOOC.C_6H_4.COOH$	*o*: 2.98
			m: 3.46
			p: 3.51

In the second ionization, however, the acids are weak mainly due to H-bonding. Another factor is destabilization of the dianion by the electron-donating inductive effect (+I) of the COO^- group.



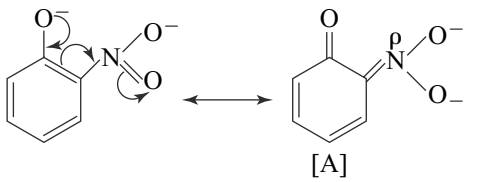
Phenols

Phenols are acidic and their acidity is influenced by the presence of substituents in the ring. *Electron-attracting groups increase the acidity of phenol when they are in the o- and p-positions*. For example, nitrophenols are more acidic than phenol.

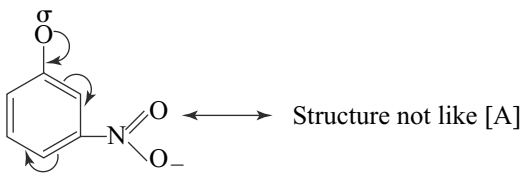
Table 4.6

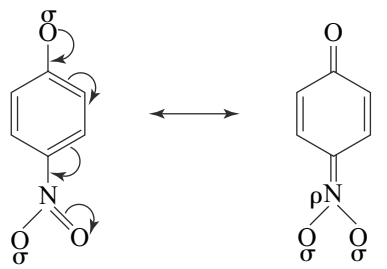
Compounds	pK_a
C_6H_5–OH	9.9
o-O_2N–C_6H_4–OH	7.2
m-$O_2N.C_6H_4$–OH	8.35
p-$O_2N.C_6H_4$–OH	7.14

It is partly (i) due to electron-attracting inductive effect of $–NO_2$ group and (ii) more by resonance stabilization of the anion, when NO_2 group is in the *o*- or *p*-position but not in the metaposition.



[A]



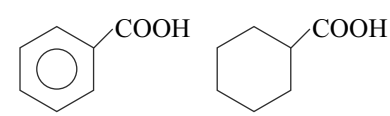


[A]

In the structures like [A], negative charge is shared by $–NO_2$ group forming more structures and, thus, resulting into more stabilization of the anion. Introduction of more $–NO_2$ groups increase acidity markedly. Thus, 2,4-dinitrophenol is a stronger acid ($pK_a = 4.01$) than phenol, whereas 2,4,6-trinitrophenol (picric acid) is very a strong acid ($pK_a = 1.02$).

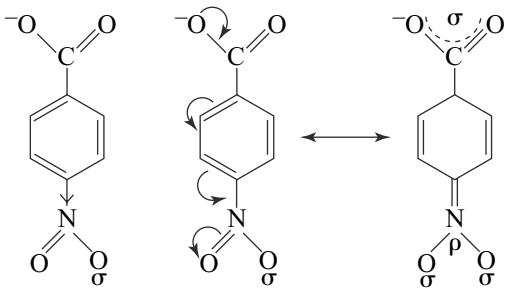
BENZOIC ACID AND ITS DERIVATIVES

Carbon in benzene is sp^2 hybridized. It is more electron attracting than sp^3-hybridized C atom. Therefore, benzoic acid is stronger than cyclohexane carboxylic acid.



$pK_a = 4.2$ $pK_a = 4.87$

The introduction of substituents into the benzene ring has an effect on the strength of the benzoic acid. The electron-attracting groups increase acid strength, especially when they are in the *o*- and *p*-positions. It is because of both the inductive effect (–I) and the resonance effect that help in the stabilization of the anion, e.g., *p*-nitrobenzoic acid.

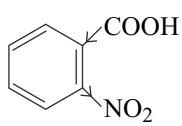


The p^{K_a} of some nitrobenzoic acids in Table 4.7, reveal the facts mentioned above.

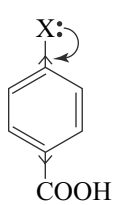
Table 4.7 p^{K_a} of some nitrobenzoic acids

Acids	p^{K_a}
C_6H_5–COOH	4.20
o-O_2N–C_6H_4.COOH	2.17
m-$O_2N.C_6H_4$.COOH	3.45
p-$O_2N.C_6H_4$.COOH	3.43

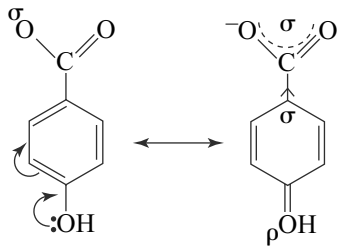
Table 4.7 shows that *o*-nitrobenzoic acid is most acidic among the three nitrobenzoic acids. It is because of the *o*-NO_2 that is at a very short distance and exerts powerful –I effect on the –COOH group.



The case for groups like halogens, –OH or OCH_3, is different. They have (i) electron-attracting inductive effect (–I) and (ii) electron-donating mesomeric effect (+M) when in *o*- or *p*-position.



The mesomeric effect causes an increase in the electron density in the COOH group, depleting dissociation of O–H bond and, thus, decreasing the acid strength. The effect is most pronounced when X is at the *p*-position.

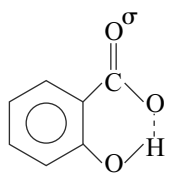


However, when X is at the *o*-position, the –I effect (due to short distance) causes increase in acid strength.

Table 4.8

	H	Cl	OH	OCH_3
o	4.2	2.94	2.98	4.09
m	4.2	3.83	4.08	4.09
p	4.2	3.99	4.58	4.47

Notes: 1. The +M effect of the OH group when at the *p*-position is most pronounced (acid-weakening effect).
2. The acids containing OCH_3 group are out of track. It may be due to the steric effect of the large OCH_3 group.
3. The presence of the –OH group at the *o*-position increases acidity, markedly. It is due to the stabilization of the anion by intramolecular H-bonding.



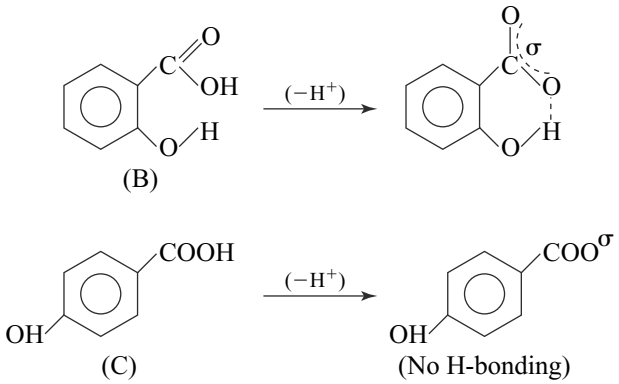
The six-atom cyclic geometry of the H-bonded structure is highly favourable. The presence of the alkyl groups in the benzene ring has very little effect on the strength of the benzoic acid.

Table 4.9

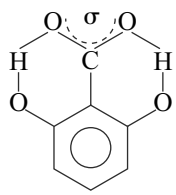
Acids	p^{K_a}
C_6H_5–COOH	4.20
m-CH_3–C_6H_4.COOH	4.24
p-CH_3.C_6H_4.COOH	4.34

H-Bonding and Acid Strength

Intramolecular H-bonding has pronounced effect on the strength of acids. It helps in the stabilization of the conjugate base leading to the increase in acid strength. Salicylic acid [B] (p^{K_a} = 3) is much stronger than *p*-hydroxybenzoic acid [C].

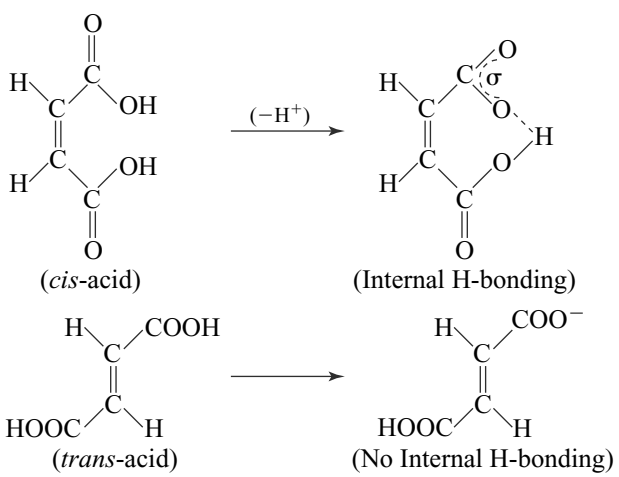


The effect is more pronounced when both the *o*-positions are occupied by –OH groups. Thus, 2,6-dihydroxybenzoic acid is very strong ($p^{K_a} = 1.3$). It is because the anion is bonded with hydrogen from both the sides.



The six-atom cyclic geometry highly favours the stabilization of the anion.

For the same reason, *cis*-butenedioic (maleic) acid is stronger ($p^{K_a} = 1.92$) than *trans*-butenedioic (fumeric) acid ($p^{K_a} = 3.02$) in its first ionization. It is because monoanion of the *cis*-acid is further stabilized by the internal H-bonding that is not possible in the *trans*-acid.



But in the second ionization, *cis*-acid is weaker ($p^{K_a} = 6.23$) than the *trans*-acid ($p^{K_a} = 4.38$). It is because of the second COOH group of the *cis*-acid that is locked in the H-bonding.

Hybridization and Acid Strength

Electronegativity (i.e. power to attract bond-pair electrons) of an atom is influenced by its hybrid nature. The greater is the s-character of the hybrid the more electronegative it is and vice versa.
Thus

$$\chi_{sp\text{-}C} > \chi_{sp^2\text{-}C} > \chi_{sp^3\text{-}C}$$

It has profound effect on acid strength. Thus, acetylene is more acidic than C_2H_4 and that, in turn, is more acidic than C_2H_6. The H of C_2H_2 is sufficiently acidic to be replaced by a metal.

Table 4.10

	C_2H_2	C_2H_4	C_2H_6
s-character of hybrid	50%	33.3%	25%
pK_a	25	36	42
Acid strength	⟶		Decreases

The situation is similar in propanoic [I], propenoic (acrylic) [II] and propynoic (propylic) [III] acids.

Table 4.11

[I]	[II]	[III]
$CH_3–CH_2–COOH$	$CH_2=CH–COOH$	$HC\equiv C–COOH$
↓	↓	↓
sp^3	sp^2	sp
$pK_a = 4.88$	$pK_a = 4.25$	$pK_a = 1.84$

It is due to the fact that α-carbon in [III] is sp hybridized and is the most electron attracting than α-carbon of [II], which, in turn, is more electron attracting than α-carbon of [I]. Therefore, the acid strength increases in the order [I] < [II] < [III].

BASES

A base accepts proton. Thus, the following equilibrium may exist in water.

$$B: + H_2O \equiv BH^+ + HO^-$$

For this equilibrium,

$$K_b = \frac{[BH^+][HO^-]}{[B:]}$$

The term $[H_2O]$ is omitted because water is present in large excess. The larger is the numerical value of K_b the stronger is the base and vice versa. For ease, pK_a is used instead of K_b, $[pK_b = -\log_{10}(K_b)]$. The smaller is the numerical value of pK_b the stronger is the base and vice versa.

The strength of a base may also be expressed in terms of pK_a to maintain the same scale for both acids and bases. The two are related, in water, as

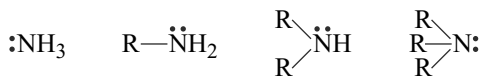
$$pK_a + pK_b = 14 \text{ (at } 25°C)$$

Base Strength

Electronic as well as steric factors affect the strength of bases. Solvent also has influence on it. But base strength can better be understood, classwise, by taking into account the above factors.

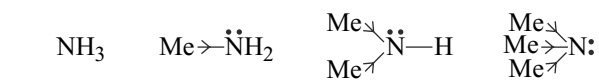
Aliphatic amines

Ammonia ($:NH_3$) is a base as it has lone pair at N (in sp^3-hybrid orbital). Amines are alkyl derivatives of NH_3. So, they are also basic because of the lone pair at N atom.



Base strength of amines in water is controlled by (i) inductive effect and (ii) solvation effect (through H-bonding).

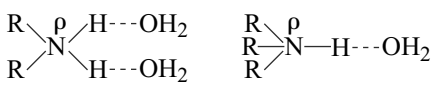
Alkyl groups have electron-donating inductive effect (+I effect) and so, amines are stronger bases than NH_3.



	NH_3	$MeNH_2$	Me_2NH	Me_3N
pK_b	4.75	3.36	3.23	4.20

It is the increasing +I effect of more R groups that makes N atom richer in electron.

However, it is seen that tert-amine is a weaker base than pri- and sec-amines. It is because the base strength of an amine in water is determined not only by electron availability at N atom but also by stabilization of the corresponding conjugate acid through H-bonding. In the second count, the conjugate acid of tert-amine is least stabilized as it has only one H at the N atom. The sec-amine is best compromised in which both the inductive effect and the solvation are favourable.



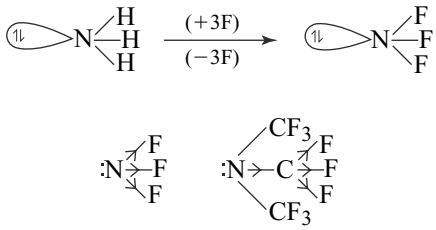
Therefore, for amines, the base strength order in water is

$$\text{Sec-amine} > \text{Pri-amine} > \text{Tert-amine}$$

However, in a solvent where H bonding cannot take place (e.g., chlorobenzene), inductive effect alone controls the base strength. And then, the base strength order is

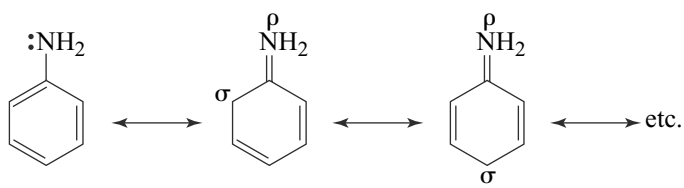
$$\underset{(3°)}{Bu_3N} > \underset{(2°)}{Bu_2NH} > \underset{(1°)}{BuNH_2} \quad (Bu = \text{butyl})$$

The presence of electron-attracting groups, –F, $–NO_2$, $–CF_3$, etc., near basic centre decreases the base strength. Thus, NF_3 and $N(CF_3)_3$ are virtually not basic. It is because of the presence of strong electron-attracting groups at N atom. The enormous –I effect shrinks lone-pair orbital decreasing its donor ability, i.e., decreasing its base strength.

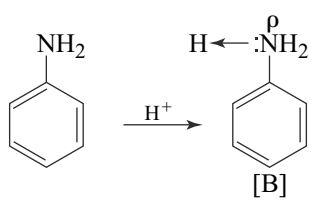


Aromatic amines

Resonance is a dominant effect to account for basic nature of aromatic amines. Aniline is a very weak base ($p^{K_b} = 9.38$) compared to methylamine ($p^{K_b} = 3.46$), cyclohexylamine ($p^{K_b} = 3.32$), etc. and even NH_3 ($p^{K_b} = 4.75$). It is due to the involvement of the electron pair on N in the mesomeric delocalization with the π-electrons of the benzene ring.

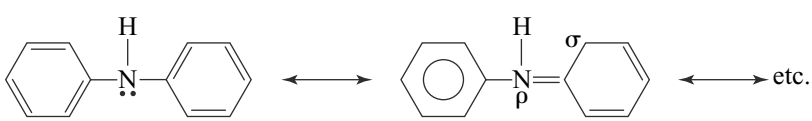


When aniline is protonated, the anilinium cation [B] loses such stabilization through delocalization as the electron pair on N is no longer available.



Aniline molecule is, thus, more stable compared to the anilinium cation. Therefore, protonation of aniline is energetically not favourable and is a very weak base.

If more phenyl groups are introduced on the N atom, its base strength further decreases. Thus, diphenylamine is an extremely weak base ($p^{K_b} = 13.2$) and triphenylamine (Ph_3N) is not basic at all. It is all due to the extensive delocalization of N electron pair over the benzene rings.



Electron-Donating Group and Base Strength

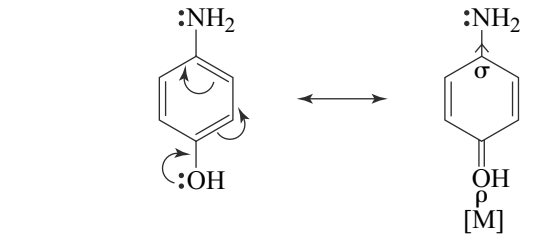
The introduction of alkyl groups (+I effect) either on the N atom or into the benzene ring has not significant effect on the base strength. It is because such substitution has little effect on the delocalization of N electron pair with the π electrons in the ring.

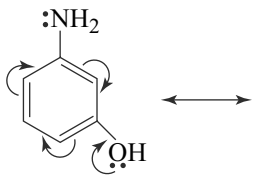
Table 4.12

	$Ph–NH_2$	$PhNH–CH_3$	$PhN(CH_3)_2$	$CH_3C_6H_4NH_2$
pK_b	9.38	9.60	9.62	*o*: 9.62
				m: 9.33
				p: 9.00

The argument given above is valid only for amines where steric factor is not operating. The effect of groups like –OH and $–OCH_3$ is different. These groups have (i) –I effect and (ii) electron-donating mesomeric effect (+M) as there are electron pairs on O atom.

The second effect dominates when the groups are in the *o*- or *p*-position but not in the *m*-position. Therefore, *o*- and *p*-isomers are stronger bases than m-isomers.





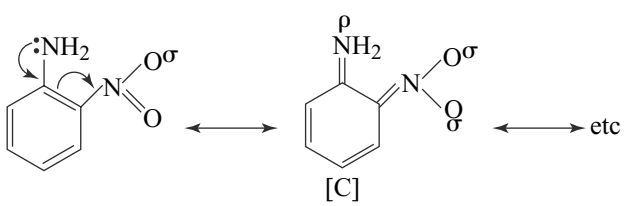
Not a structure like 'M' is possible

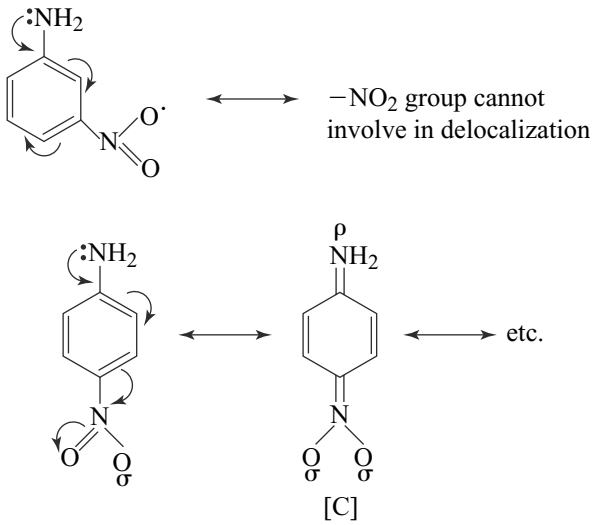
Table 4.13

	$PhNH_2$	$HO.C_6H_4–NH_2$	$CH_3OC_6H_4NH_2$
pK_b	9.38	*o*: 9.28	*o*: 9.51
		m: 9.83	*m*: 9.80
		p: 8.50	*p*: 8.71

Electron-Attracting Groups and Base Strength

Electron-attracting groups in the ring (NO_2, –CN, etc.) decrease the base strength significantly, e.g., nitroanilines are weaker bases than aniline itself. The effect is more pronounced when $–NO_2$ group is in the *o*- or *p*-positions. It is because both (i) the π-electrons in the ring and (ii) the NO_2 group involve mesomeric delocalization with the N electron pair and, additionally, stabilize the neutral molecule.





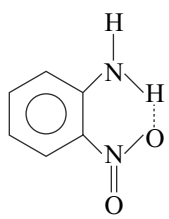
No structure like [C] is possible with *m*-nitroaniline.

Table 4.14

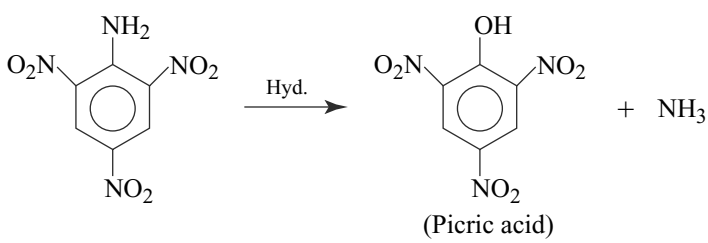
	$PhNH_2$	$O_2NC_6H_4.NH_2$		
pK_b	9.38	*o*: 14.28	*m*: 11.53	*p*: 13.02

The *o*-isomer is exceptionally a weak base. It is due to

1. short distance of NO_2 group over which its –I effect is operating,
2. H-bonding of NO_2 group with NH_2 group and
3. steric effect.



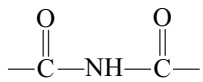
The introduction of more of NO_2 groups into the ring is significant towards base-weakening effect. Thus, 2,4,6-trinitroaniline is not basic and is compared with an amide. It is called *picramide*, as it is readily hydrolyzed to picric acid.



Amides and imides

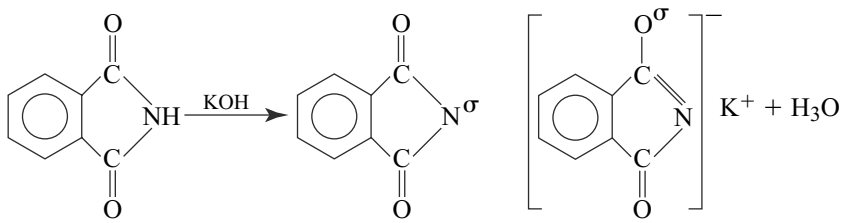
Amides are not basic as electron pair at N atom is involved in mesomeric conjugation with C=O group.

Imides contain the unit



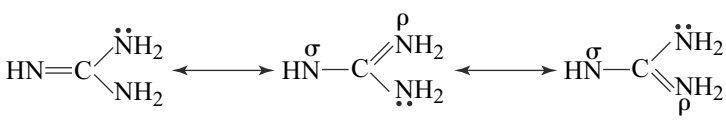
The two strong electron-attracting C=O groups kill its basicity.

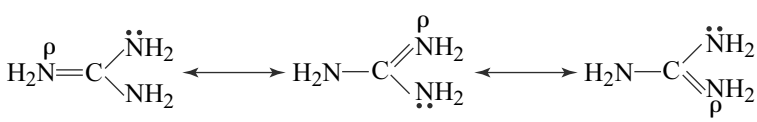
The imides are sufficiently acidic to form salt. It is because the conjugate base of an imide is stabilized by the mesomeric effect, e.g., phthalimide and succinimide.



Basicity of guanidine (aminomethanamidine)

Gnanidine, $HN{=}C(NH_2)_2$, is a very strong organic base. It is due to the mesomeric effect. Both the free molecule and its conjugate acid (cation) are stabilized by the delocalization of the electrons.



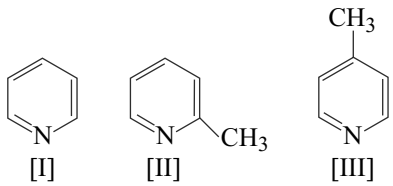


The delocalization in the free molecule produces charge-separated structure, which is not a profitable process. But in the cation, delocalization produces three equivalent structures that have more resonance stabilization. Thus, protonation of guanidine is energetically highly favourable making it a strong base.

Steric Factor and the Base Strength

Non-bonded repulsion between groups or atoms is called steric hindrance. It affects the strength of a base to an appreciable degree. For example,

1. The base strength of the pyridine and some of its methyl derivatives towards proton follows the given order below.



[I] [II] [III]

[II] ≈ [III] > [I] is due to the +I effect of CH_3 group. But with respect to $B(CH_3)_3$, the order is [I] ≈ [III] >> [II].

It is due to the steric hindrance between methyl groups of $B(CH_3)_3$ and the *o*-methyl group of the base.

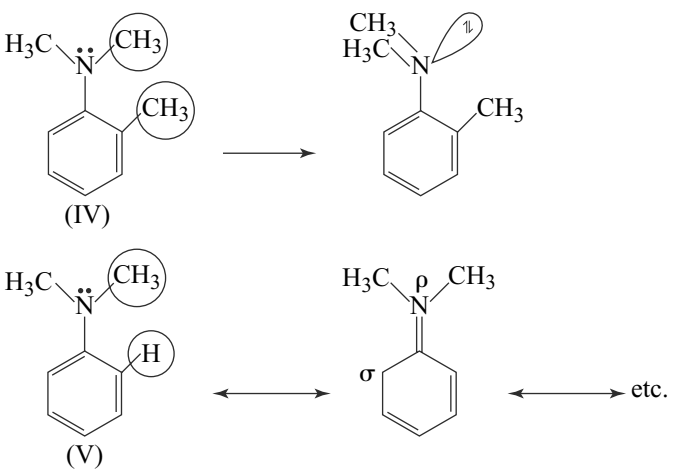
2. The N,N-dimethyl *o*-toluidine [IV] ($p^{K_b} \approx 8$) is a stronger base than N,N-dimethylaniline [V] ($p^{K_b} \approx 9$). It is due to the larger steric effect in [IV] over [V].

The *o*-methyl group (large in size) in [IV] pushes one of the CH_3 groups in a conformation that results into

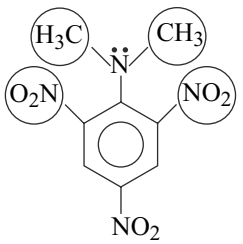
(a) projection of electron pair at one side and

(b) coplanarity of N with ring C that is destroyed (a condition needed for the delocalization of N electron pair with ring π-electron system).

On the other hand, in [V], steric effect is not operating as H at *o*-position is very small in size. Thus, [IV] is a stronger base than [V].

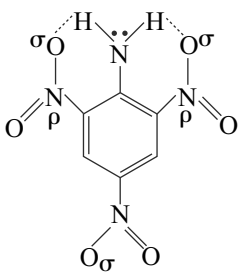


3. For the same reason 2,4,6-trinitro-N, N-dimethylaniline [VI] is a much stronger base than 2,4,6-trinitroaniline [VII].



(VI)

The steric destroys the coplanarity of N with ring C atom. It inhibits resonance of N lone pair with ring π electrons. It is thus free to be donated, making the compound a stronger base.



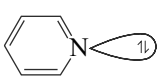
(VII)

H-bonding keep Ncoplanar with the ring C atom. Delocalization of electron pair at N takes place with ring π electrons. It reduces the bases strength.

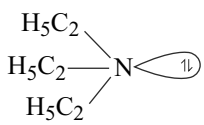
Heterocyclic bases

Heterocyclic compounds of nitrogen are basic. Their base strength depends on many factors. They are as follows:

Hybrid nature of N and base strength Pyridine is a tertiary base. But unlike aliphatic tert-amines, it is much weaker in base strength.

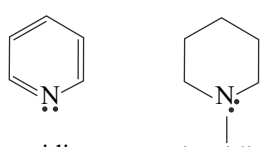


$pK_b = 8.96$



$pK_b = 3.12$

It is due to the difference in the hybrid nature of N atom in the compounds. The N in pyridine and in Et_3N is sp^2 and sp^3 hybridized, respectively. The sp^2 hybrid has larger s-character (33.3%) than sp^3 hybrid (25%). Therefore, nucleus of N has greater attraction for electron pair in pyridine. It is less available for coordination with a proton compared to Et_3N electron pair. Thus, pyridine is a weaker base. It is even weaker than NH_3 ($pK_b = 4.75$). However, the reduction product of pyridine, i.e., pipyridine, is a stronger base than pyridine.

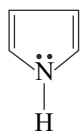


pyridine pipyridine

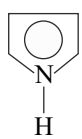
In pipyridine, N is sp^3 hybridized and that is why it is a stronger base than pyridine. The effect of electron-pair hybrid is so pronounced on base strength that alkyl cyanides (N ⟶ sp hybrid) are not basic at all. The order of the base strengths is as follows:

$$R_3N > C_5H_5N > R.C \equiv N$$
$$(sp^3) \quad (sp^2) \quad (sp)$$

Basicity of pyrrole Pyrrole is a five-membered N-heterocyclic compound.

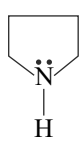


It has aromatic character. To achieve aromaticity, the molecule uses electron pair on N for the formation of aromatic sextet, i.e., $(4n + 2)$ π electrons.



The electron pair on N atom is not free to coordinate with a proton and so it is not basic ($pK_b = 13.6$).

But pyrrolidine, the fully reduced product of pyrrole, is a strong base ($pK_b = 2.73$). It is because pyrrolidine is not aromatic and electron pair on N atom is, now, in an sp^3-hybrid orbital.



(Pyrrolidine)

PROBLEMS

Objective-Type Questions

1. Which of the following is the correct order of decreasing acidity of H_2O, ROH, HC≡CH, NH_3 and RH?
(a) $H_2O > HC{\equiv}CH > ROH > NH_3 > RH$
(b) $H_2O > ROH > HC{\equiv}CH > NH_3 > RH$
(c) $HC{\equiv}CH > ROH > H_2O > RH > NH_3$
(d) $NH_3 > H_2O > ROH > RH > HC{\equiv}CH$

2. Which of the following represents the decreasing order of their acidity?

1. PhCOOH
2. o-$O_2NC_6H_4COOH$
3. p-$O_2NC_6H_4COOH$
4. m-$O_2NC_6H_4COOH$

(a) 2 > 4 > 1 > 3 (b) 1 > 2 > 3 > 4
(c) 2 > 4 > 3 > 1 (d) 2 > 3 > 4 > 1

3. Mark the decreasing order of the acidity of the following compounds.
1. *o*-$O_2NC_6H_4COOH$
2. *o*-$CH_3OC_6H_4COOH$
3. C_6H_5COOH

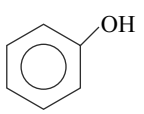
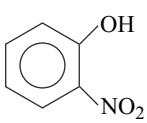
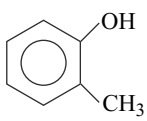
(a) 1 > 3 > 2 (b) 2 > 1 > 3
(c) 3 > 2 > 1 (d) 1 > 2 > 3

4. The correct order of acidity of the given acids is
1. CH≡C–COOH
2. CH_2=CHCOOH
3. CH_3CH_2COOH

(a) 2 > 1 > 3 (b) 1 > 3 > 2
(c) 3 > 2 > 1 (d) 1 > 2 > 3

5. Which of the following is the least basic anion?
(a) $HC\equiv C^{\sigma}$ (b) NH_2^{σ}
(c) OR^{σ} (d) R^{σ}

6. Pyridine is less basic than triethylamine because
(a) pyridine has aromatic character
(b) nitrogen in pyridine is sp^2 hybridized
(c) pyridine is a cyclic system
(d) in pyridine, lone pair of nitrogen is delocalized

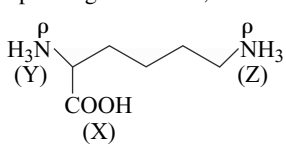
7. Which one of the following compounds is the most acidic?
(a) Cl–CH_2–CH_2–OH (b) 
(c)  (d) 

8. Which one of the following order of acid strength is correct?
(a) RCOOH > ROH > HOH > HC≡CH
(b) RCOOH > HOH > ROH > HC≡CH
(c) RCOOH > HOH > HC≡CH > ROH
(d) RCOOH > HC≡CH > HOH > ROH

9. Which of the following compounds is more basic than aniline?
(a) Triphenylamine (b) *p*-Nitroaniline
(c) Benzylamine (d) Diphenylamine

10. Which is the most basic compound among the following?
(a) Benzylamine (b) Aniline
(c) Acetanilide (d) *p*-Nitroaniline

11. In the compound given below,



the correct order of acidity of the positions X, Y and Z is
(a) Z > X > Y (b) X > Y > Z
(c) X > Z > Y (d) Y > X > Z

12. Which of the following orders is correct regarding the basicity of NH_2 group in benzene?
(a) $CH_3NH_2 > (CH_3)_2NH > (CH_3)_3N$
(b) $CH_3NH_2 < (CH_3)_2NH < (CH_3)_3N$
(c) $CH_3NH_2 > (CH_3)_2NH < (CH_3)_3N$
(d) $CH_3NH_2 < (CH_3)_2NH > (CH_3)_3N$

13. What is the decreasing order of the strength of the bases OH^-, NH_2^-, $HC\equiv\bar{C}$ and $CH_3\bar{C}H_2$?
(a) $CH_3-CH_2^- > NH_2^- > H-C\equiv C^- > OH^-$
(b) $H-C\equiv C^- > CH_3-CH_2^- > NH_2^- > OH^-$
(c) $OH^- > NH_2^- > HC\equiv C^- > CH_3-CH_2^-$
(d) $NH_2^- > H-C\equiv C^- > OH^- > CH_3-CH_2^-$

14. Which of the following orders of the base strength is correct?
(a) $R^- > NH_2^- > HC\equiv\bar{C} > RCOO^-$
(b) $R^- > NH_2^- > RCOO^- > HC\equiv\bar{C}$
(c) $R^- > RCOO^- > NH_2^- > HC\equiv\bar{C}$
(d) $HC\equiv\bar{C} > NH_2^- > RCOO^- > R^-$

15. The correct sequence regarding the base strengths of aliphatic amines in aqueous solution is
(a) $R_3N > R_2NH > RNH_2 > NH_3$
(b) $R_2NH > RNH_2 > R_3N > NH_3$
(c) $R_2NH > R_3N > RNH_2 > NH_3$
(d) $RNH_2 > R_2NH > R_3N > NH_3$

16. The correct sequence regarding the base strengths of aliphatic amines in gaseous phase is
(a) $R_3N > R_2NH > RNH_2 > NH_3$
(b) $R_3N > RNH_2 > R_2NH > NH_3$
(c) $R_2NH > R_3N > RNH_2 > NH_3$
(d) $R_2NH > RNH_2 > R_3N > NH_3$

17. Increasing order of basicity of $CH_3CH_2CH_2NH_2$, H_2C=$CHCH_2NH_2$ and HC≡CCH_2NH_2 is
(a) $CH_3CH_2CH_2NH_2 < HC\equiv CCH_2NH_2 < H_2C=CHCH_2NH_2$
(b) $CH_3CH_2CH_2NH_2 < H_2C=CHCH_2NH_2 < CH\equiv CCH_2NH_2$
(c) $HC\equiv CCH_2NH_2 < H_2C=CHCH_2NH_2 < CH_3CH_2CH_2NH_2$
(d) $HC\equiv CCH_2NH_2 < CH_3CH_2CH_2NH_2 < H_2C=CHCH_2NH_2$

18. Which is the strongest acid among the following compounds?
(a) HC≡CH (b) C_6H_6
(c) C_2H_6 (d) CH_3OH

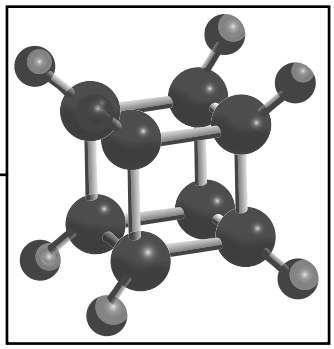
19. Which of the following has the most acidic hydrogen?
(a) 3-Hexanone (b) 2,4-Hexanedione
(c) 2,5-Hexanedione (d) 2,3-Hexanedione

20. Which of the following is the strongest base?
(a) $C_6H_5NH_2$ (b) p-$NO_2C_6H_4NH_2$
(c) m-NO_2–$C_6H_4NH_2$ (d) $C_6H_5CH_2NH_2$

Answers

1. (b)	2. (d)	3. (d)	4. (d)	5. (c)
6. (b)	7. (c)	8. (b)	9. (c)	10. (a)
11. (b)	12. (b)	13. (a)	14. (a)	15. (b)
16. (a)	17. (c)	18. (d)	19. (b)	20. (d)

CHAPTER 5



Reaction Mechanism

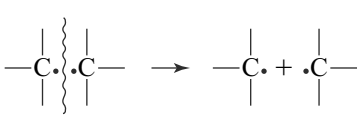
Organic compounds contain covalent bonds. Organic reactions, thus, involve breaking and making of covalent bonds. Breaking a bond requires energy while bond formation releases energy. In many reactions, covalent bonds are broken to give reaction intermediates, which form products. In some reactions, bond formation and bond breaking are simultaneous processes. Such reactions are called concerted processes (e.g., S_N2 reactions).

BREAKING OF A COVALENT BOND

Covalent bonds can break in two ways: homolytic cleavage and heterolytic cleavage.

Homolytic Cleavage

The symmetrical breaking of a covalent bond in which each part keeps one electron is called 'Homolytic Cleavage'. Each fragment, thus, contains an unpaired electron. These are called *free radicals*.

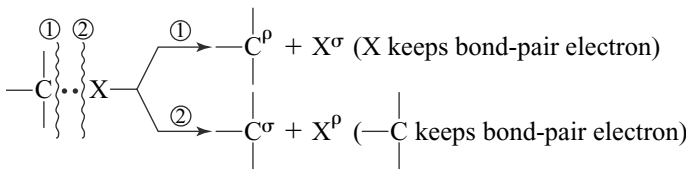


Free radicals

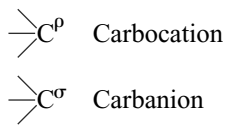
The energy required for bond fission is supplied in the form of either heat or light (UV). The reactions in which radicals are involved are called free-radical reactions. Such reactions are generally gaseous or take place in nonpolar solvents.

Heterolytic Cleavage

The unsymmetrical breaking of a covalent bond in which only one part retains both the electrons is called 'Heterolytic Cleavage'.



It produces ions. The species through which carbon carries positive charge is called 'carbonium ion' or 'carbocation' and the C^{σ} species is called 'carbanion'.



Reactions involving heterolytic cleavages are ionic in nature. They are favoured in polar solvents.

REAGENTS

The reaction site in a molecule may be electron rich, electron poor or a centre where one unpaired electron (i.e., a free radical) is present. This is preferred by different types of reagents. Broadly, reagents may be classified into three groups: (i) electrophiles, (ii) nucleophiles and (iii) free radicals.

Electrophiles

The reagents that attack electron-rich centres of organic compounds (substrate) are called 'electrophiles' or 'electrophilic reagents', i.e., electrophiles are electron-seeking (or -loving) reagents. Examples of electrophiles include the following.

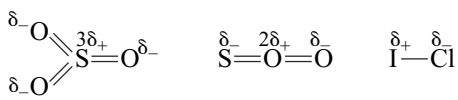
1. Positively charged species.

$$H^{\rho},\ H_3O^{\rho},\ NO^{\rho},\ NO_2^{\rho},\ R_3C^{\rho},\ PhN_2^{\rho} \text{ etc.}$$

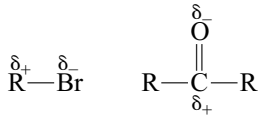
2. Species that possess an electron-deficient atom.

$$B_2H_6,\ AlCl_3,\ SO_3,\ CO_2,\ ICl, \text{ etc.}$$

B_2H_6 and $AlCl_3$ are electron-deficient species as B and Al have no octet. On the other hand, S in SO_3, C in CO_2 and I in ICl are electron poor as they have polar bonds.



3. Species containing polarizable functional groups.



Here, alkyl and carbonyl C atoms are electrophilic centres as the bonds are polar covalent. Thus, all Lewis acids are electrophiles.

Nucleophiles

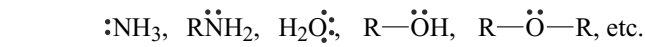
The reagents that attack electron-poor centre in a substrate are called 'nucleophiles' or 'nucleophilic' reagents, i.e., they search site in a substrate to sit in.

Nucleophiles include the following:

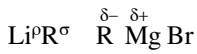
1. Negatively charged ions.

$$H^{\sigma}, HO^{\sigma}, CN^{\sigma}, RO^{\sigma}, HSO_3^{\sigma}, RCOO^{\sigma}, RC\equiv\overset{\sigma}{C} \text{ etc.}$$

2. Species that contain lone-pair electrons.



3. Some organometallics.



Here, alkyl moieties are nucleophilic. Thus, all Lewis bases are nucleophiles.

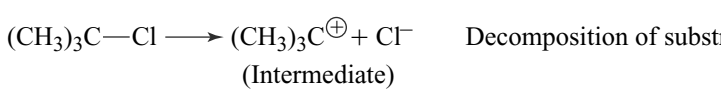
Free Radicals

The reagents that have unpaired electron at an atom are called free radicals. They attack free-radical centre in the substrate. Examples of free radicals are

$$Cl^{\bullet}, R^{\bullet}, HO^{\bullet}, RO^{\bullet}, \text{ etc.}$$

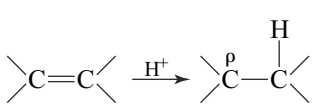
REACTION INTERMEDIATES

A great majority of organic reactions involve intermediates. They are formed either by the decomposition of the organic compound (the substrate) or by the attack of the reagent on the substrate.



Decomposition of substrate

(Intermediate)



By attack of the reagent

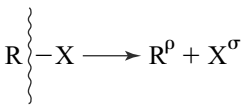
(Intermediate)

The intermediates, in general, are short-lived but some are stable enough to be isolated. The common reaction intermediates are

1. Carbocation
2. Carbanion
3. Free radicals
4. Carbenes

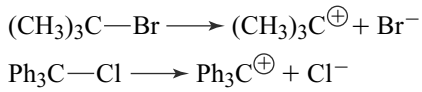
Carbocation

An intermediate having positive charge at C atom is called carbocation. It is also called carbonium ion. They are formed by heterolytic cleavage of a covalent bond.



Formation

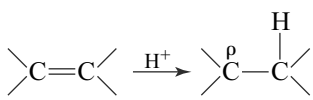
1. *By ionization*



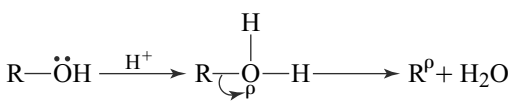
Such ionizations are favoured in polar protic solvents.

2. *By protonation of substrates*

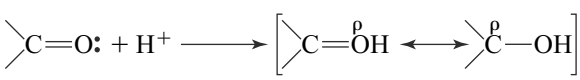
(a) Protonation of >C=C<



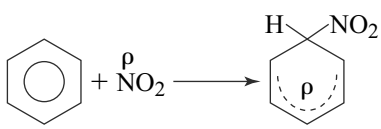
(b) Protonation followed by dehydration of alcohols



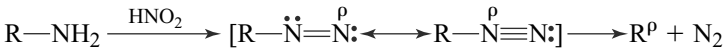
(c) Protonation of >C=O compounds



3. *Addition of electrophile to aromatic compounds*

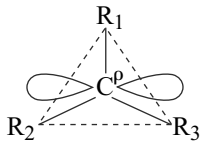


4. *Ionization of cation*
Deamination of aliphatic amines by HNO_2 produces carbocation.



Structure

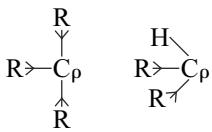
The carbonium ion in carbon has three substituents and an empty p-orbital. The carbonium ion in the C atom is, thus, sp^2 hybridized and it is a trigonal planar.



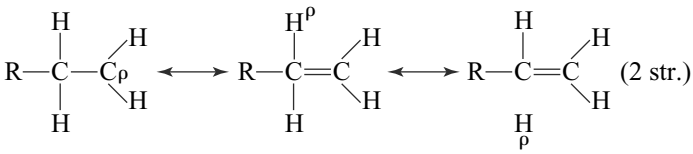
Stability

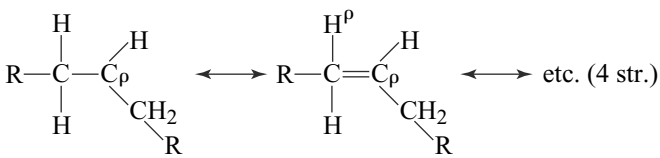
The carbonium ion in carbon bears positive charge. Any effect that reduces positive charge on carbon confers stability to a carbocation. Inductive effect, hyperconjugation and resonance all can do that.

Inductive effect and hyperconjugation explain stability of alkyl carbocation. Alkyl groups are electron-donating groups. They increase electron density at the carbon having positive charge. This results into the dispersal of positive charge over all the alkyl groups that increase the stability.

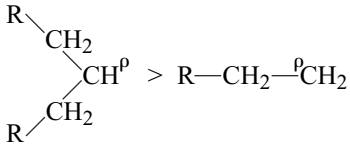


The hyperconjugative effect is also partly responsible for stability. The C–H σ-electrons can delocalize into empty p-orbital of the carbocation, spreading it over all alkyl groups and, thus, stabilizing it. The larger is the number of C–H bonds, α- to the positive carbon, the larger is the number of hyperconjuagative structures and more stable is the carbocation.

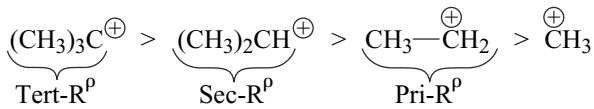




As there are more structures possible for the second carbocation, it is more stable than the first, i.e.,

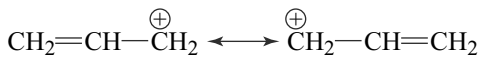


In general, decreasing order of stability of alkyl carbocations is



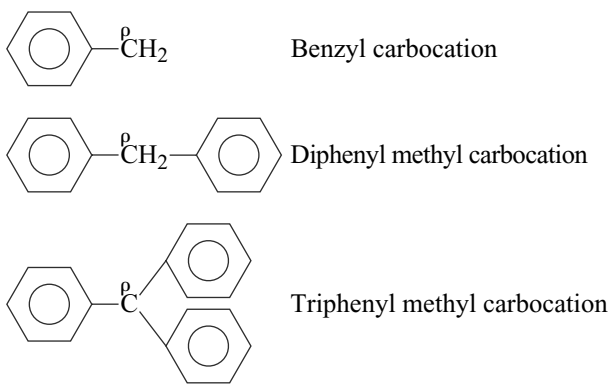
Methyl and primary carbocations are, generally, not found.
Resonance is important stability-deciding factor for carbocations that contain unsaturated and conjugated systems. For example,

1. Stability of allyl carbocation

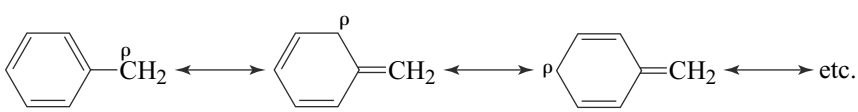


The declocalization of positive charge to produce equivalent structure is the reason for its stability.

2. Carbocations containing phenyl groups.

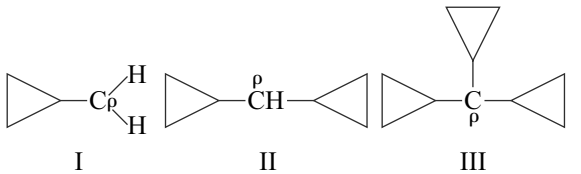


These carbocations are very stable due to the delocalization of positive charge into the benzene rings.



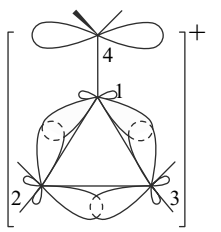
The larger the number of phenyl groups at the positive carbon, the more stable is the carbocation. Thus, triphenylmethyl carbocation is stable enough to form salt. Example,

3. Cyclopropyl methyl carbocations are very stable.



I II III

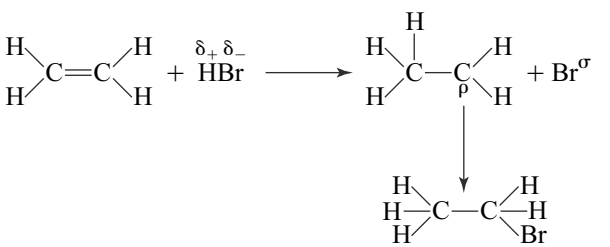
It is due to the conjugation between vacant p-orbital of the positive carbon and bent orbitals of the cyclopropyl rings, the stability order being III > II >I.



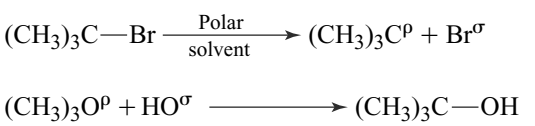
Reactions

Carbocations generally undergo the following types of reactions:

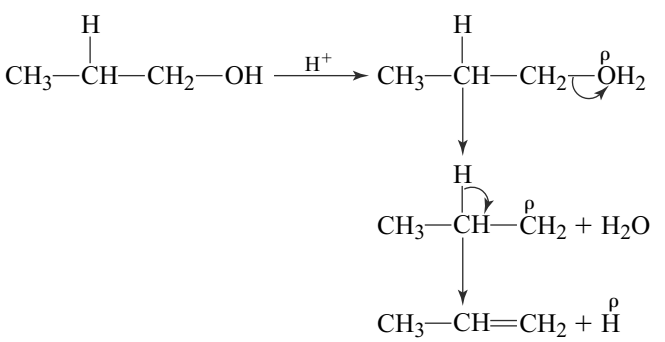
1. *Addition reaction to C=C*



2. *Combination with a nucleophile (S_N1rk)*



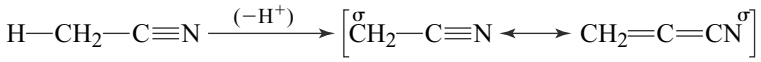
3. *Elimination of a proton (E^1 reaction)*



4. *Rearrangement reaction*
Many rearrangements involve carbocations (see Chapter *Rearrangement*).

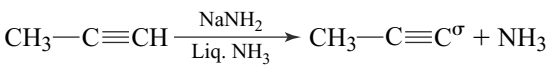
Carbanion

A reaction intermediate that carries negative charge at C is called carbanion. They are generated by heterolytic cleavage of a covalent bond. The most common method is heterolysis of a C–H bond. It becomes possible when carbon having C–H bond is attached with an electron-attracting group (NO_2, CN, >C=O, etc.). The loss of proton gives anions that are resonance stabilized.

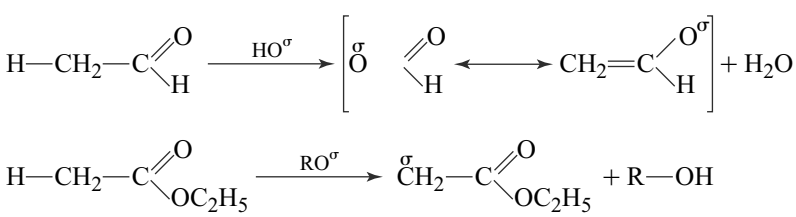


Formation

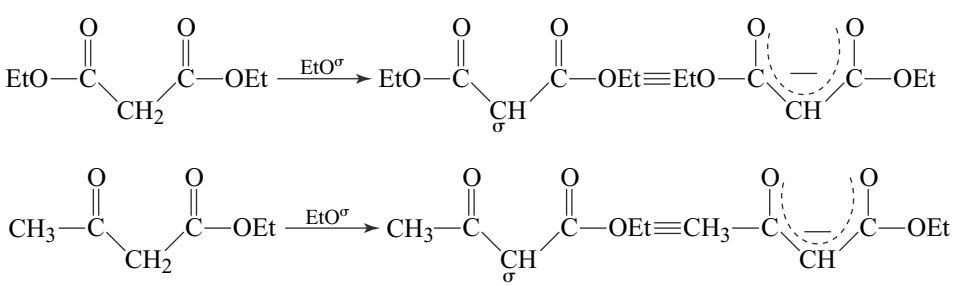
1. *From terminal alkynes*
Alkynes that contain R at one of the C atom of C≡C are called terminal alkynes, e.g. CH_3–C≡CH. The H atom of ≡C–H is acidic. It reacts with a base to form carbanion.



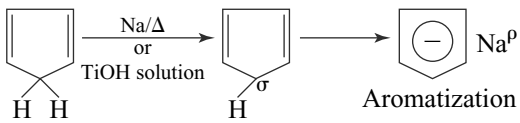
2. *From carbonyl compounds*
Aldehydes, ketones, esters, etc., that have α-hydrogen form carbanion. It is because of the fact that electron-attracting property of >C=O group makes α-H atom slightly acidic. They are easily lost to a base producing carbanion.



3. *From active methylene compounds*
The $>CH_2$ group is called the methylene group. When it is flanked by two electron-attracting groups, it is called 'active methylene group'. It is because in this case, both the H atoms become acidic. Therefore, such compounds easily form carbanions.

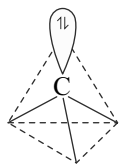


4. *Through aromatization*
The species that can aromatize by loss of a proton forms carbanion easily, e.g., cyclopentadiene forms cyclopentadienide ion very easily.



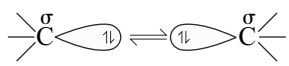
Structure

Carbanion carbon has three bonds and a lone pair. To keep these four electron pairs, C is sp^3 hybridized and the ion is trigonal pyramidal.

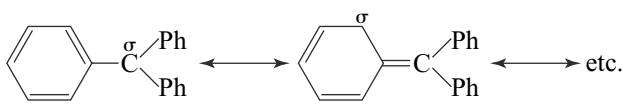


The bond angle is less than tetrahedral angle (109°28′) due to lp–bp (lone pair–bonding pair) repulsion.

If C is sp^3 in a carbanion, then an asymmetric carbanion of the type $R_1R_2R_3C^-$ should form an enantiomeric pair. But the enantiomers have never been isolated even at very low temperature. It is due to the rapid interconversion (i.e., umbrella effect).



The resonance-stabilized carbanions are nearly planar, e.g., triphenyl methyl carbanion. It is because of the resonance that requires coplanarity in the structure.



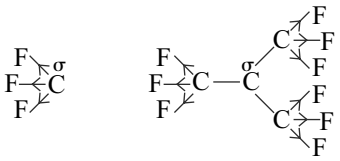
Stability

Various factors control stability of a carbanion, such as

1. inductive effect
2. delocalization of carbanion electron pair with π-electron (i.e., resonance effect)
3. hybrid nature of the carbanion carbon
4. aromatization

I effect and stability Electron-attracting groups increase and electron-donating groups decrease the stability of the carbanion. For example,

1. CF_3^- and $(CF_3)C^-$ carbanions are very stable. It is because of the fact that strong electron-attracting groups disperse negative charge from C and stabilize the ion.

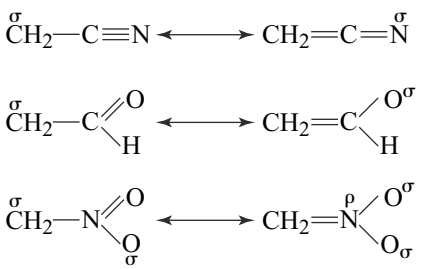


2. When carbanion carbon carries R groups, (+I effect) stability is decreased. Thus, the decreasing order of stability is

$$CH_3^{\sigma} > R{-}CH_2^{\sigma} > R_2CH^{\sigma} > R_3C^{\sigma}$$

Resonance effect and stability The delocalization (i.e., resonance) of negative charge at the carbanion carbon imparts stability to the carbanion.

1.

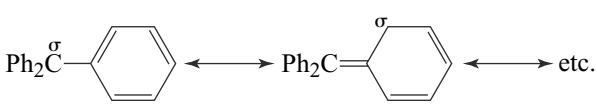


The C=O group in aldehydes and ketones is more effective in carbanion stabilization than –COOR group. It is due to the electron-donating conjugative ability of the lone pair at OR group.

The effectiveness of various groups for stabilising the carbanion is

$$-NO_3 > -C(=O)-H\ (\text{or R}) > -C(=O)-OR > -CN \approx CONH_2 > \text{Halogen}$$

The triphenyl methyl carbanion is very stable due to the delocalization of negative charge over three phenyl groups.



Thus, it is easily formed.

$$Ph_3C{-}H \xrightarrow{Na} (Ph)_3C^{\sigma}.Na^{\rho} + \tfrac{1}{2}H_2$$

Hybrid nature of carbon and its stability The stability of carbanions increases with an increase in the s-character of the hybrid keeping the electron pair (of the C^-). The s-orbital is closer to the nucleus than the corresponding p-orbitals and, hence, is of lower energy. This is present even in the hybrids. The s-character of the hybrids is as follows:

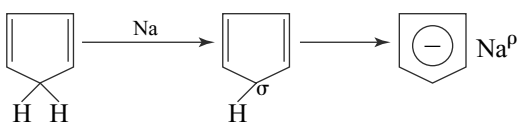
sp	sp^2	sp^3
50%	33.3%	25%

That is, the electron pair in an sp hybrid is held closer and tightly by the carbon nucleus than an electron pair in an sp^2 or sp^3 hybrid. Thus, sp-hybridized C stabilizes the carbanion the most. The decreasing order of stability of different carbanions is,

$$R{-}C{\equiv}\overset{\sigma}{C} > R_2C{=}\overset{\sigma}{C}H \approx \overset{\sigma}{Ar} > R_3C{-}CH_2^{\sigma}$$

(R may be H also)

Aromatization and stability Aromatic systems are highly stable. Therefore, a change from non-aromatic to aromatic is strongly favoured. For example, cyclopentadiene (A) loses a proton very easily to form a carbanion (B). The non-bonded electron pair in B forms a $(4n + 2)$ π-electron system with two π-bonds. This aromatization is responsible for the stability of the anion (B).



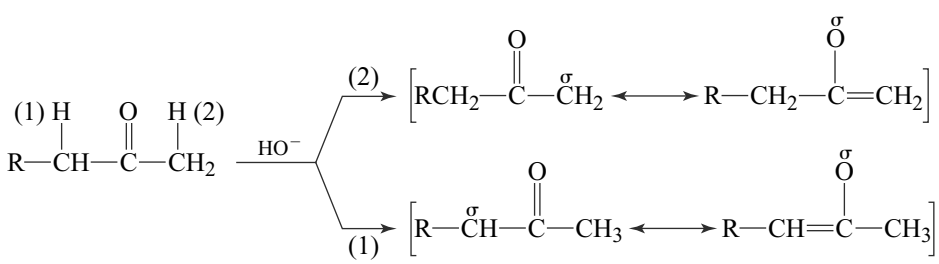
Reactions

The reactions of carbanions are of great synthetic utility (many times C–C bonds are formed). Examples of such reactions are given below.

1. Aldol condensation, Claisen condensation and others alike (see name reactions)
2. Benzoin condensation (see name reactions)
3. Michael reaction (see name reactions)
4. Halogenation of ketones
   Halogenation of ketones involves the carbanion intermediate.

(see haloform reaction)

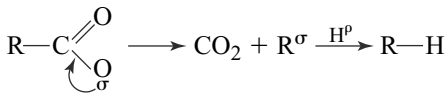
With ketones, which have alternative groups of α-H atoms, selective halogenation takes place, e.g.,



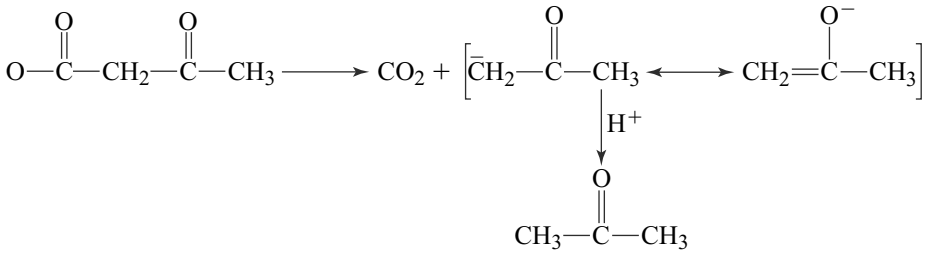
The route (2) is preferred as the R group (+I effect) that will make the H atoms of the CH_2 group less acidic.

5. Decarboxylation

The loss of CO_2 from $-COO^{\sigma}$ anion is believed to proceed through carbanion intermediate.



Such reactions are promoted by electron-attracting groups in R. Therefore, nitro, cyano and β-keto acids undergo easy decarboxylation.

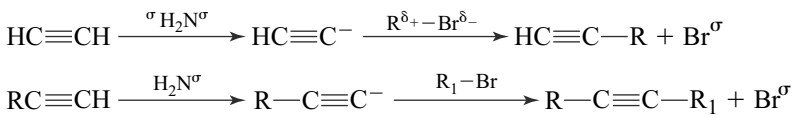


6. Grignard reagents

They are a good source of carbanions in substitution reactions (see synthesis of alcohols).

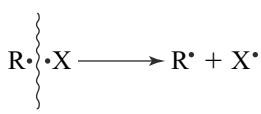
7. Acetylide anion

$HC{\equiv}C^{\sigma}$ is a good carbanion for the synthesis of higher alkynes of the type RC≡CH and RC≡CR (both alkyl groups can be different).



Carbon-Free Radicals

A reaction intermediate that has unpaired electron at C atom is called 'free radical'. They are formed by homolytic cleavage of a covalent bond.

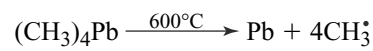


The energy required for bond fission is supplied either in the form of heat or light (UV). Radicals are paramagnetic as they contain unpaired electron.

Formation

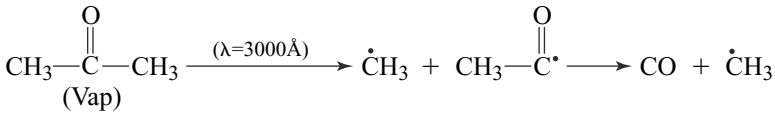
1. *Thermolysis*

Homolysis of a covalent bond by the effect of heat is called thermolysis. Compounds having relatively weak covalent bonds give radicals on heating.



2. *Photolysis*

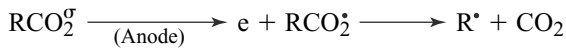
Fission of a covalent bond by visible or ultraviolet light is called 'photolysis'. It produces radicals. This method is preferred over thermolysis because it can produce more selective product.



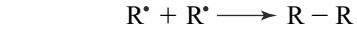
This reaction produces methyl-free radical.

3. *Redox reaction*

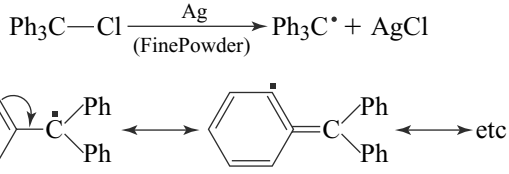
Single-electron redox reactions generate radicals. The common example is Kolbe electrolytic synthesis of hydrocarbons.



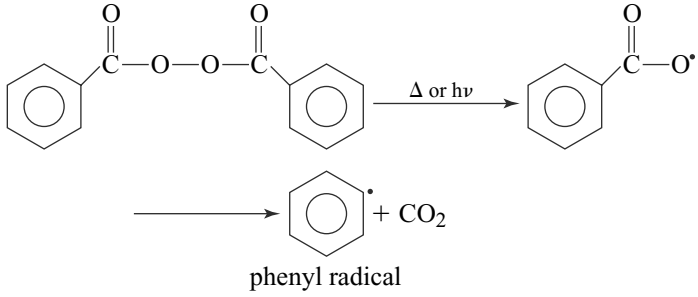
The R′-free radicals dimerize to an alkane.



The above-said radicals are not very stable. However, stable radicals like triphenyl methyl radical, $Ph_3C^{\bullet}$, is also known. Its stability is due to the extensive delocalization of single electron over three benzene rings.

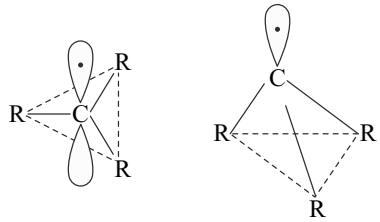


Fragmentation in oxygen-containing radicals is common. It results into the formation of new radicals and a non-radical fragment, e.g. phenyl radical from benzoyl peroxide.

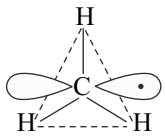


Structure and shape

Carbon radicals are either (a) trigonal planar or (b) trigonal pyramidal.



Therefore, alkyl radicals are trigonal planar and C is sp^2 hybridized. The p-orbital keeps the unpaired electron.

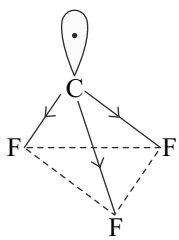


(H may be R also)

The bond angle in this structure is 120°. This large bond angle over tetrahedral angle (109°28′) reduces strain and favours this structure when H is R. The $\dot{C}H_3$ radical is also trigonal planar.

Resonance-stabilized radicals such as $Ph\dot{C}H_2$ and $Ph_2\dot{C}H$ are also trigonal planar. It is the resonance that requires planarity in the structure.

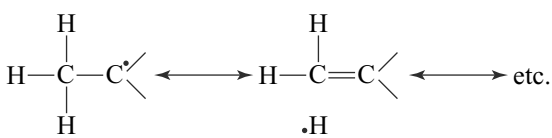
On the other hand, trifluoromethyl radical, $^{\bullet}CF_3$, is trigonal pyramidal and single electron is housed in an sp^3-hybrid orbital.



In this radical, F is more electronegative than C. Bond pairs shift towards F atoms. It reduces repulsion between them. Thus, the radical remain tetrahedral in structure and trigonal pyramidal in shape.

Stability

Radicals are stabilized by hyperconjugation as well as by resonance through π-electron systems. Simple alkyl radicals are stabilized by hyperconjugation. A radical that forms more hyperconjugative structures is more stable and vice versa.



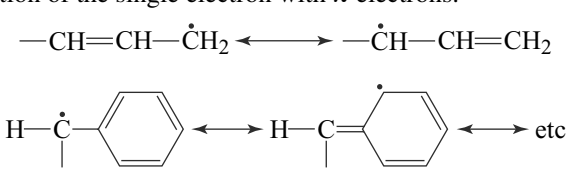
Thus, a tertiary radical is more stable than a secondary radical.

$$R_3C^{\bullet} > R_2\dot{C}H > R\text{–}\dot{C}H_2 > \dot{C}H_3$$

Radicals of the type

$$\text{—CH=CH—}\dot{C}\text{ and Ph}\dot{C}\text{H}$$

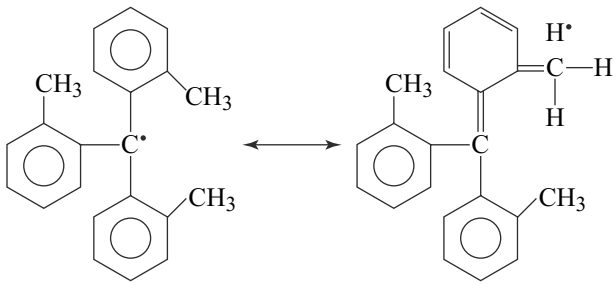
are stabilized by delocalization of the single electron with π-electrons.



Thus, relative stability of phenyl group containing radicals follows the order

$$PH_3\dot{C} > Ph_2\dot{C}H > Ph_2\dot{C}H_2$$

The tri (o-tolyl) methyl radical is even stabler than triphenyl methyl radical.
It is because CH_3 groups may share free-radical electron to form more structures.



Tri (*o*-tolyl) methyl radical

Reactions

1. Some of the reactions involving radicals are given below:

(a) *Chlorination of alkanes*

This group of reactions involve free radicals.

Initiation $Cl—Cl \xrightarrow{h\nu} 2Cl^{\bullet}$

Propagation
$CH_4 + Cl^{\bullet} \longrightarrow HCl + \dot{C}H_3$
$^{\bullet}CH_3 + Cl_2 \longrightarrow CH_3—Cl + Cl^{\bullet}$

Termination
$Cl^{\bullet} + Cl^{\bullet} \longrightarrow Cl_2$
$^{\bullet}CH_3 + {}^{\bullet}CH_3 \longrightarrow CH_3—CH_3$

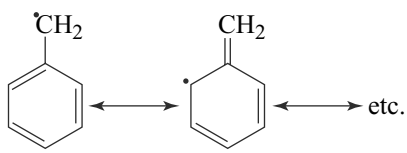
(b) *Chlorination of alkyl benzenes*

The light-induced chlorination or bromination of alkyl benzenes gives substitution on the side chain not on the ring.

$$C_6H_5—CH_3 \xrightarrow[h\nu]{Cl_2} C_6H_5CH_2—Cl \xrightarrow[h\nu]{Cl_2} C_6H_5CCl_3$$

Benzotrichloride

The effect of phenyl ring is to stabilize the radical intermediate.



2. Addition reactions

(a) *Addition of Cl_2 to C=C*

Under the influence of light, C_{12} adds to C=C in a free-radical manner. Such reactions generally take place in the gaseous phase or in the nonpolar solvent (CCl_4).

Initiation $Cl_2 \xrightarrow{h\nu} 2Cl^{\bullet}$

Propagation $Cl^{\bullet} + H_2C{=}CH_2 \longrightarrow ClCH_2{-}\dot{C}H_2 + Cl^{\bullet}$

$Cl{-}CH_2{-}\dot{C}H_2 + Cl_2 \longrightarrow Cl{-}CH_2{-}CH_2{-}Cl + Cl^{\bullet}$

Termination $Cl^{\bullet} + Cl^{\bullet} \longrightarrow Cl_2$

(b) *Addition of HBr to CH_3–$CH{=}CH_2$*

HBr adds to unsymmetrical alkenes under thermal condition in a free-radical manner. It is popularly known as anti-Markownikoff addition. The reaction proceeds in the presence of a peroxide.

Initiation $R{-}O{-}O{-}R \xrightarrow{h\nu} 2R{-}O^{\bullet}$

$RO^{\bullet} + HBr \longrightarrow R{-}OH + Br^{\bullet}$

Propagation $CH_3{-}CH{=}CH_2 + Br^{\bullet} \longrightarrow CH_3{-}\dot{C}H{-}CH_2{-}Br$

$CH_3{-}\dot{C}H{-}CH_2{-}Br + HBr \longrightarrow CH_3{-}CH_2{-}CH_2{-}Br + Br^{\bullet}$

Termination $R^{\bullet} + R^{\bullet} \longrightarrow R{-}R$

$Br^{\bullet} + Br^{\bullet} \longrightarrow Br_2$

3. Autoxidation

Slow oxidation of organic compunds by atmosphereic oxygen is termed as autoxidation. One of such reactions is oxidation of benzaldehyde to benzoic acid. This reaction is catalysed by light and the radical initiators ($R^{\bullet}$). It is also catalysed by metal ions capable of one-electron transfer, Fe^{3+} and Co^{+3}.

$$Ph{-}\overset{\overset{O}{\|}}{C}{-}H + Fe^{3+} \longrightarrow Ph{-}\overset{\overset{O}{\|}}{C}{}^{\bullet} + H^{\oplus} + Fe^{+2}$$

$$Ph{-}\overset{\overset{O}{\|}}{C}{-}O{-}O^{\bullet} + Ph{-}\overset{\overset{O}{\|}}{C}{-}H \longrightarrow Ph{-}\overset{\overset{O}{\|}}{C}{-}O{-}OH + Ph{-}\overset{\overset{O}{\|}}{C}{}^{\bullet}$$

$$Ph{-}\overset{\overset{O}{\|}}{C}{-}O{-}OH + Ph{-}\overset{\overset{O}{\|}}{C}{-}H \longrightarrow 2Ph{-}\overset{\overset{O}{\|}}{C}{-}OH$$

(Benzaldehyde often fails silver mirror test due to its oxidation to benzoic acid.)

4. Radical polymerization

Many synthetic polymers are made by radical processes, e.g., vinyl polymerization. The most common initiators in such reactions are radicals, formed by thermal (or photochemical) decomposition of peroxides or azo compounds.

$$Ph{-}\overset{\overset{O}{\|}}{C}{-}O{-}O{-}\overset{\overset{O}{\|}}{C}{-}Ph \longrightarrow 2Ph{-}\overset{\overset{O}{\|}}{C}{-}O^{\bullet} \longrightarrow 2Ph^{\bullet} + 2CO_2$$

The polymerization process may be summarized as

$$X_2 \xrightarrow{\Delta \text{ or } h\nu} 2X^{\bullet}$$

$$X^{\bullet} + Ph{-}CH{=}CH_2 \longrightarrow \begin{cases} Ph{-}\overset{\bullet}{C}H{-}CH_2{-}X \quad [I] \\ Ph{-}CH(X){-}CH_2^{\bullet} \quad [II] \end{cases}$$

The intermediate (I) is favoured over (II) as it is a benzyl-type radical (II is the alkyl type).
Polymerization then gives a product that has phenyl groups on alternate carbons (head to tail addition).

$$X{-}CH_2{-}\overset{Ph}{\underset{\bullet}{C}}H + Ph{-}CH{=}CH_2 \longrightarrow X{-}CH_2{-}\overset{Ph}{C}H{-}CH_2{-}\overset{Ph}{\underset{\bullet}{C}}H$$

$$\longrightarrow X{-}CH_2{-}\overset{Ph}{C}H{-}CH_2{-}\overset{Ph}{C}H{-}CH_2{-}\overset{Ph}{\underset{\bullet}{C}}H \text{ etc.}$$

This process may be terminated either by combination or by disproportionation of radicals.
To control the molecular weight of the polymer, chain-terminators are added to the reaction mixture.

Carbene

The divalent, electron-deficient intermediate of the type CX_2 is known as 'Carbene'. The simplest carbene is methylene, CH_2. Carbenes have very short lifelime (less than 1 sec). They may be of two types: (a) singlet and (b) triplet.

Singlet: If the two non-bonded electrons are paired, the carbene is called a singlet.

Triplet: If the two non-bonded electrons are unpaired, the carbene is called a triplet. It is, thus, a biradical.

Singlet Triplet

Formation

1. Thermal or photochemical decomposition
   Diazo compounds on thermal or photochemical decomposition give carbenes.

$$CH_2{=}\overset{\rho}{N}{=}\overset{\sigma}{N}: \xrightarrow{\Delta \text{ or } h\nu} :CH_2 + N_2$$

Ketenes also react in the same way.

$$R_2C{=}C{=}O: \longrightarrow R_2C: + CO$$

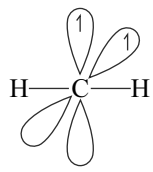
2. α-Elimination
   An α-elimination may produce a carbene, e.g. dichlorocarbene is formed when $CHCl_3$ is treated with an aq. base.

$$HO^- + H{-}C(Cl)(Cl)(Cl) \xrightarrow{(-H_2O)} :\overset{\sigma}{C}(Cl)(Cl)(Cl) \longrightarrow :CCl_2 + Cl^{\sigma}$$

Structure and shape

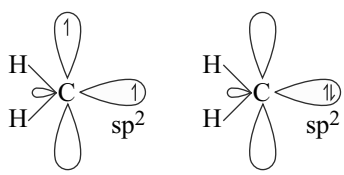
A carbene carbon is bonded to two groups and has two non-bonded electrons. For such a species two types of structures are possible.

1. A carbene carbon may be sp hybridized with linear or near linear geometry. The two sp hybrids are used for bond formation. The two p-orbitals remain pure atomic orbitals and following Hund's rule each has one electron. Hence, the ground state of a linear carbene is expected to be a triplet state.



I

2. A carbene carbon may also approximate sp^2 state. The unhybridized p-orbital is perpendicular to the plane. This situation may have two electron configurations.



II (Triplet) II (Singlet)

Spectroscopic studies show that triplet as well as singlet carbenes are bent. The triplet state has lower energy and is, thus, the ground state of a carbene (Table 5.1).

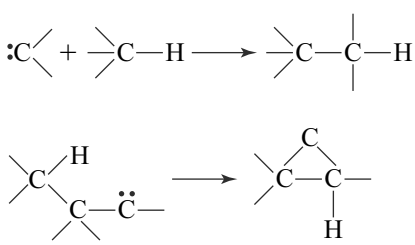
Table 5.1 Bond angle in some carbenes

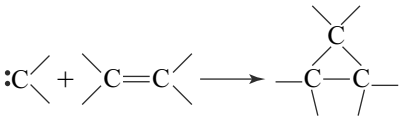
Carbene	State	Bond angle (°)
CH_2	Triplet	136
	Singlet	103
CCl_2	Singlet	100
CBr_2	Singlet	114

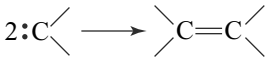
Reactions

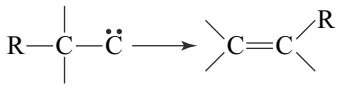
General reactions of carbenes are summarized below.

Insertion into C–H bond

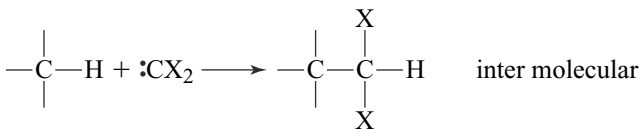


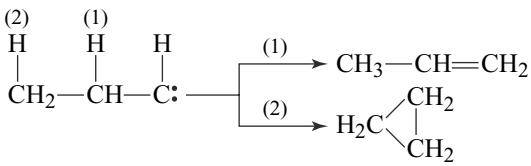
Addition 

Dimerization 

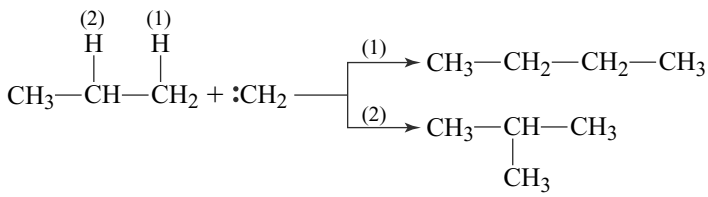
Rearrangement 

Insertion reaction A carbene may insert into C–H bond, both in aliphatic and aromatic. The reaction may be inter- or intramolecular (rearrangement).


inter molecular

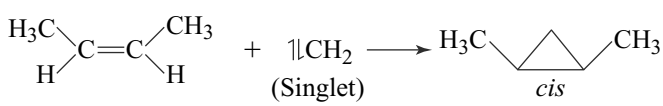

intra molecular

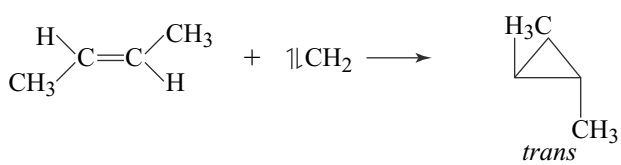
Thus, $:CH_2$ reacts with propane to give n-butane and isobutene.

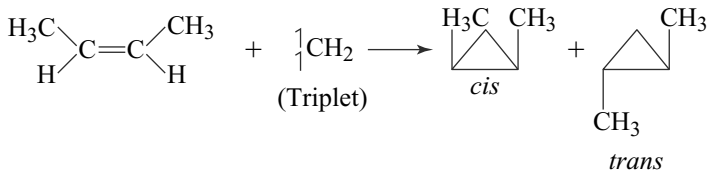


Dihalocarbenes (CCl_2 or Br_2) generally do not give insertion reactions. The above reactions are useless for synthetic purposes but show extreme reactivity of carbene.

Addition The addition of $:CH_2$ to C=C gives cycloalkane. The two carbenes (singlet and triplet) add differently. The addition of a singlet carbene is stereospecific whereas a triplet carbene adds in a non-stereospecific manner.

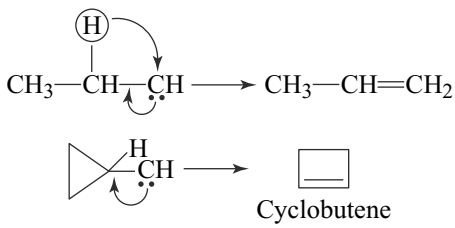

(Singlet) *cis*


trans

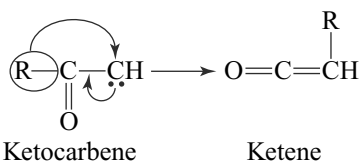


As the stereochemistry of these cyclo additions is specific, the reactions may be used to identify singlet and triplet carbenes.

Rearrangements Alkyl carbenes may rearrange with migration of H or alkyl group. The products are stable species. Some examples are



Migration of an alkyl group may also take place in a ketocarbene to form a ketene. This is called 'Wolff Rearrangement'.



TYPES OF ORGANIC REACTIONS

Organic compounds generally undergo four types of reactions.

1. Addition reactions
2. Substitution reactions
3. Elimination reactions
4. Rearrangement reactions

Addition Reactions

An addition reaction is that in which two substances combine to form a single product. It is the characteristic of unsaturated (C=C, C≡C, C=0, etc.) compounds. Addition reactions are further calssified as electrophilic, nucleophilic and radical addition. In such reactions, a single π-bond converts into two σ-bonds, i.e. an energetically favourable process.

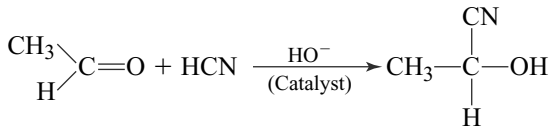
Electrophilic addition reaction

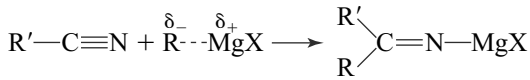
When an addition reaction is initiated by an electrophile, it is called 'Electrophilic Addition' reaction. It is the characteristic of C=C or C≡C bonds.

$$CH_2{=}CH_2 + Br_2 \longrightarrow Br{-}CH_2{-}CH_2{-}Br$$
$$CH_2{=}CH_2 + HBr \longrightarrow CH_3{-}CH_2{-}Br$$

Nucleophilic addition reaction

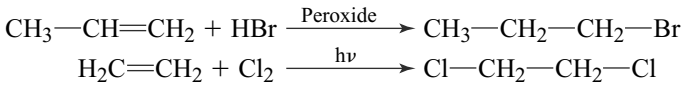
When an addition reaction is initiated by a nucleophile it is called nucleophilic addition reaction. It is characteristic of C=O, C≡N etc, that is, carbon–heteroatom multiple bonds.





Radical addition reaction

In the presence of peroxides, addition of HBr to C=C proceeds by a radical mechanism (see anti-Markownikoff's rule).

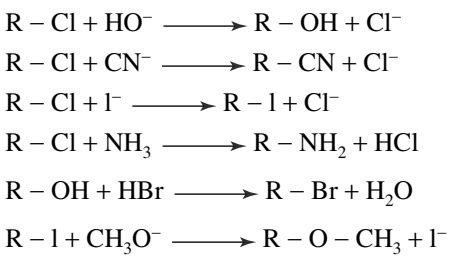


Substitution Reactions

In a substitution reaction, another atom or a group replaces an atom or a group. A substitution reaction may either be nucleophilic, electrophilic or a free-radical reaction.

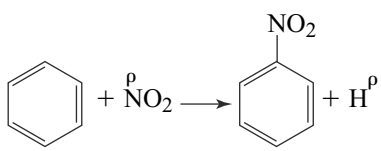
Nucleophilic substitution reaction

In a nucleophilic substitution reaction, a nucleophile replaces the leaving group (as a nucleophile) from the substrate. Such reactions are common in saturated substrates. Some examples are



Electrophilic substitution reaction

In electrophilic substitution reactions, the attacking reagent is an electrophile. The leaving group departs also as an electrophile. Such reactions are characteristic of the aromatic compounds.



Radical substitution reaction

Substitution of a group or an atom by a free radical is termed as radical substitution reaction, e.g. chlorination of alkanes.

$$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + HCl$$
$$\rightsquigarrow CCl_4 + 3HCl$$

Elimination Reactions

Elimination reactions are reverse of addition reactions. Thus, in such reactions a saturated substrate converts into an unsaturated product. The most common examples are

1. Dehydrohalogenation of alkyl halides
   Such reactions take place with a base.

$$CH_3 - CH_2 - CH_2 - Br + NaOH \longrightarrow CH_3 - CH = CH_2 + H_2O + Na^+ + Br^-$$

2. Dehydration of alcohols
   Dehydration of alcohols is acid catalysed.

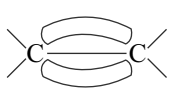
$$CH_3—CH_2—OH \xrightarrow{H^{\oplus}/\Delta} CH_2=CH_2—H_2O$$

Rearrangement

Rearrangements are reactions in which an atom or a group migrates from one centre to the other in the same molecule (see rearrangements in *Name Reactions*)

ADDITION TO CARBON–CARBON MULTIPLE BONDS

The carbon–carbon multiple bonds include both σ- and π-bonds. The σ-electrons are held strongly but the π-electrons are held loosely by the carbon nuclei. The π-orbitals are divided in two parts by the bond axis. It is, therefore, easily polarizable.



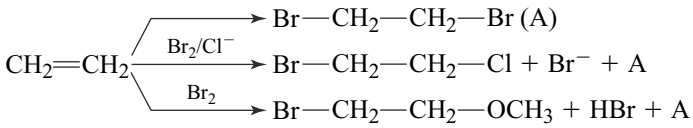
π-orbital

This electronic situation in a π-bond makes the reaction easy with an elelctrophile. The reaction is basically an addition reaction as a π-bond converts into two σ-bonds, an energetically favourable process. Thus, electrophilic addition is characteristic reaction of C=C and C≡C. However, nucleophilic or radical addition may also take place but only in selective substrates and in special conditions (see later in the Chapter).

ADDITION OF BR_2 TO C=C

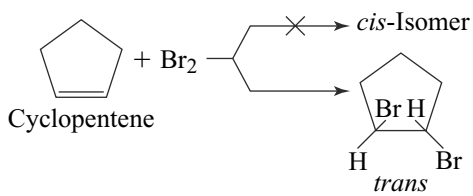
The addition of Br_2 to C=C is a two-step stereospecific reaction. The following observations prove the above fact.

1. When ethylene is treated with Br_2 in the presence of other nucleophiles, a mixture of products is obtained.



   In the presence of other nucleophiles, there is competetion between Br^{σ} and the other nucleophile; so, mixed products are obtained.

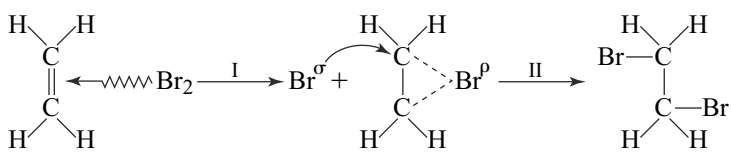
2. The addition of Br_2 to cycloalkenes always gives *trans*-dibromo alkane and not the *cis*-isomer.



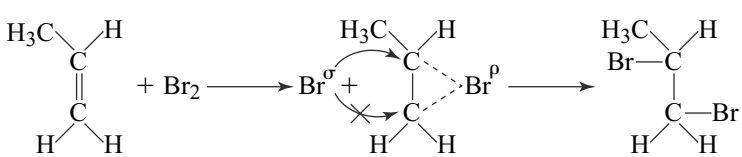
   It shows that the addition is stereospecific, i.e., a *trans* addition.

MECHANISM OF ADDITION

To account for a two-step stereospecific addition, the following mechanism has been suggested. Bromine molecule is nonpolar. But under the influence of loosely held π-electrons, it undergoes polarization. The polarized bromine molecule forms a π-complex with alkene that finally transforms into a cyclic intermediate, the brominium ion and Br^- parts with. This is the first step of the reaction. The second step involves the attack by the Br^- from the backside of the bridging bromine atoms. The frontside attack is sterically hindered due to bulky bromine atom of the bridge.

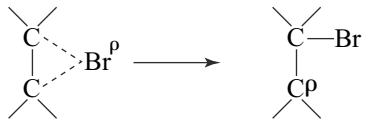


If the carbon atoms of the intermediate bromonium ion are symmetrically substituted, attack by Br^- (i.e., a nucleophile) occurs at either carbon. But in the case of the intermediate derived from an unsymmetrical alkene, the nucleophile attacks the more substituted carbon.



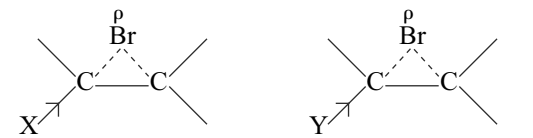
Effect of the Substituent at Unsaturated Carbon Atoms and the Rate of Addition

Electrophilic addition to C=C proceeds through an intermediate (bromonium ion or carbonium ion) that is cationic in nature.



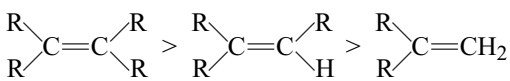
Bromonium ion Carbonium ion

Therefore, electron-donating groups will stabilize the intermediate, i.e., they will increase the rate of electrophilic additions. Conversely, electron-attracting groups (NO_2, CN, Br, COOH) will destabilize the intermediate and will decrease the rate of the electrophilic addition.



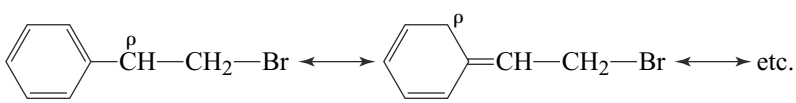
X = electron donating (Stabilization) Y = electron attracting (Destabilization)

The following order of reactivities is found for different alkenes.



$$> R{-}CH{=}CH_2 > CH_2{=}CH_2 > CH_2{=}CH{-}Br$$

The presence of phenyl group at the unsaturated carbon also increases the rate of the electrophilic addition. It is due to the fact that phenyl group stabilizes the intermediate by delocalization of the positive charge in the ring.



Howetxver, the rate of catalytic hydrogenation falls with increasing substitution in the alkene. The decreasing order found is

$$CH_2{=}CH_2 > RCH{=}CH_2 > R_2C{=}CH_2 > R_2C{=}CHR > R_2C{=}CR_2$$

It shows that hydrogenation is affected by steric factors.

Addition of HX and Markownikoff's Rule

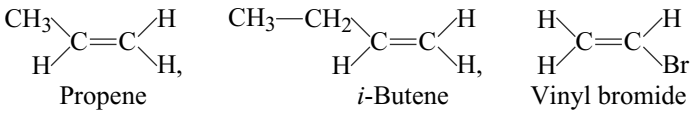
Markownikoff's rule deals with the addition of unsymmetrical reagent to unsymmetrical alkene (i.e. orientation of addition in polar condition).

The HX molecule is unsymmetrical, with respect to both atoms and polarity.

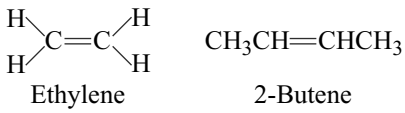
$$\overset{\delta+}{H}{-}\overset{\delta-}{X} \text{ where X = Br, } OSO_2\text{, OH, etc.}$$

Unsymmetrical alkene

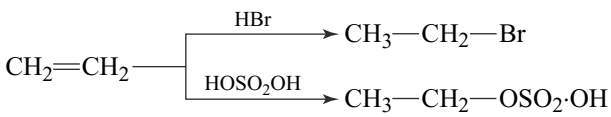
An alkene that carries different substituents at unsaturated carbon atoms is called unsymmetrical alkene.



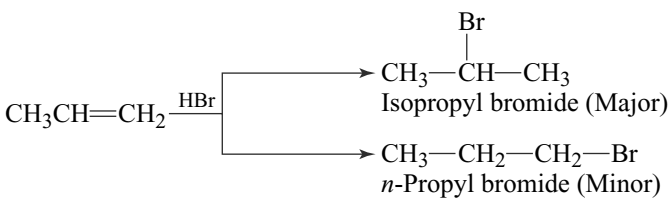
If substituents at unsaturated C atoms are similar, the alkene is said to be symmetrical.



The addition of HX to symmetrical alkenes gives only one product.



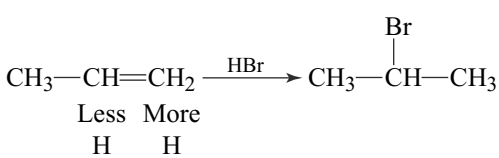
However, addition of HX to an unsymmetrical alkene can give only two products.



The major product is isopropyl bromide. To account for orientation of such addition reactions, Markownikoff proposed a generalization that is known as Markownikoff's rule. It states that—'During the addition of HX to unsymmetrical alkene, H of HX goes to that C which contains larger number of H atoms'

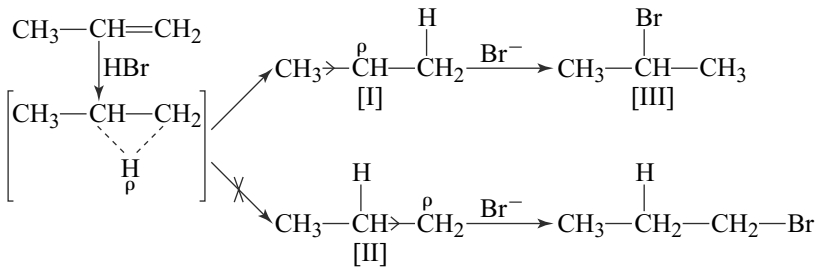
or,

'The negative part of the addendum adds on to that C which is joined with the least number of H atoms'. Thus, isopropyl bromide is the major additional product when HBr reacts with propene.



Electronic explanation of Markownikoff's rule

The addition of HBr to propene is a two-step reaction. In the first step, the partially positive H atom of HBr forms the protonium ion intermediate. The intermediate may, however, be taken as a carbonium ion. Then the relative stability of the possible carbonium ions determines the course of addition.



The secondary carbonium ion (I) is more stable than the primary carbonium ion (II). Thus, (I) is formed in preference to (II), leading to the formation of isopropyl bromide (III) as the major product.

However, the mode of addition is reversed in the presence of peroxides.

$$CH_3—CH=CH_2 \xrightarrow[R—O—O—R]{HBr} CH_3—CH_2—CH_2—Br$$

This is known as anti-Markownikoff addition or peroxide effect or Kharasch effect. The reverse addition is due to the free-radical addition in the presence of a peroxide.

Peroxides decompose to give radicals.

$$R—O—O—R \xrightarrow{\Delta} 2RO^{\bullet}$$

The $RO^{\bullet}$ radical can react with HBr in two ways.

$$HBr + RO^{\bullet} \begin{cases} \longrightarrow R—OH + Br^{\bullet} & \Delta H = \sigma \\ \longrightarrow R—OBr + H^{\bullet} & \Delta H = \rho \end{cases}$$

The first process is exothermic and so is energetically favourable. Thus, $Br^{\bullet}$-free radical initiates a chain reaction.

$$CH_3—CH=CH_2 + Br^{\bullet} \begin{cases} \longrightarrow CH_3—\dot{C}H—CH_2—Br \quad (IV) \\ \longrightarrow CH_3—\underset{\displaystyle Br}{\underset{|}{CH}}—\dot{C}H_2 \quad (V) \end{cases}$$

The intermediate radical (IV), a secondary radical, is more stable than a primary radical (V). Therefore, (IV) is formed preferentially and determines the course of the reaction. The reaction completes as

$$CH_3—CH=CH_2 + Br^{\bullet} \longrightarrow \underset{(IV)}{CH_3—\dot{C}H—CH_2—Br}$$

$$CH_3—\dot{C}H—CH_2—Br + HBr \longrightarrow CH_3—CH_2—CH_2—Br + Br^{\bullet}$$

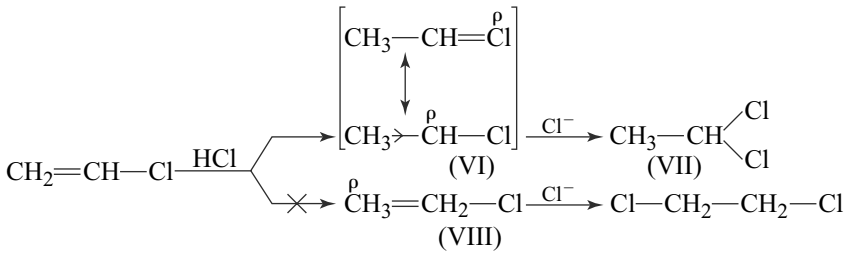
The reaction in the presence of inhibitors (diphenyl, quinines, etc.) stops, which supports radical mechanism.

$$Br^{\bullet} + Br^{\bullet} \longrightarrow Br_2$$
$$R^{\bullet} + R^{\bullet} \longrightarrow R—R$$

The peroxide has no effect on the addition of HCl or HI. It is because HCl bond that is stronger (103 kCal/mole) than HBr bond (87 kCal/mole) is not homolysed by the free radical. The HI bond is weaker (71 kCal/mole) but iodine atom forms I_2 rather than being added to the double bond.

Addition of HCl to Vinyl Chloride

Vinyl chloride is CH_2=CH–Cl. This addition, thus, is the addition of an unsymmetrical reagent (HCl) to an unsymmetrical alkene. It proceeds through a carbonium ion intermediate.

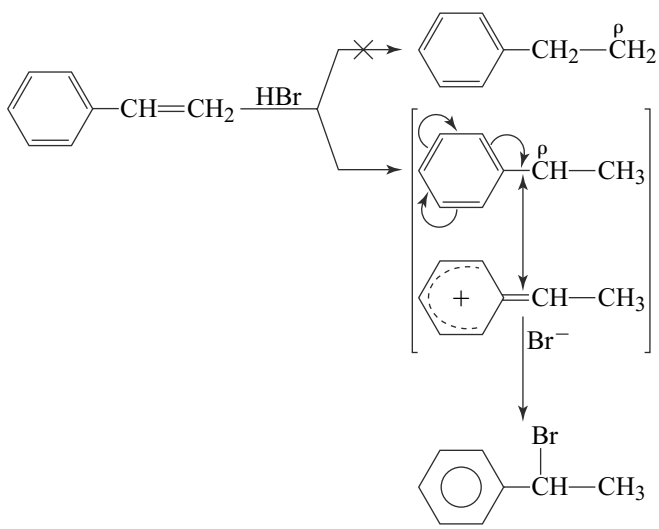


The formation of (VIII) seems to be probable as Cl has –I effect. But (VIII) is a primary carbonium ion as well. On the other hand, (VI) is a secondary carbonium ion and so is more stable than (VIII). In addition to that, electron pairs at Cl can enter into mesomeric delocalization with the positive C atom giving greater stability (VI).

The addition, therefore, proceeds according to the Markownikoff's rule. But the –I effect of Cl makes the reaction slow.

Addition of HBr to C_6H_5–CH=CH_2

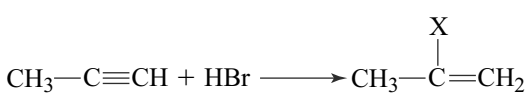
The addition is similar to the addition of HCl to vinyl chloride.

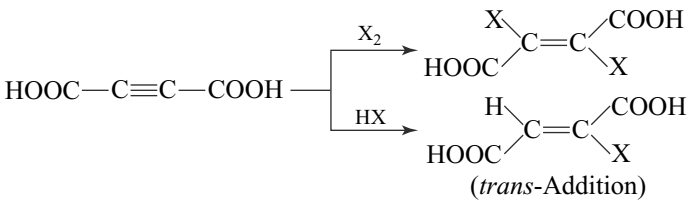


Many other addition reactions of C=C will be discussed in the Chapter *Alkene*.

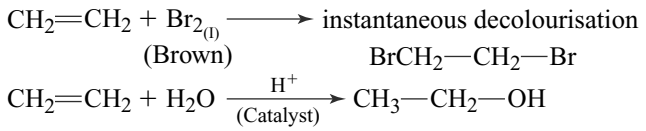
Reaction of C≡C

The electrophilic addition reactions of alkynes are very similar to alkenes. The stereochemistry is also similar and the reactions follow Markownikoff's rule.

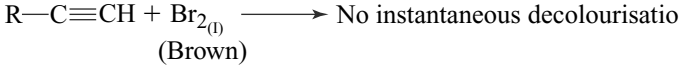




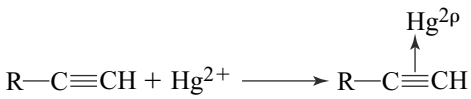
But the reaction rates of alkynes with the electophilic reagents are less than alkenes.



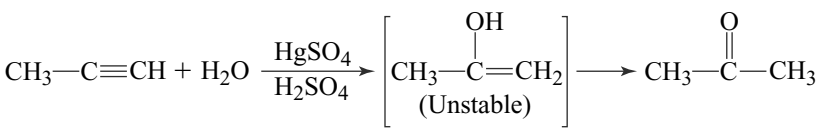
The deep brown colour of liquid bromine persists for a few minutes with most alkynes.



Similarly, the addition of water to alkynes not only requires acid catalyst but also mercuric ions. The mercuric ion forms complex with triple bond and makes the addition possible.



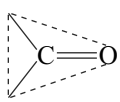
The hydration of propyne can be written as



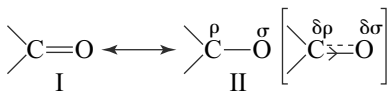
Many other important reactions are given in the Chapter *Alkynes*.

Reactions of C=O and C≡N

The carbonyl group (>C=O) is trigonal planar (C is sp^2 hybridized).

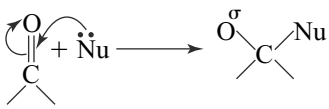


As O atom is more electronegative than C atom and the >C=O group is polar. The dipolar resonance form best represents the reaction with oxygen being negative and carbon positive.

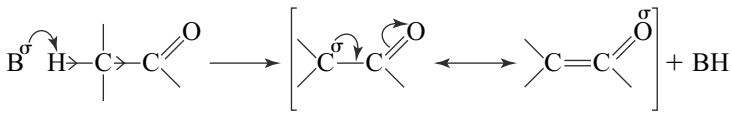


The positive nature of the carbonyl carbon makes the carbonyl group electron attracting (–I effect) as a whole. The polar nature of >C=O group works in two ways towards its reactions.

1. The C atom of the >C=O group is attacked by a nucleophile.



2. The electron-attracting effect of >C=O group makes the α-H atom acidic. It is, thus, taken up by a base to give resonance-stabilized carbanion.

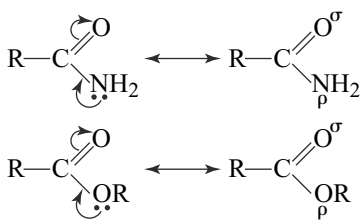


It is the first step in many condensation reactions (e.g., aldol and Claisen condensations). The carbonyl compounds fall in two categories:

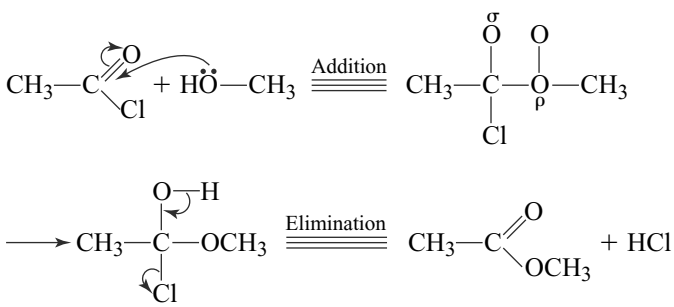
(a) Aldehydes and Ketones
(b) Carboxylic acids and their derivative (esters, acid chlorides, amides, etc.)

Aldehydes and ketones give many nucleophilic addition reactions.

But carboxylic acids or their derivatives do not give addition reactions due to the conjugation of >C=O group with electron pair of the heteroatom linked to the carbon of the >C=O group.

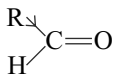


(This resonance reduces positive nature of the carbonyl carbon.)
Acid and their derivatives generally give addition–elimination reactions.

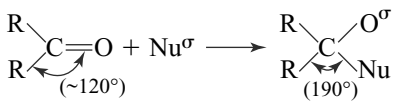


Structure and Reactivity of Aldehydes and Ketones

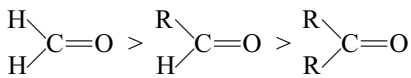
The reactions of aldehydes and ketones are influenced by both electronic and steric factors. The alkyl groups are electron donating. They decrease the positive nature of the carbonyl C atom and makes it less susceptible to be attacked by a nucleophile.



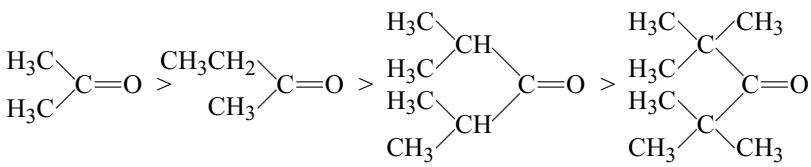
Thus, the presence of R group at the C atom of the >C=O group causes a decrease in the reactivity. On the other hand, the bulk of the R group inhibit the approach of the nucleophile to the C atom of the >C=O group. It is because in the transition state, bond angle is reduced to ~109° from ~120° in the substrate. Thus, transition state is energetically unfavourable that makes the reactions slow.



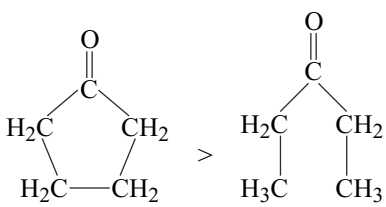
Thus, the overall reactivity of aldehydes and ketones is



Formaldehyde is most reactive, as H has neither +I effect nor steric hindrance. For ketones, as the bulk of R increases, their reactivity also decreases. It is due to the greater steric hindrance caused by the bigger R groups. On this basis, the decreasing reactivity with increasing bulk of R is



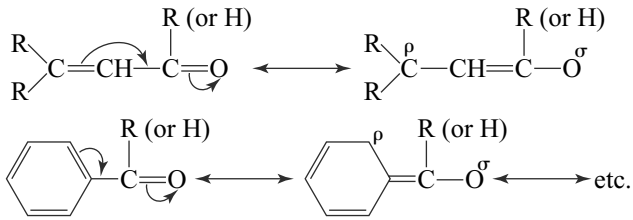
Cyclic ketones are more reactive in addition reactions than their open-chain analogues, e.g.



It is because the R groups of the open-chain compounds have more freedom of motion and produce greater steric hindrance.

Conjugated >C=O and Reactivity

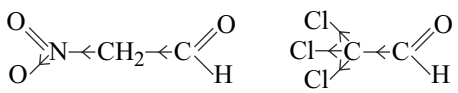
When the >C=O group is conjugated with C=C or with a benzene ring, the reactivity (of aldehydes or ketones) is decreased. It is because of the resonance stabilization in the carbonyl compound.



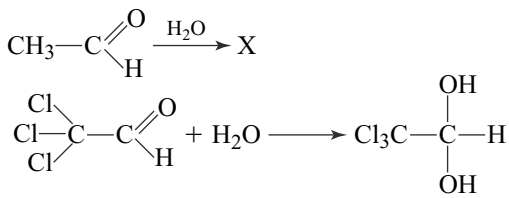
This type of resonance reduces positive nature of the carbonyl carbon, decreasing reactivity of the carbonyl compound.

Electron-Attracting Groups and Reactivity

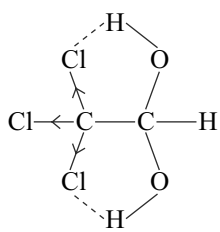
Electron-attracting groups (–NO_2, –CN, –Cl, etc.) at α-position increase the rate of nucleophilic addition reactions of aldehydes and ketones. It is because such groups increase the positive nature of the carbonyl carbon.



Because of the above effect, trichloro acetaldehyde (chloral) forms crystalline hydrate, whereas acetaldehyde fails that reaction.

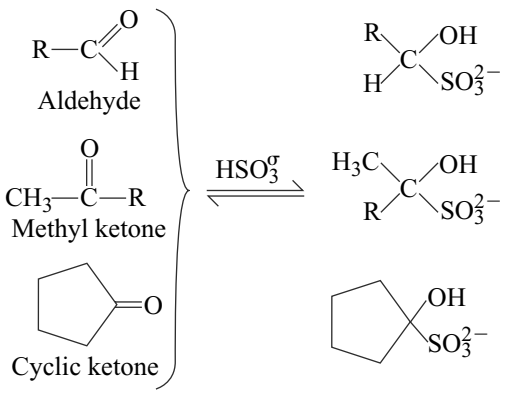


The hydrate is stabilized partly by electron-attracting effect of Cl atoms and partly by H bonding.



Size of the Nucleophile and Reactivity

The size of the nucleophiles also affects the rate of addition reactions of aldehydes and ketones. The larger is the size of the nucleophile slower is the reaction. It is because a large nucleophile cannot approach the carbonyl carbon easily. For example, the rate of addition of SO_3^{2-} to $(CH_3CH_2)_2C{=}O$ is much smaller than the rate of the addition of CN^- (SO_3^{2-} larger than CN^-). Actually, bisulphite addition compounds are formed only by aldehydes, methyl ketones and cyclic ketones.



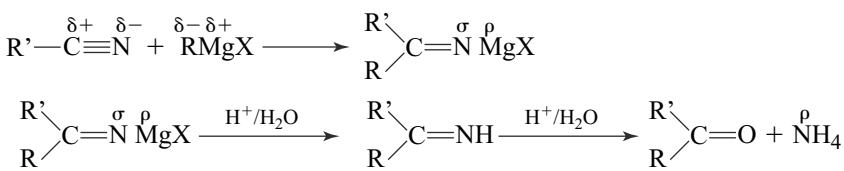
Reactions will be given in the Chapter *Aldehydes and Ketones*.

The C≡N group

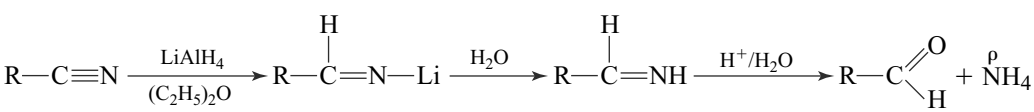
The cyanide group is polar as N is more electronegative than C (C is sp hybridized in C≡N). It is best represented by the resonance structures.

This polarity makes C≡N group highly reactive (like C=O). It gives variety of reactions. Some examples are as follows.

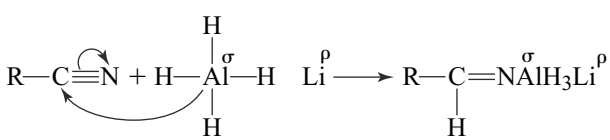
1. Cyanides add Grignard reagents to form salt of ketimines that can be hydrolyzed to ketones.



2. A cyanide can be converted to an aldehyde by $LiAlH_4$.



3. Cyanides can also be reduced to a primary amine by $LiAlH_4$.
The reaction proceeds as



Thus, overall reaction can be written as

$$2R{-}C{\equiv}N + LiAlH_4 \longrightarrow [R{-}CH_2{-}N]_2\overset{\sigma}{Al}\,\overset{\rho}{Li} \xrightarrow{H^+/H_2O} RCH_2{-}NH_2 + \overset{3\rho}{Al} + \overset{\rho}{Li}$$

(Primary amine)

ALIPHATIC NUCLEOPHILIC SUBSTITUTION

A substitution reaction involves replacement of one functional group by another.

$$R{-}X + Y \longrightarrow R{-}Y + X$$

When the reagent (Y) is a nucleophilc (i.e., an electron pair-donating reagent), the reaction is termed as nucleophilic substitution reaction, e.g.,

$$HO^{\sigma} + CH_3 - Br \longrightarrow H_3C - OH + Br^{\sigma}$$

In this reaction, the electron pair of the C–O bond is provided by the HO^-, whereas bromine departs with electron pair of C–Br bond. This type of reactions is abbreviated as S_N, S for substitution and N for nucleophilic. These reactions are of great synthetic utility.

Variety of nucleophilic reagents is found in S_N reactions. A nucleophile may be an anion, $Y:^{\sigma}$, or a neutral molecule, Y or HY. A substrate may be neutral or positively charged.

Nucleophilic substitution reactions are widespread and substrates may include alkyl halides, alcohols, ethers, esters and onium salts, such as

Tetraalkylammonium	$R_4N^{\oplus}$
Trialkyl carbonium	$R_3N^{\oplus}$
Alkyl diazonium	$R - \overset{\oplus}{N} \equiv N:$

Table 5.2 Some SN-substitution reactions

Alkyl compound, RX	Reaction
Alkyl chloride	
Alkyl bromide	$R{-}Br + I^{\sigma} \longrightarrow R{-}I + Br^{\sigma}$
Alkyl iodide	$R{-}I + CH_3O^{\sigma} \longrightarrow R - OCH_3 + I^{\sigma}$
Alcohol	$R{-}OH + HBr \longrightarrow R{-}Br + H_2O$
Ether	$R{-}O{-}R' + HI \longrightarrow R{-}I + R'{-}OH$
Ester	$CH_3{-}\overset{\overset{O}{\|}}{C}{-}OR + H_2O \longrightarrow R{-}OH + CH_3{-}\overset{\overset{O}{\|}}{C}{-}OH$
Ammonium ion	$R{-}N^{\rho} + HO^- \longrightarrow R{-}OH + R_3N$
Diazonium ion	$R{-}\overset{\rho}{N}{\equiv}N + H_2O \longrightarrow R{-}OH + N_2 + H^{\rho}$
Alkyl chloride	$R{-}Cl + CN^{\sigma} \longrightarrow R{-}CN + Cl^{\sigma}$
Alkyl chloride	$R{-}Cl + HC{\equiv}C^{\sigma} \longrightarrow R{-}C{\equiv}CH + Cl^{\sigma}$
Alkyl chloride	$R{-}Cl + NO_2^{\sigma} \longrightarrow R{-}NO_2 + Cl^{\sigma}$

Many S_N reactions can be carried out using the solvent as the nucleophile. These reactions are called 'solvolysis'. For example, solvents such as water, alcohol and acetic acid cause hydrolysis, alcoholysis and acetolysis, respectively.

$$R–Cl + H_2O \longrightarrow R–OH + Cl^- \quad \text{(hydrolysis)}$$
$$R–Cl + CH_3–OH \longrightarrow R–OCH_3 + Cl^- \quad \text{(alcoholysis)}$$
$$R–Cl + CH_3COOH \longrightarrow CH_3–COOR + Cl^- \quad \text{(acetolysis)}$$

The following two mechanisms are common in S_N reactions.

1. Two-step reaction, S_N1

$$R—X \longrightarrow \underset{\text{Transition state}}{[R^{\delta+}\cdots X^{\delta-}]} \xrightarrow{I} R^{\rho} + X^{\sigma}$$
$$\text{II}\uparrow \; Y^{\sigma} \longrightarrow R—Y$$

2. One-step reaction, S_N2

$$R—X + Y^{\sigma} \longrightarrow \underset{\text{Transition state}}{[Y^{\delta+}\cdots R\cdots X^{\delta-}]} \longrightarrow RY + X^{\sigma}$$

These symbols (S_N1 and S_N2) were used by Ingold.

Common nucleophiles

Y^{σ}=HO^{σ}, Cl^{σ}, Br^{σ}, I^{σ}, RO^{σ}, CN^{σ}, R^{σ}, NO_2^{σ}, NH_2^{σ}, RCO_2^{σ}

Y=R_3N, …, R_2S

HY=H_2O, …, R–OH, …, NH_3

Easily displaced groups

X^{σ}=Cl^{σ}, Br^{σ}, I^{σ}, RSO_3^{σ}, RCO_2^{σ}

Z=H_2O, …, N_2, …, R_3N

S_N2 Reactions

Nucleophilic substitution reactions that follow second-order kinetics are called S_N2 reactions. For example,

$$CH_3–Br + HO^{\sigma} \longrightarrow CH_3–OH + Br^{\sigma}$$

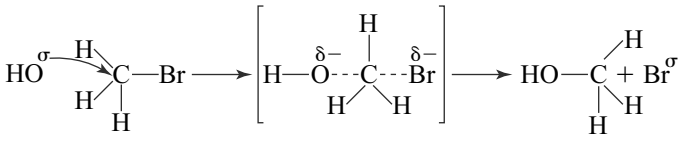
The rate of this reaction is found to be dependent on the concentrations of both CH_3–Br and OH^{σ}.

$$\text{Rate} = K_2\,[CH_3–Br]\,[HO^{\sigma}], \text{ i.e., a second-order reaction.}$$

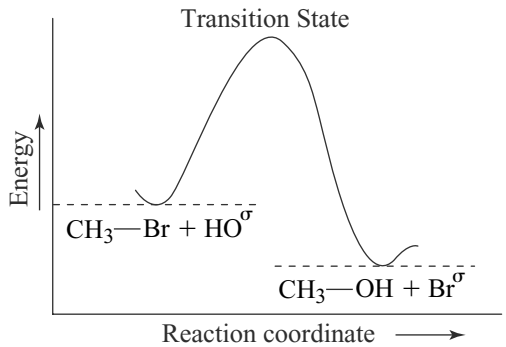
Thus, it is an S_N2 reaction.

Mechanism

The S_N2 reaction is a one-step process, in which no intermediate is formed. The process of bond making and bond breaking occurs simultaneously. The nucleophile attacks the substrate from the back of the leaving group. The course of the reaction can be formulated as



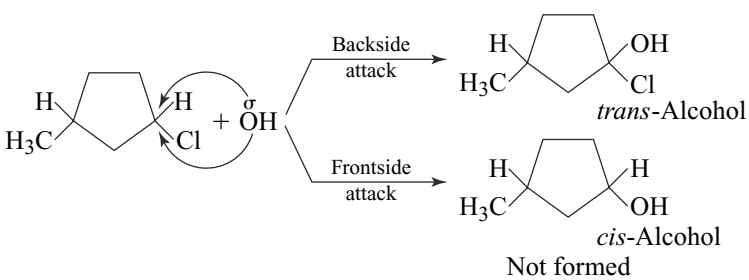
The energy profile for the reaction may be represented as



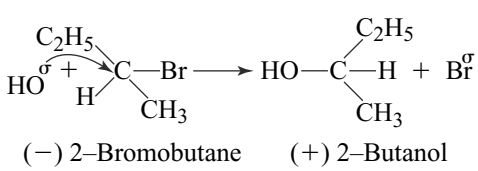
Stereochemistry of S_N2 reactions

The backside attack of nucleophile has been proposed in the mechanism. The following points are in favour of the backside attack.

1. Oxygen and Br atoms are well separated in the transition state, i.e., the charge (δ–) is dispersed. The frontside attack would not disperse the negative charge to the same extent and, hence, would be less favourable.
2. An S_N2 reaction between *cis*-1-chloro-3-methylcyclopentane and HO^{σ} would give *cis*-alcohol by frontside attack but the *trans*-alcohol by backside attack. The actual product is the *trans*-alcohol. Thus, it proves the backside attack.



3. The backside attack predicts inversion of configuration when substitution occurs at a chiral carbon (i.e., asymmetrically substituted). It is found in many cases. For example, the hydrolysis of 2-bromobutane gives alcohol having the configuration opposite to the halide.



Thus, S_N2 reaction proceeds with stereochemical inversion. This inversion of the configuration is called Walden inversion.

S_N1 Reactions

A nucleophilic substitution reaction that follow first-order kinetics is called S_N1 reaction. For example, hydrolysis of tert-butyl bromide to tert-butyl alcohol by NaOH.

$$(CH_3)_3C{-}Br + HO^{\sigma} \longrightarrow (CH_3)_3C{-}OH + Br^{\sigma}$$

The rate of this reaction depends only on the concentration of $(CH_3)_3C{-}Br$, i.e.,

$$\text{Rate} = K_1\,[(CH_3)_3C{-}Br]$$

Thus, it is a first-order reaction.

Mechanism

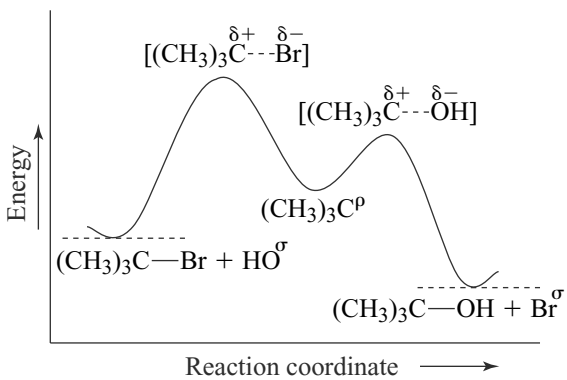
The S_N1 reaction proceeds by a two-step mechanism. It involves

1. ionization of tert-butyl bromide (slow step) to tert-butyl carbocation due to dipole–dipole interaction with polar solvent and
2. fast reaction of carbocation with HO^{σ}.

$$(CH_3)_3C{-}Br \xrightarrow{\text{Slow}} (CH_3)_3C^{\rho} + Br^{\sigma}$$

$$(CH_3)_3C^{\rho} + HO^{\sigma} \xrightarrow{\text{fast}} (CH_3)_3C{-}OH$$

The energy profile for an S_N1 reaction is shown below.

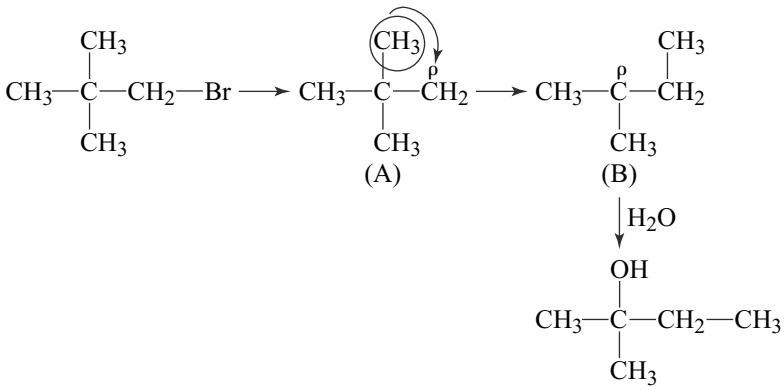


The energy profile shows two transition states. The first corresponds to the formation of the intermediate carbocation, $(CH_3)_3C^{\rho}$, and the second with a low barrier indicates rapid reaction between the carbocation and HO^{σ}.

Rearrangement and S_N1 mechanism

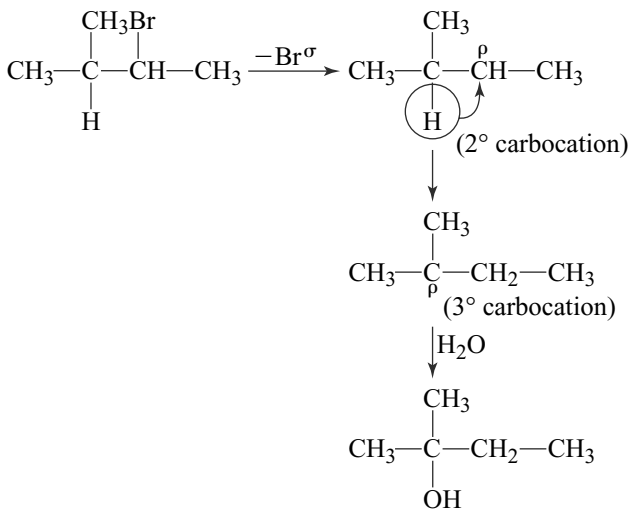
The S_N1 reactions proceed through carbonium ion intermediate. An important aspect of carbonium ion chemistry is rearrangement. It always happens when the initially formed carbonium ion rearranges to a more stable ion. For example,

1. The S_N1 hydrolysis of neopentyl bromide gives 2-methylbutan-2-ol not neopentyl alcohol (2,2-dimethyl propanol). It is because of the greater stability of the tertiary carbonium ion (B) that is produced from the initially formed carbonium ion (A).



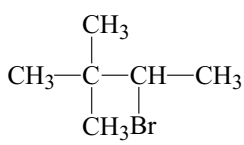
Here, a methyl group migrates with its bonding pair of electron from the β to the α-carbon converting an unstable primary carbonium ion to a stable tertiary cation. These types of rearrangements, in carbon skeleton, are known as '*Wagner–Meervwein Rearrangement*'.

2. Rearrangements involving shifts of H (as H^{Γ}) may also occur.



Problem

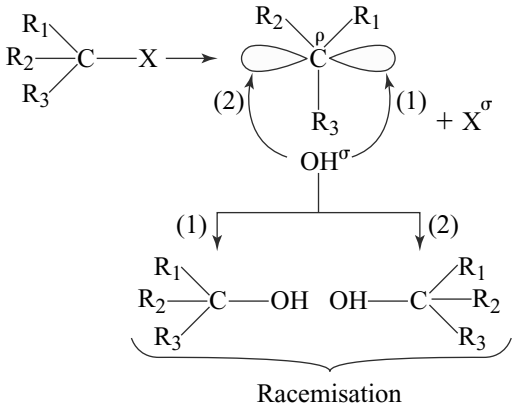
Predict real product in the SN^1 hydrolysis of the following bromide,



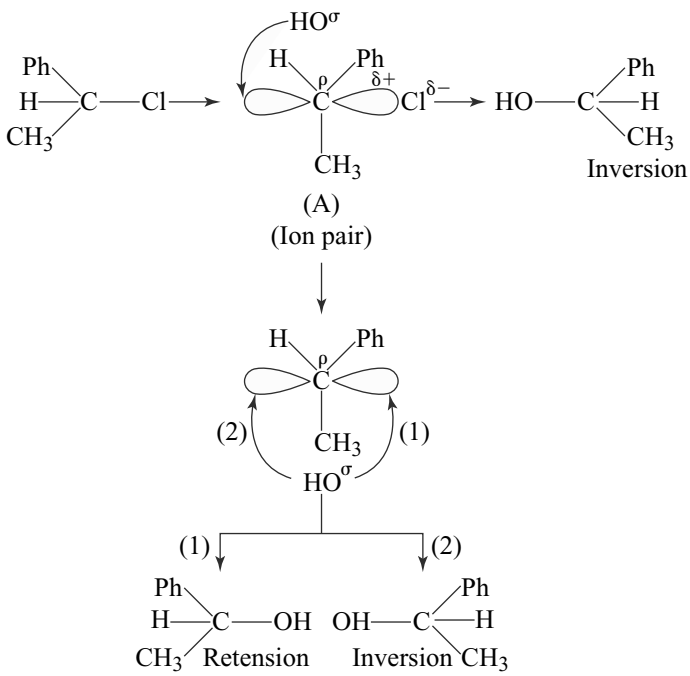
Suggest a mechanism and name the reaction.

Stereochemistry of S_N1 reactions

The S_N1 reaction involves carbocation intermediate. It is a trigonal planar and the C^{ρ} carbon is sp^2 hybridized. It has an empty p-orbital that is perpendicular to the plane of the three sp^2-orbitals. Either lobe of the empty p-orbital can interact with the nucleophile. Attack on either lobe is probably equal. Thus, a carbocation formed from an asymmetric carbon atom would give equal proportions of products with retension and inversion of configuration, i.e. the reaction will result into racemization. It is practically true for very stable carbocation, i.e. tertiary carbocation.



But with secondary carbocation, some inversion also takes place and the product is not pure racemic form. It is due to the presence of ion pair-like species (A) during ionization that makes easy, backside attack giving product with some inversion of configuration, e.g.



FACTORS AFFECTING S_N REACTION

The following factors affect reactivity in S_N reactions.

1. Structure of the alkyl group
2. The nature of the leaving group
3. The nature of the nucleophile
4. The nature of the solvent

Structure of the Alkyl Group

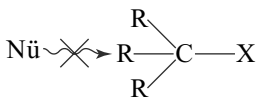
The rates of S_N2 reaction of R–X are found to follow the given order.

$$CH_3–X > \text{primary R} > \text{secondary R} > \text{tertiary R}$$

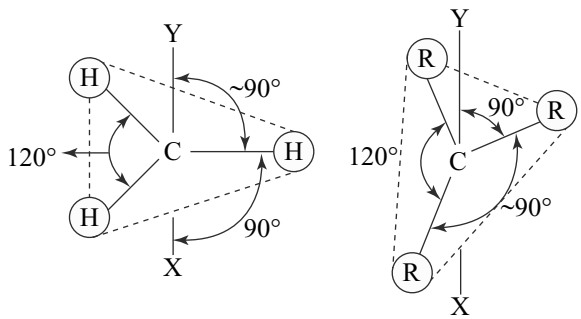
Electron-donating or electron-attracting group in R has no effect on the rate.

The S_N2 reactions are greatly influenced by steric hindrance around the C site where displacement has to take place. The steric hindrance can be seen to operate in two ways:

1. Heavily substituted reactive sites will restrict backside approach of the nucleophile.



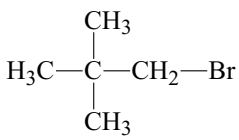
2. The greater nonbonded interaction in the transition state between the larger group (R instead of H) and the entering and leaving groups will make transition state less stable. On going from ground state to the transition state in an S_N2 reaction, the angle HCH in CH_3X increases from about 109° to about 120°, but at the same time the angles H–C–X and Y–C–H decreases to about 90°. The overall effect is the decrease in the rate of reaction.



Less steric hindrance of H with X and Y

Large steric hindrance of R with X and Y

Neopently halides, which are primary halides, are very unreactive in S_N2 reactions due to steric hindrance.



Neopentyl bromide

The following table shows average relative rates for different alkyl groups in S_N2 reactions.

R in R–X	Relative rate	R in R–X	Relative rate
CH_3	30	CH_3–CH_2–CH_2–CH_2	0.4
CH_3–CH_2	1	$(CH_3)_2CH$–CH_2	0.03
CH_3–CH_2–CH_2	0.4	$(CH_3)_3C$–CH_2	10^{-5}
$(CH_3)_2CH$	0.025		

S_N1 Reactivity

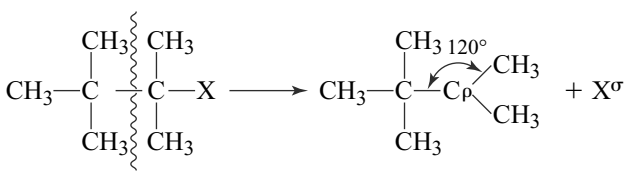
The rates of S_N1 reactions of alkyl halides follow the order

$$\text{tertiary R} > \text{secondary R} > \text{primary R} > CH_3\text{–X}$$

The rate-determining step in an S_N1 reaction is the formation of a carbocation intermediate. Therefore, the factors that favour formation and stability of these ions would increase the reactivity. The stability order of carbocations is

$$\text{tertiary } C^{\rho} > \text{secondary } C^{\rho} > \text{primary } C^{\rho}$$

It is because of the alkyl groups that are electron donating. They disperse charge on C^{ρ} carbon and ultimately stabilize the carbocation. Hyperconjugation, in part, also stabilizes carbocations, i.e. S_N1 reactions are affected by electronic effects. Reactivity of alkyl groups shows that steric hindrance is unimportant in S_N1 reactions. However, *steric acceleration* is found in the solvolysis of highly branched alkyl halides. It is because of the bond angle R–C–X (about 109°) in the substrate that increases to about 120° in the carbocation. It reduces steric strain and stabilizes the carbocation.



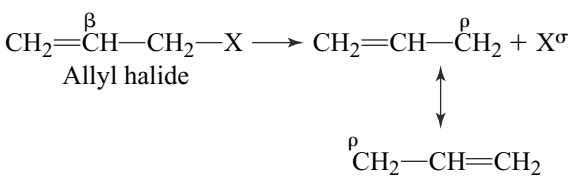
Steric crowding Relief of strain

The overall effect is increased in the rate of the reaction.

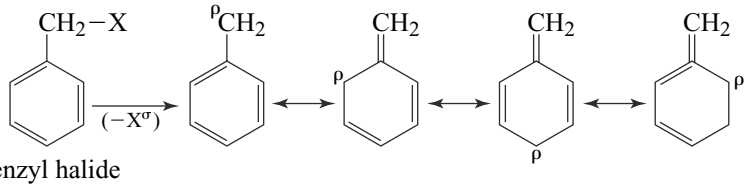
In general, tertiary halides react by S_N1 mechanism and primary halide by S_N2 mechanism. Secondary halides react either by S_N1 or S_N2 or both, depending on reaction conditions.

Allylic and benzylic compounds

Allylic and benzylic halides react fast in S_N1 reactions. It is because of the resonance stabilization of the carbocation. It becomes possible due to the unsaturation at the β-carbon atom.



Allyl halide



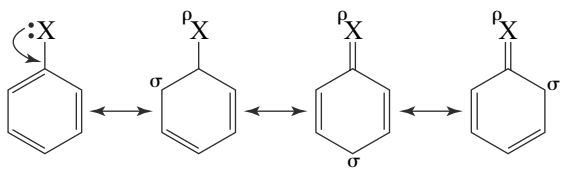
Benzyl halide

Vinyl halide and aryl halide

Vinyl and aryl halides have unsaturated α-C atom. Halogens have electron pairs. The electron pair at X and unsaturated α-C establish resonance. It makes C–X bond strong being a multiple bond. Therefore,

1. the ionization is not easy, which makes S_N1 reaction slow, and
2. the direct displacement of X is also not easy making S_N2 reaction slow.

Vinyl halide



The nature of the leaving group

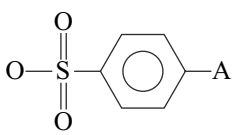
In a nucleophilic substitution reaction, the leaving group departs (or separates) with the bond-pair electron, i.e., as a base. Therefore, the species that can hold (or keep) the bond-pair electron with ease is a good leaving group and vice versa.

Good leaving groups

1. Conjugate bases of the strong acids, i.e., weak bases, are good leaving groups. Thus I^- is the best leaving group and F^- is the poorest among the halides. It is because of the H–X that the acid strength order is HI > HBr > HCl > HF. Thus, for R–X, S_N2 reactivity order is

$$R–I > R–Br > R–Cl > R–F.$$

The best leaving groups are the anions of strong acids, e.g.



A = CH_3 Tosylate
= Br Brosylate
= NO_2 Nosylate

Some fluorinated compounds are still better leaving groups, such as

$–OSO_2CF_3$	$OSO_2C_4F_9$
Trifluoromethanesulphonate	Nonafluorobutane sulphonate
(Triflates)	(Nonaflates)

2. The best leaving group is N_2. It may be because of the high stability of N_2.

$$R{-}NH_2 \xrightarrow{HNO_2} R\,.\overset{\rho}{N}_2 \longrightarrow \overset{\rho}{R} + N_2\uparrow$$

Poor leaving groups The stronger bases are poor leaving groups, e.g., HO^-, RO^- and H_2N^-. The atoms bonded to carbon are N or O. These are (i) small, (ii) of high electronegativity and (iii) of low polarizability (i.e., hard bases in the Lewis sense). They are bonded to carbon strongly and so are poor leaving groups. However, the above groups become good leaving groups in the presence of strong acids. Acid protonates HO^-, RO^- and H_2N^- to form H_2O, R–OH and NH_3, which are good leaving groups.

Therefore, alcohols, which are unreactive in SN reactions, become reactive in the presence of strong acids.

$$\begin{array}{l} \overset{\sigma}{Br} + R{-}OH \not\longrightarrow \text{No. reaction} \\ \qquad\quad \downarrow H^+ \\ \overset{\sigma}{Br} + R{-}\overset{H}{\underset{\rho}{O}}H \longrightarrow R{-}Br + H_2O \end{array}$$

Hydroiodic acid cleaves ethers for the same reason.

$$CH_3{-}O{-}Ph \xrightarrow{HI} CH_3{-}\overset{H}{\underset{\rho}{O}}Ph \xrightarrow{I^-} CH_3I + Ph{-}OH$$

The decreasing order of some of the leaving groups is as follows.

$$RN_2^{\rho} > \text{Nonaflates} > \text{Triflates} > \text{Tosylates}$$
$$\approx \text{brosylates} \approx \text{Nosylates} > Rl > RBr > ROH_2 > R{-}F > R{-}OH > R{-}OR$$

Metal halide as leaving groups

Heavy-metal salts, particularly those of Ag, Hg, Cu, etc., catalyse S_N1 reactions of alkyl halides. It is because of the metal ion that complexes with electron pair of the halide, making the leaving group a metal halide rather than the halide itself. It is a heavy-metal catalysis.

$$R{-}X \xrightarrow{Ag^{\oplus}} [R{-}X\!:\!\cdots Ag]^{\rho} \xrightarrow[(-AgX)]{} R^{\rho} \xrightarrow{y^-} R{-}Y$$

This reaction finds use in qualitative test for alkyl halides with silver nitrate in ethanol solution. Silver halide precipitates. The reactivity of halides in these reactions is

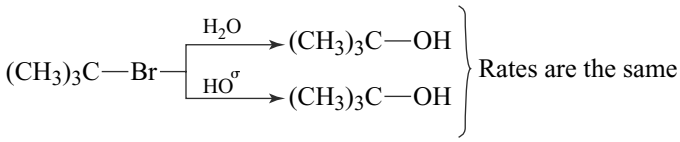
$$\text{tertiary halide} > \text{secondary halide} > \text{primary halide}$$

The nature of nucleophiles

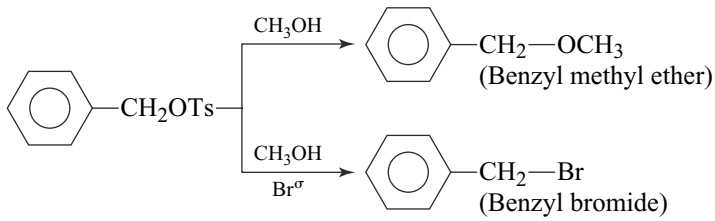
Nucleophiles contain unshared electron pair, i.e., they are Lewis bases. They may be a negative ion or a neutral species, e.g., HO^{σ}, CN^{σ}, H_2O or NH_3.

S_N1 Reaction and Nucleophiles

The rates of S_N1 reactions are independent of nucleophiles. It is because they do not take part in the rate-determining step of the reaction.



However, a change in the nucleophile may change the product.



Here Br^{σ} is a better nucleophile, so the product in the presence of Br^{σ} is benzyl bromide (not the ether).

S_N2 Reactions and Entering of Nucleophiles

The S_N2 reactions are greatly influenced by entering of nucleophiles. The entering of nucleophile uses its electron pair to form bond with the substrate to push away the leaving group with its bonding pair of electrons. Thus, a good nucleophile is one that readily forms the bond, allowing rapid reaction.

Nucleophilicity

The ability of a nucleophile to donate its electron pair to C (or another atom) is termed as nucleophilicity. It is kinetic in nature.

Basicity

The ability of a base to donate its electron pair to H^+ is called basicity. It is thermodynamic in nature. Basicity is not affected but nucleophilicity is greatly affected by steric factors. Both do not run parallel all the time. The following are found to be good nucleophiles:

1. A negative ion is always a better nucleophile than its conjugate acid. Thus, OH^- is stronger than H_2O, EtO^{σ} is stronger than EtOH, NH_2^- is stronger than NH_3, etc. as nucleophiles.
2. If attacking atom is the same, stronger the base more powerful is the nucleophile. Thus,

$$EtO^{\sigma} > PhO^{\sigma} > CH_3COO^{\sigma} > NO_3{}^{\sigma}$$

3. Highly polarizable ions are good nucleophiles. For example,

$$I^{\sigma} > Br^{\sigma} > Cl^{\sigma} > \text{ and } RS^{\sigma} > RO^{\sigma}.$$

Large and less electronegative atom is more polarizable. Thus, I^{σ} is more polarizable than Br^{σ}. It is because the nucleus of a large atom has weaker hold on its peripheral electrons.

Overall nucleophilicity order for S_N2 reactions

$$RS^{\sigma} > I^{\sigma} > CN^{\sigma} > HO^{\sigma} > \ Br^{\sigma} > Cl^{\sigma} > ACO^{\sigma} > H_2O$$

Ambident nucleophiles

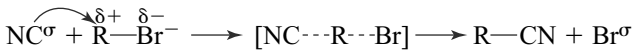
Nucleophiles that can bond through two different atoms are called 'Ambident Nucleophiles', e.g. CN^{σ}, $NO_2{}^{\sigma}$ and SCN. The CN^{σ} can bond either through C or N.

R–CN (alkylcyanide)
R–NC (alkyl isocyanide)

AgCN gives alkyl isocyanide. It is because Ag^+ promotes the formation of R^+ by precipitating Ag halide (a good leaving group). Then, the carbonium ion is attacked by the atom of the nucleophile where electron density is high. Thus, the reaction is S_N1 in nature.

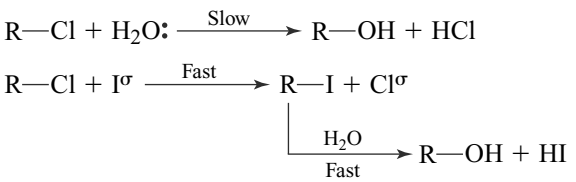
$$R{-}Br + AgCN \longrightarrow AgBr + R^+ + CN^{\Gamma} \longrightarrow R - NC$$

But with NaCN (or KCN) R–Br gives alkyl cyanide. The reaction in this case is S_N2 type. NaCN cannot promote ionization of halide to form R^+ by precipitating NaBr. In S_N2 type reaction, nucleophilicity counts. In CN^{Γ}, the C centre is more nucleophilic as C is more polarizable (C has less nuclear charge than N). Thus, the product is alkyl cyanide.



Nucleophilic catalysis

A nucleophile that is both a good leaving and a good entering group may catalyse a slow substitution reaction. It is called the nucleophilic catalysis. For example, the iodide ion (I^{Γ}) is both a good leaving and a good entering group. The following reaction shows the catalytic effect of I^{σ}.



THE NATURE OF THE SOLVENT

The rates of the nucleophilic substitution reactions are influenced by the solvent.

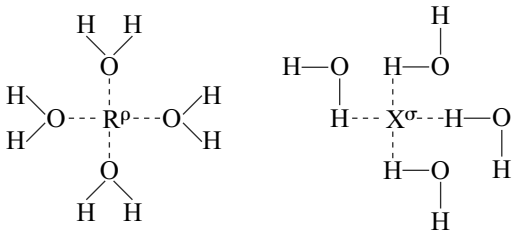
S_N1 Reactions and Solvent

The rates of the most S_N1 reactions are sensitive to change in solvent. The S_N1 reactions proceed through carbonium ion (R^+) intermediate. Therefore, ionizing solvents favour formation of the intermediate. Two factors are important for the solvent.

1. *Dielectric constant* ($\in$)
   A high dielectric constant increases the ionizing power of the solvent. It is because the force between the charged particles is inversely related to dielectric constant of the medium. Thus, water (dielectric constant, $\in = 82$) is much more effective than a hydrocarbon ($\in = 2$). Ionizing power of some solvents are given below.

	H_2O	HCOOH	CH_3OH	$CH_3{-}CH_2{-}OH$	CH_3COOH
$\in$	(82)	(48)	(33)	(25.8)	(7.1)

2. *Solvating power of the solvent*
   Cations are solvated through coordination with electron pairs and anions are solvated through H bonding.



Cation solvation Anion solvation

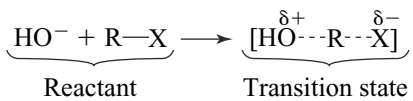
This situation decreases the energy of the transition state. Therefore, the rate of S_N1 reactions increases. Examples of such solvents are water, alcohol and carboxylic acid.

Conclusions

1. The S_N1 reactions are most favoured in polar protic solvents.
2. Nonpolar solvents are not favourable for S_N1 reaction, e.g. benzene and CCl_4 hydrocarbons.
3. Polar aprotic solvents are also less important.

S_N2 Reactions and Solvents

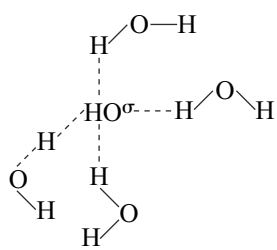
The S_N2 reactions are also influenced by the solvents. In S_N2 reactions, charge (σ charge) is not created but the charge in the reactant is more concentrated than in the transition state.



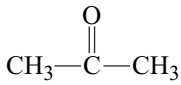
Reactant Transition state

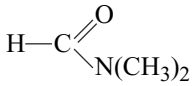
The change of solvents has the following effect.

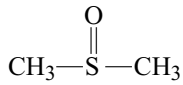
1. *Non-polar solvents (C_6H_6, CCl_4, etc.)*
   Non-polar solvents decrease the rate of the S_N2 reactions.
2. *Polar protic solvents*
   Polar protic solvents are those that have protonic hydrogen (water, alcohol, etc.). They decrease the rate of S_N2 reactions. It is because they solvate the reagent (the nucleophile HO^-, CN^-, etc.) through H bonding and decrease its effectiveness.



3. *Polar aprotic solvents*
   Polar aprotic solvents are those that are polar but have no protonic hydrogen. Examples are

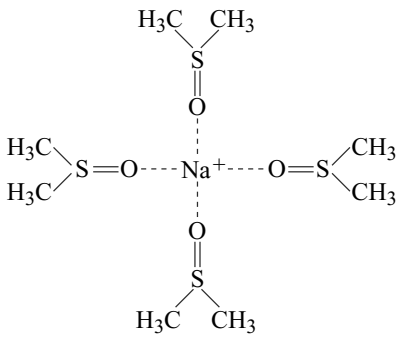
Acetone 

Dimethyl formamide (DMF) ($\in$=38) 

Dimethyl sulphoxide (DMSO) ($\in$=42) 

They enormously increase the rate of the S_N2 reactions. It is because aprotic solvents dissolve ionic reagent but (i) solvate cation only and (ii) leave the anion (i.e., nucleophile) free, i.e., highly reactive.

$$NaOH \xrightarrow{DMSO} Na^+ + HO^-$$



The nucleophile (HO^{σ}) is not solvated and is left free.

Thus, aprotic solvents have remarkable effect on the rates of many S_N2 reactions. For example, the S_N2 reaction of CH_3I with Cl^-

$$Cl^{\sigma} + CH_3{-}I \longrightarrow [\overset{\delta+}{Cl}\cdots CH_3\cdots \overset{\delta-}{I}] \longrightarrow ClCH_3 + I^-$$

is a million times faster in dimethylformamide than in water.

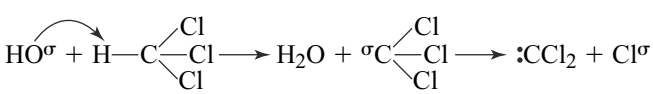
ELIMINATION REACTIONS

Elimination reactions are the reverse of addition reactions. They may be classified as

1. α-elimination
2. β- (or 1,2) elimination
3. 1,3; 1,4; 1,5; etc., eliminations.

α-Elimination

In α-elimination, both groups leave from the same carbon. For example, the formation of dichlorocarbene from $HCCl_3$ by the action of NaOH.



(See Reimer-Tieman reaction)

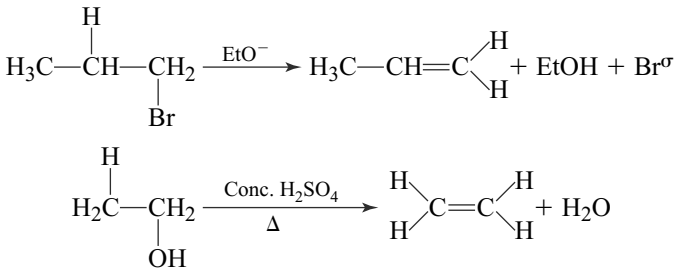
β- (or 1,2) Elimination

The elimination reactions in which atoms or groups are lost from adjacent carbon atoms are known as β-eliminations. It leads to the formation of a π-bond, i.e., an unsaturated compound. In the majority of cases, a proton is lost from one carbon atom and a nucleophile from the other.

The most common examples of β-eliminations are

1. dehydrohalogenation of alkyl halides (base induced) and
2. dehydration of alcohols (acid catalysed).

The product, in both the above cases, is an alkene.

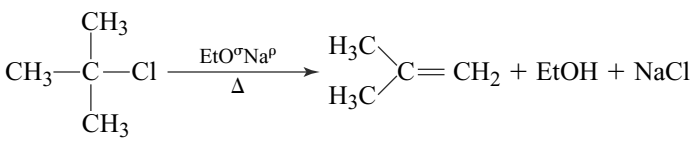


Different mechanisms may operate in β-eliminations.

(a)	E_1	Reactions	Common types
(b)	E_2	Reactions	
(c)	E_1CB	Reactions	Rare

E_1-Eliminations

Unimolecular β-elimination reaction are called E_1 reactions. For example, *t*-butyl chloride when heated with sodium ethoxide forms isobutene.

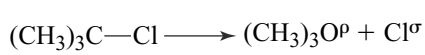


Rate = $k_1[(CH_3)_3C–Cl]$. It is, thus, a unimolecular reaction, i.e., E_1.

Mechanism

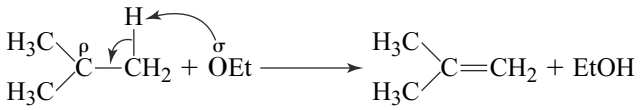
The E_1 reactions are a two-step process.

1. Ionization of t-halide to form carbonium ion.

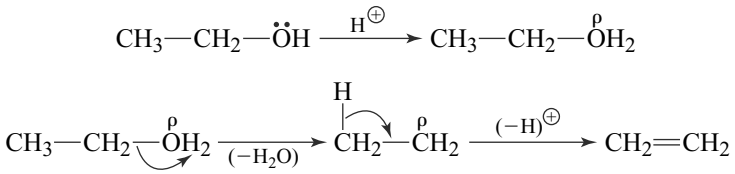


It is slow-step process (bond breaking requires energy).

2. The carbonium ion, in the second step, loses a proton to the base to give the product.



Acid-catalysed dehydration of alcohols to alkenes is another example of E_1 reactions. This reaction proceeds as



Effect of structure on rate of E_1 reaction

Structural effects on E_1 reactions are as follows:

1. The rate of R–X follow the order

$$R\text{–}I > R\text{–}Br > R\text{–}Cl > R\text{–}F$$

It is because ionization is easy when halogen is large (the larger is the halide ion better leaving group it is).

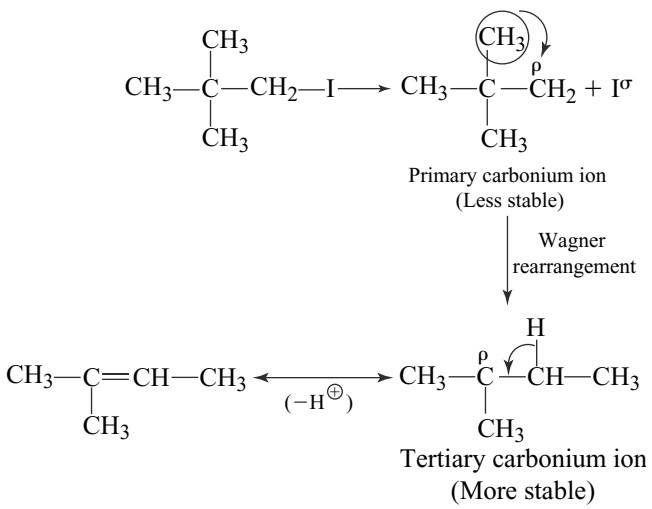
2. Tertiary halides react faster than secondary halides and secondary halides react faster than primary halides, i.e.,

$$\text{tertiary R} > \text{secondary R} > \text{primary R}$$

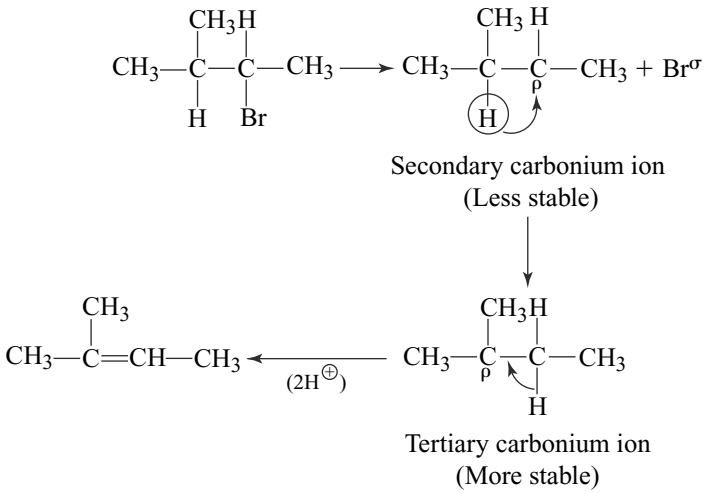
The reason for the above sequence is the stability of the carbonium ions. The stability order of carbonium ions is

$$\text{tertiary } C^{\rho} > \text{secondary } C^{\rho} > \text{primary } C^{\rho}$$

Another feature of E1 reactions is the rearrangement in the carbonium ion. It always takes place when initially formed carbonium ion rearranges to a more stable ion. Thus, the final product is from the stable ion, e.g.,

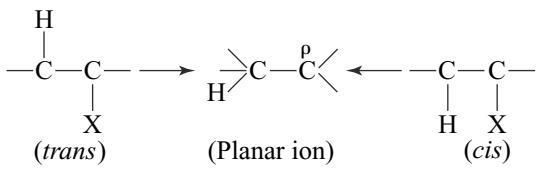


Rearrangements that involve shift of hydrogen (as H^-) may also take place, e.g.,



Stereochemistry of E_1 reactions

The E_1 reactions are not stereospecific. These reactions proceed through planar carbonium ion intermediates. *Cis*- and *trans*-isomers produce the same carbonium ion. Therefore, the product remains the same with either of the isomers.



E_2 Reactions

Bimolecular β-eliminations are called E_2 reactions. For example,

$$CH_3—CH_2—Br + EtO^- Na^+ \xrightarrow{\Delta} CH_2=CH_2 + EtOH + NaBr$$

Rate = $k_2[CH_3–CH_2–Br]\,[EtO^-]$
Thus, a bimolecular reaction is an E_2 elimination.

Mechanism

Two types of mechanisms may operate in E_2 reactions:

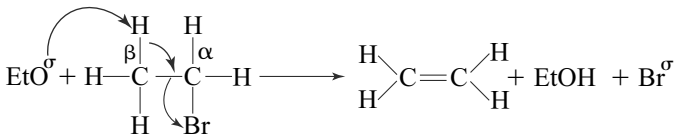
1. One-step E_2 reaction (i.e., concerted mechanism). It is of a common type.
2. Two-step E_2 reaction denoted as E_1CB (Ingold). The notation E_1CB stands for elimination unimolecular conjugate base. It is rare.

E_2 mechanism

Ethyl bromide when heated with sodium ethoxide forms ethylene.

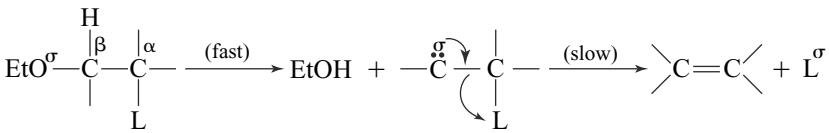
$$CH_3—CH_2—Br + EtO^{\sigma} Na^{\rho} \xrightarrow{\Delta} CH_2=CH_2 + EtOH + NaBr$$

This reaction is bimolecular. It completes in one step. Removal of H as H^+ by the base (from β-carbon), formation of π-bond and loss of Br (from α-carbon) with bond pair (i.e. as Br^-) take place in a single step.

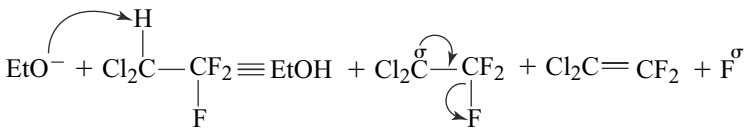


E_1CB mechanism

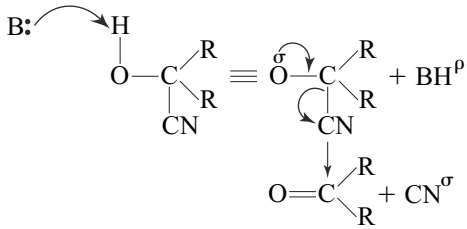
In this mechanism, the base removes H^+ from the β-carbon to produce a carbanion. This carbanion loses the leaving group to form the product.



But this mechanism operates when α and β both carbon atoms carry electron-attracting group. Thus, 1,1,1-trifluoro-2,2-dichloro ethane undergoes elimination by E_1CB mechanism.



Another example, of E_1CB is the formation of a carbonyl compound from cyanohydrins (i.e. reverse of cyanohydrin formation).



Reactions following E_1CB mechanism are rare.

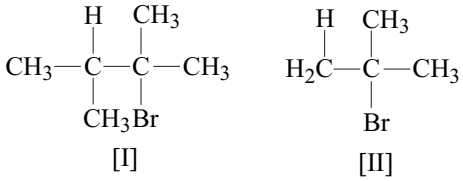
Effect of structure on the rate of E_2 reactions

The substrates that have alkyl substitution at both α- and β-carbon atoms promote E_2 reactions. It is because they lead to more substituted alkene (i.e. more stable alkene). The ease of elimination follows the order.

tertiary R > secondary R > primary R

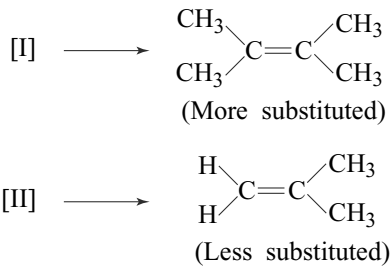
Thus, E_2 reactions (unlike S_N2) are not influenced by the steric factor.

Thus, [I] will react faster than [II].



[I] [II]

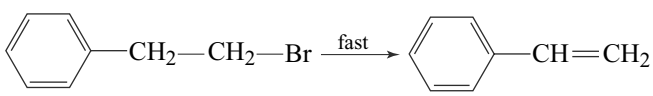
It is because [I] will give more stable alkene compared to the product from [II].



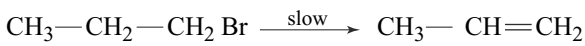
(More substituted)

(Less substituted)

The presence of phenyl group (C_6H_5-) at α- and β-carbon atoms also promote E_2 reactions. It is because the π-electrons of the phenyl group can establish conjugation with the alkene π-electrons leading to more stable alkene. Thus, [III] reacts faster as compared to [IV].

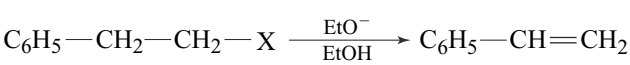


[III]



[IV]

The bond strength of the carbon-leaving group is also a feature of E_2 reactivity. The substrates containing weaker C-leaving group bond (C–X) react fast. Thus, the relative rate observed with $C_6H_5–CH_2–CH_2–X$ is



X =	F	Cl	Br	I
Rate =	1	70	4×10^3	2.7×10^4

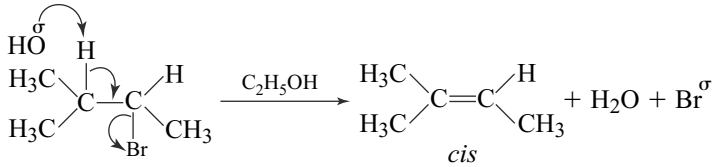
The C–X bond strength depends on the size of X. Thus, larger is the X the weaker is the C–X bond.

X	C–X (kJ/mole)
F	439
Cl	347
Br	276
I	238

The electron-attracting groups (–NO_2, –CN, >C=O, etc.) promote elimination reactions.

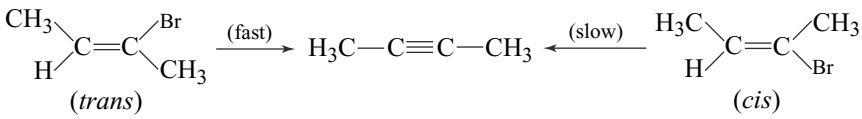
Stereochemistry of E_2 reactions

Most E_2 reactions are stereospecific. The group being removed arrange themselves as far apart as possible at the time of their departure, i.e. *trans*-elimination takes place. Here, *trans* refers disposition of the leaving groups at the time of reaction and not to the configuration of the alkene formed.



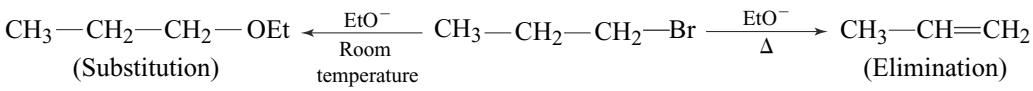
Trans elimination occurs because of the incoming electron pair (by loss of H^+ which forms π bond) and outgoing electron pair (with leaving group) which is kept as far apart as possible.

The following example shows the effectiveness of *trans* elimination.



Temperature, base strength and E_2 reactions

High temperature favours E_2 reactions (S_N2 is favoured at relatively low temperature).



The strength of the base also affects the rate of E_2 reactions. The stronger is the base used higher is the rate of E_2 reactions. Thus, effectiveness of the bases observed for E_2 reactions is

$$H_2N^{\sigma} > C_2H_5O^{\sigma} > HO^{\sigma} > CH_3COO^{\sigma}$$

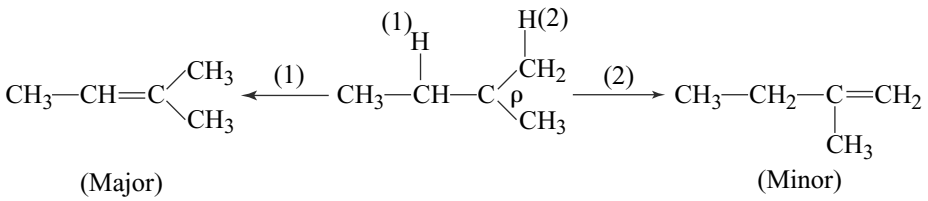
DIRECTION OF ELIMINATION

Unsymmetrical substrates generally give mixture of elimination products. There are two rules to decide the amount of the major product. They are (i) Saytzeff's rule and (ii) Hofmann's rule.

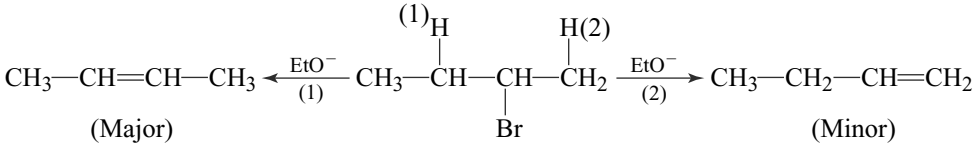
Saytzeff's Rule

It deals with the neutral substrates like alkyl halides. The rule states that 'Neutral substrates give most alkyl substituted alkene as the major product'. This rule applies to E_1 and also to most E_2 reactions.

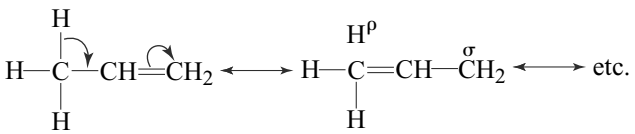
E_1 reactions



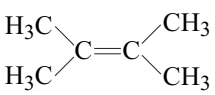
E_2 reaction



The preferential formation of most alkyl-substituted alkene is explained on the basis of hyperconjugation.



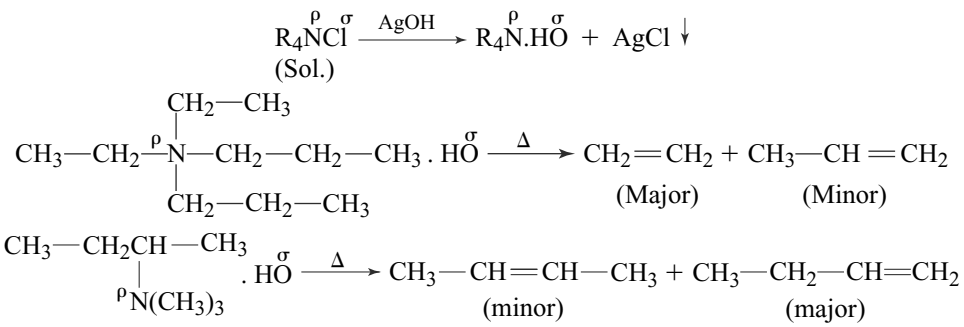
Thus, most stable alkene is



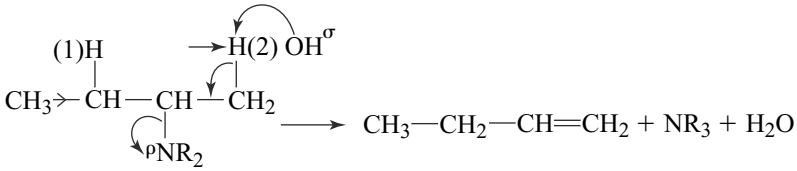
as it will produce the largest number of hyperconjugative structures (12 structures).

Hofmann's Rule

It deals with the charged substrates like quaternary ammonium salts, $R_4N^+X^-$. The rule states that 'Quaternary ions give least substituted alkene as the major product'. Quaternary hydroxide is the actual substrate that is generally prepared by the addition of moist silver oxide to a water solution of a quaternary ammonium halide.

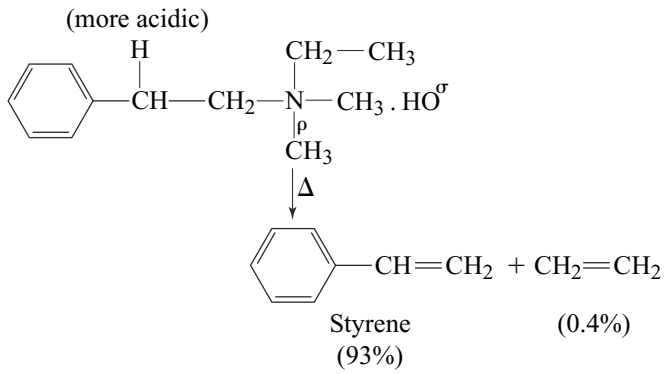


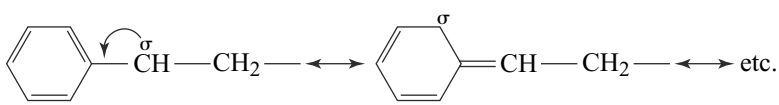
Hofmann elimination is influenced on the acidity of the hydrogen removed as a proton (the –I effect of N^{ρ} causes acidity in H). Acidity is lowered due to the presence of alkyl groups (+I effect) for H at the point of the reaction.



1. H less acidic H due to +I effect of CH_3.
2. H more acidic as carbon has no R.

   Other groups that have acid-strengthening effect also increase the ease of elimination, e.g.



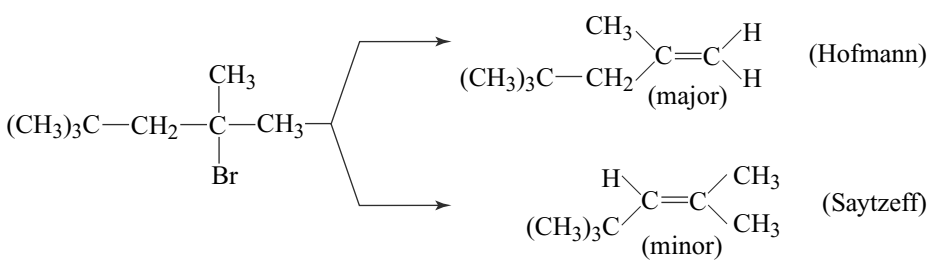


STRUCTURAL EFFECTS ON DIRECTION OF ELIMINATIONS

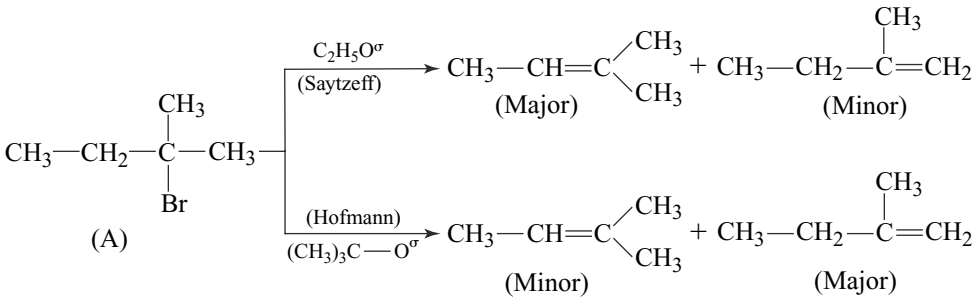
Branching in the substrate and size of the attacking base both have effect on the direction of elimination. It is found that E_2 eliminations of alkyl halides are forced to follow Hofmann type of elimination by (i) increasing the extent of branching in the substrate or (ii) increasing the size of the attacking base.

The above effects are seen in the examples given below.

Branching in Substrate



Size of the Base

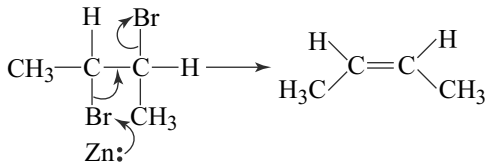


Thus, the extent of Hofmann-type elimination for the above substrate (A) increases in the order given below

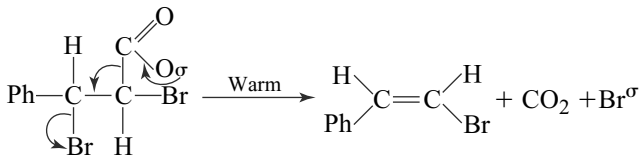
Base = EtO^{σ}	$(CH_3)_3C–O^{\sigma}$	$(C_2H_5)_3C–O^{\sigma}$
30%	72%	78%

DEHALOGENATION

Elimination reactions are not limited only to those substrates in which one of the leaving groups is a H. Other eliminations are also known. For example, elimination of 1,2-dihalides takes place in the presence of active metals (Zn, Mg, etc.) to give alkenes. These reactions are of E_2 type and proceed in a *trans* manner.



Another example of elimination, not involving H, is the elimination of Br^{-} and CO_2 from cinnamic acid dibromide. This reaction is very easy requiring no reagent.



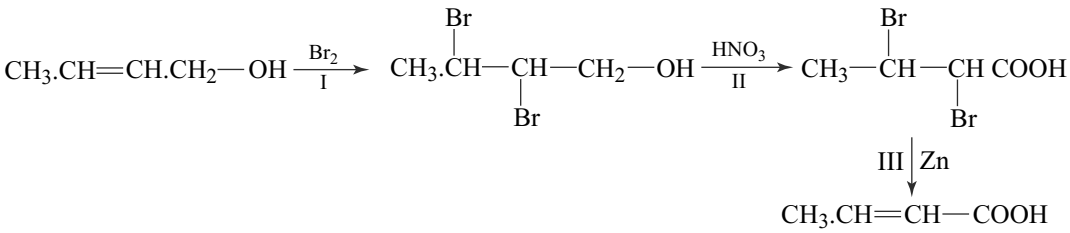
Problem

Carry out the following conversion in three steps:

$CH_3—CH=CH—CH_2—OH \longrightarrow CH_3—CH=CH—COOH$

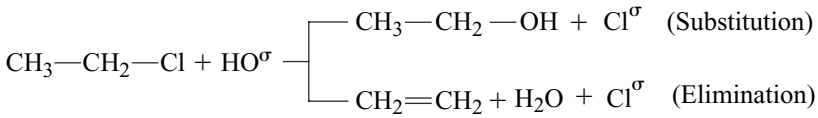
Solution

An unsaturated alcohol cannot be oxidized directly to the acid due to the double bond (the alcohol will decompose). The double bond is protected by bromination, then oxidation is done and at last debromination is carried out. The steps are



COMPETITION BETWEEN SUBSTITUTION AND ELIMINATION REACTIONS

Substitution and elimination generally take place together (i.e. concurrently). For example,



Thus, substitution and elimination are competing reactions. It is because substitution and elimination have closely related mechanisms. But suitable reaction conditions may favour one of the reactions. The following conclusions are observed.

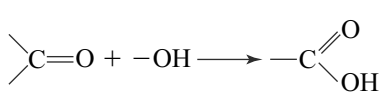
1. Elimination is favoured over substitution
   (a) with strong bases of low polarizability and effectiveness parallels base strength $H_2N^{\sigma} > C_2H_5O^{\sigma} > HO^{\sigma} > CH_3COO^{\sigma}$ and
   (b) at high temperature
2. Substitution is favoured over elimination
   (a) with weak bases like CH_3COO^{σ} and highly polarizable nucleophiles like iodide ion (I^{σ}) and
   (b) at low temperatue

REACTIONS OF –COOH GROUP AND ITS DERIVATIVES

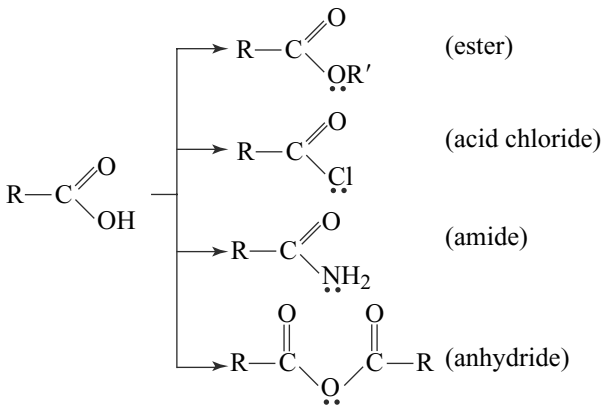
Carboxyl group (–COOH) may be thought of as a combination of two groups:

(i) the carbonyl, >C=O, group and

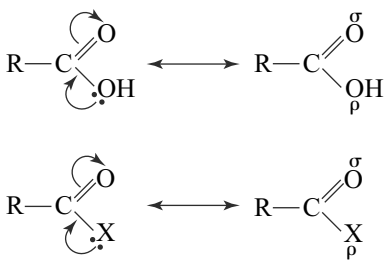
(ii) the hydroxyl, –OH, group.



But this combination is so close that neither of the group behaves independently.
The derivatives of carboxylic acid are ester, acid chloride, amide, acid anhydride, etc.



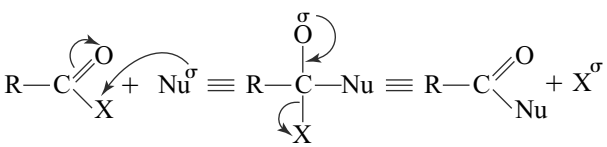
The above structures show that groups attached to >C=O have lone pairs. The lone pair establishes resonance with >C=O group



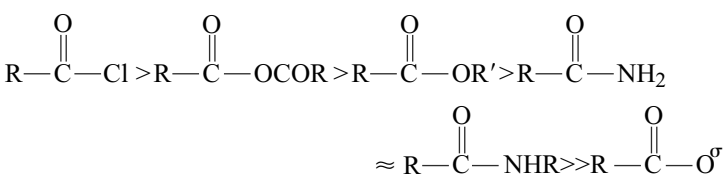
where X = –OH, –OR, NH_2 and –OCOR. This resonance effect reduces the positive nature of carbonyl carbon.

In spite of this effect, many reactions of carboxylic acids (and derivatives) involve attack on carbon of carbonyl group by nucleophiles. But the reactions are not nucleophilic addition like aldehydes and ketones. They are actually addition-elimination reactions.

It is due to the fact that X groups are good leaving groups (or become good leaving groups during the reaction). Therefore, the reactions are nucleophilic substitution at unsaturated carbon. The general reaction may be outlined as



The general reactivity order, in such reactions, is



Reaction of COOH Group

The main reactions of carboxylic acids take place at two sites:

1. Reactions at the carbonyl carbon of –COOH group.
2. Reactions at the 2-position (or α-carbon) of carboxylic acids.

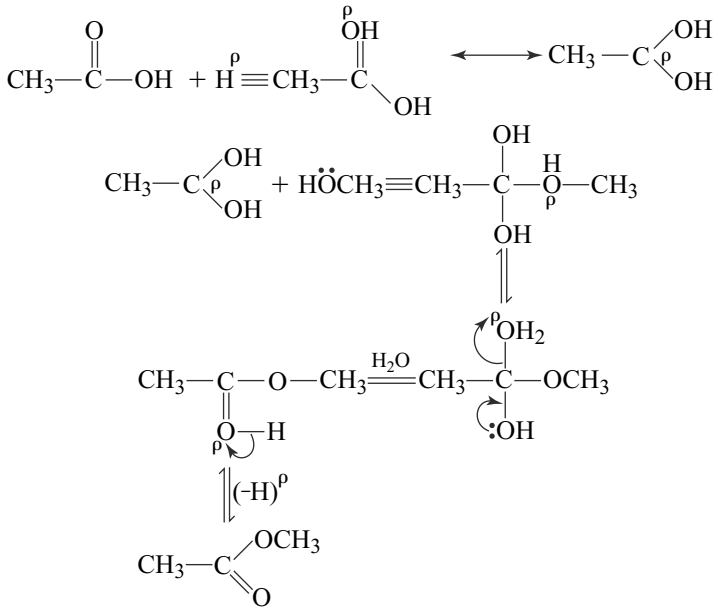
Ester formation

It is a reaction that takes place at the carbonyl carbon of the carboxylic acid. Esters are formed by the reaction of alcohol with carboxylic acid (or acid chloride or acid anhydride).

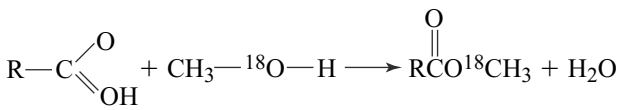
Acid chloride reacts fast and the reaction is more complete. It is because acid chloride has more positive carbonyl carbon due to the polarization of the C–O and C–Cl bonds.

Acid + Alcohol reaction

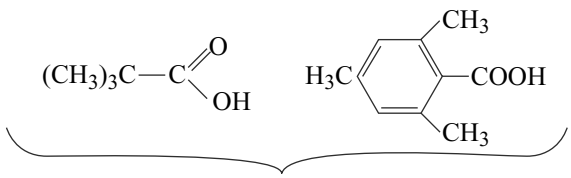
Strong proton acids (conc. H_2SO_4) catalyse this reaction. The reaction is addition–elimination that proceeds as



Using alcohol-containing ^{18}O (heavy isotope), it has been shown that ^{18}O is incorporated in the ester and not in the water. This indicates that acid loses its –OH group during esterification.

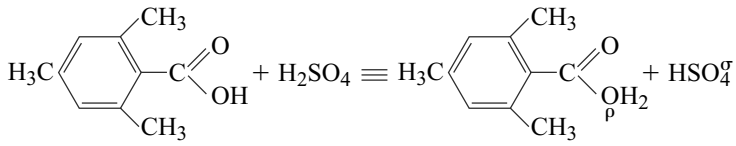


However, esterification, (or hydrolysis) of sterically hindered acids, is somewhat different. In these cases, protonation of –OH (instead of >C=O) takes place leading to the formation of the acyl cation (oxycarbonium ion), a planar ion that is attacked by R–OH.

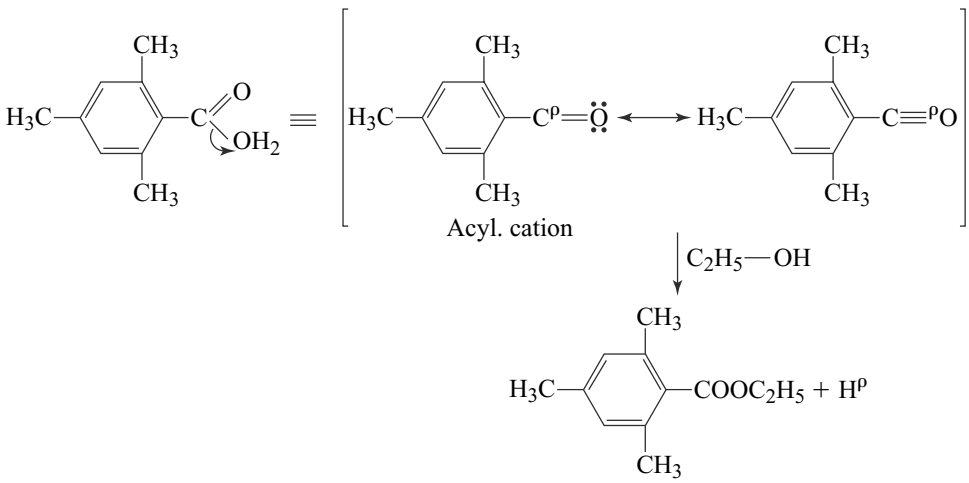


Sterically hindered acids

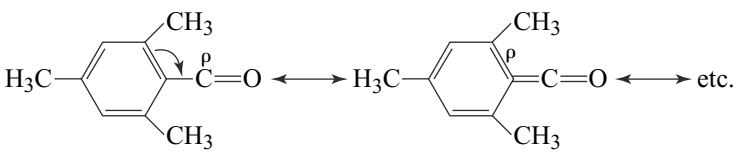
A well-known reaction of this type is esterification of mesitoic acid (2,4,6-trimethyl benzoic acid).



[I]

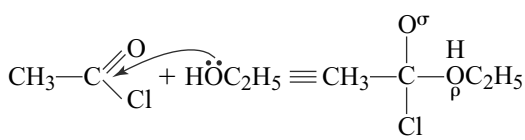


The acylcation is stabilized by the resonance.



Acid chloride + Alcohol

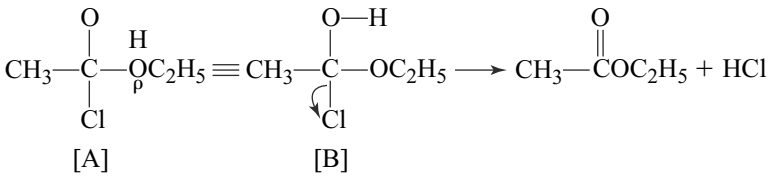
The more polarized carbonyl carbon of acid chloride is attacked by the alcohol (a nucleophile) easily. The reaction is addition–elimination that proceeds as



[A]

The addition product [A] contains both an acid group ($C_2H_5—\overset{\oplus}{O}(H)—$) and a basic group ($—\overset{|}{\underset{|}{C}}—O^{\sigma}$)

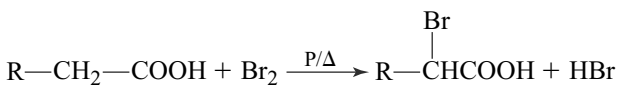
Therefore, proton shift occurs and [B] is formed that rapidly loses HCl to form the ester.



[A] [B]

Reaction at the 2-position of carboxylic acid

An useful reaction is the formation of 2-bromo acid.



This reaction is known as Hell–Volhard–Zelinsky (H–V–Z reaction) reaction.

Derivatives of COOH Group

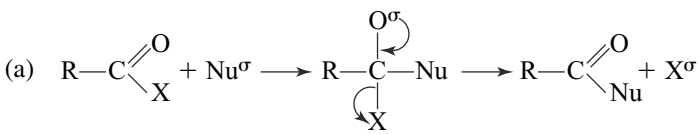
A functional derivative of COOH group is a compound formed by the replacement of –OH of the acid by X (X = OR, Cl, NH_2, OCOR) that can be hydrolyzed back to the parent acid.

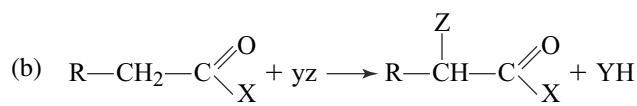
Thus, $R—\overset{O}{\overset{\|}{C}}—R'$ is not a functional derivative of a carboxylic acid as it cannot be hydrolyzed back to R–COOH.

The important derivatives are esters, acid chlorides, acid amides, acid anhydrides, etc. The two main types of reactions of acid derivatives are

1. Replacement of X by a nucleophile (Nu^-) at carbonyl carbon.
2. Substitution at the 2-carbon.

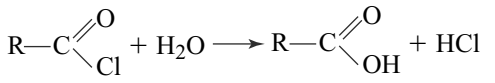
General reactions can be outlined as



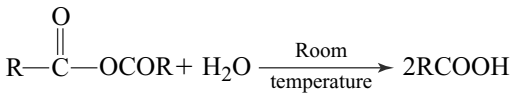


Replacement reactions

All the derivatives of acids may be hydrolyzed under one or another set of conditions. These reactions are generally acid or base catalysed, but acid chlorides and anhydrides usually hydrolyze rapidly without any catalyst.

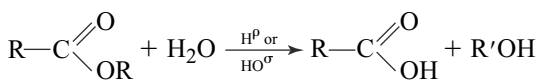


(Fumes in air)



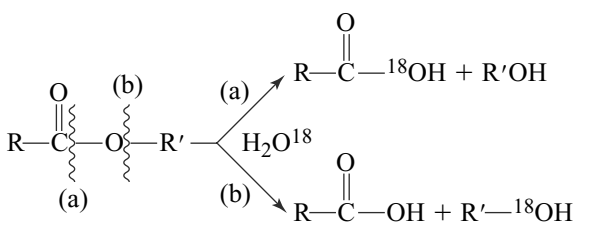
Hydrolysis of esters

Ester hydrolysis is both acid and base catalysed.



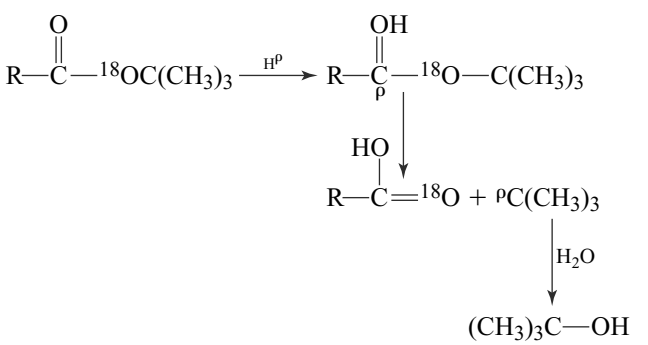
The hydrolysis can proceed by cleavage of either

1. acyl–oxygen bond or
2. alkyl–oxygen bond.



The reaction in ^{18}O-enriched water shows that most simple esters contain acids having ^{18}O, i.e., the hydrolysis is following acyl–oxygen bond cleavage path.

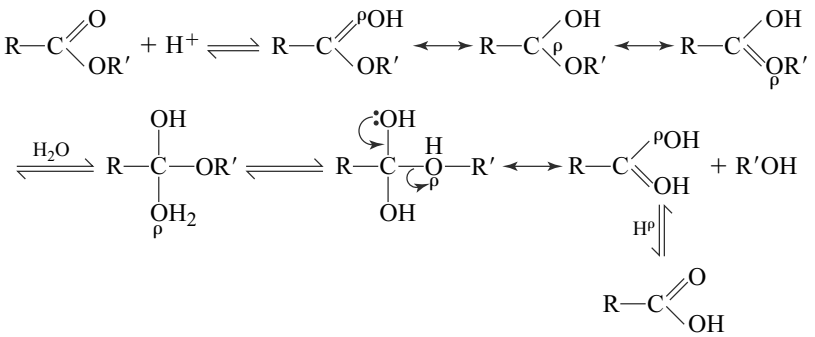
On the other hand, esters, R–COOR′, where R′ can form stable carbocation, hydrolyze by alkyl–oxygen bond cleavage.



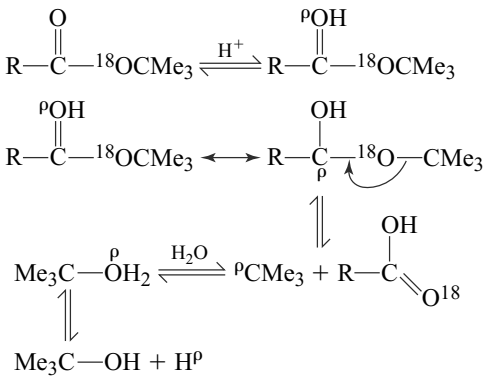
The O–C bond (i.e., alkyl–oxygen) breaks in the ester [$^{18}OC(CH_3)_3$]. Therefore, ^{18}O remains in the acid.

Acid-catalysed hydrolysis

Esters are hydrolyzed when heated with catalytic amount of acid in aqueous solution. The reaction is reversible. The general reaction proceeds by acyl–oxygen bond cleavage.



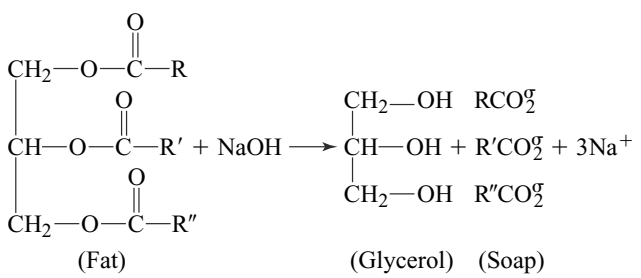
Esters, RCOOR′, where R′ can form stable carbocation, hydrolyze by alkyl–oxygen bond cleavage. It has been shown by the hyrolysis of ^{18}O-levelled ester.



Base-catalysed hydrolysis

Alkali also catalyse ester hydrolysis. This hydrolysis reaction is often termed as saponification (as soap is made this way).

$$CH_3COOC_2H_5 + NaOH \xrightarrow{\Delta} CH_3COONa + C_2H_5{-}OH$$

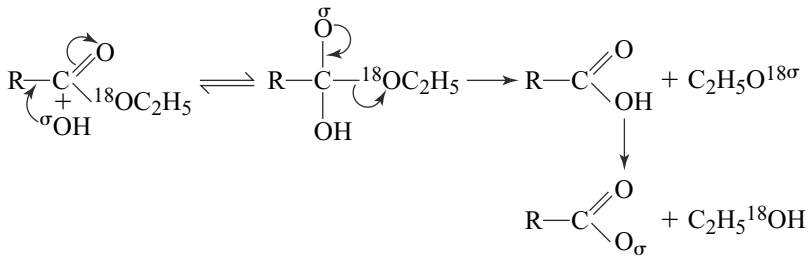


(Fat) (Glycerol) (Soap)

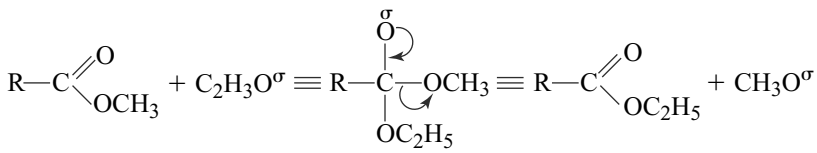
The R, R′ and R″ are long-chain saturated and unsaturated alkyl groups.

Mechanism of Alkaline Hydrolysis

The HO^{σ} ion attacks the carbonyl carbon of the ester. It is the first step. In the second step, OR′ departs to form the product. Hydrolysis of ^{18}O-levelled ester shows that the reaction preceedes by the acyl–oxygen bond cleavage.



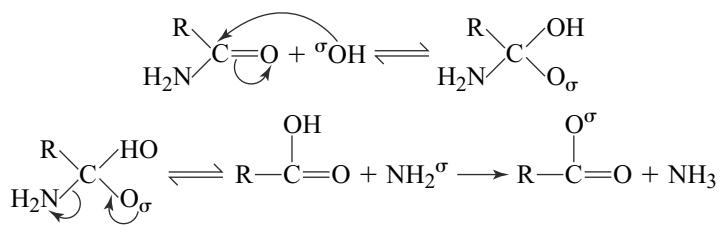
A quite similar reaction is transesterification (or ester interchange) when a nucleophile is RO^{σ} instead of HO^{σ}.



Hydrolysis of amides

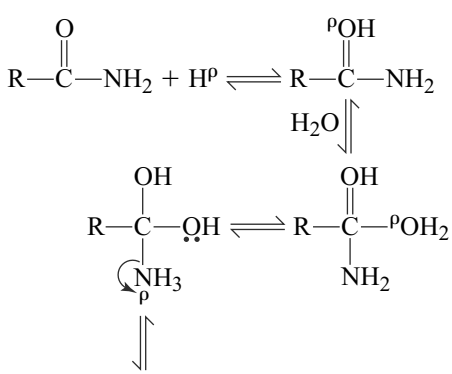
Amides are harder to hydrolyze than esters. Acid or base catalysis is required for hydrolysis. Alkaline hydrolysis is rather rapid. The reactions take place on heating.

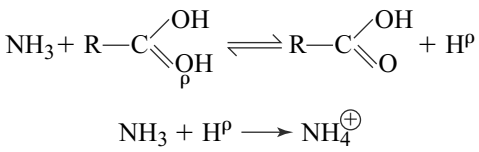
Base hydrolysis



Acid hydrolysis

Study of the reaction using physical methods show protonation of cabonyl oxygen.

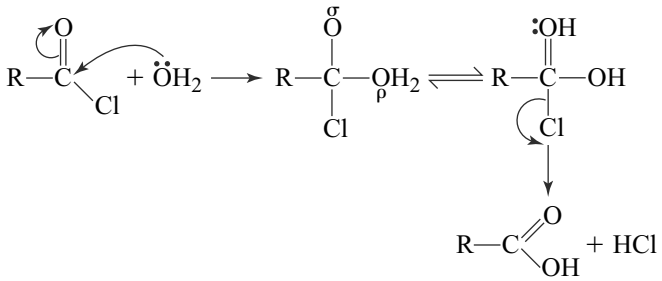




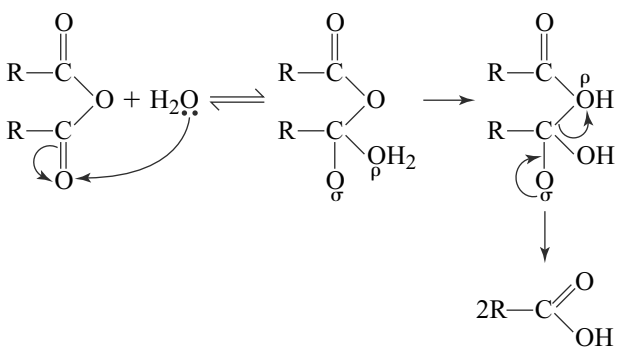
Hydrolysis of acid chloride and acid anhydrides

The hydrolytic reactivity of acid chlorides and anhydrides is greater than carboxylic esters and amides. The mechanisms are given below.

Acid chloride

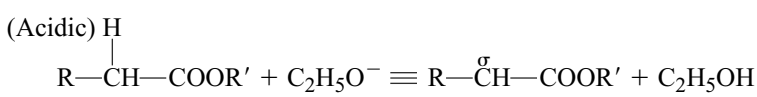


Acid anhydride

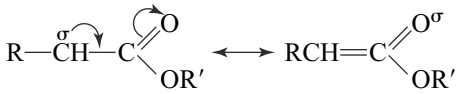


Reactions at the 2-position (α-carbon) of acid derivatives

1. Acidic nature of esters with α-hydrogen
The α-hydrogens of an ester, like R–CH_2–COOR′, are weak acidic. They are replaced by a strong base ($C_2H_5O^-$) to produce ester anion.

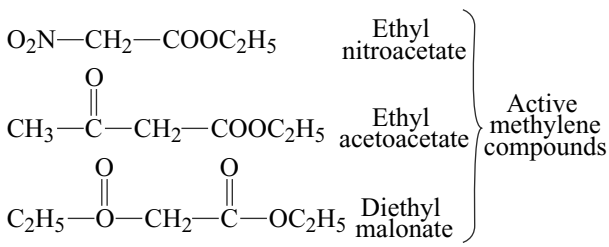


The anion is stabilized partly due to the –I effect of ester oxygen and partly due to the resonance.

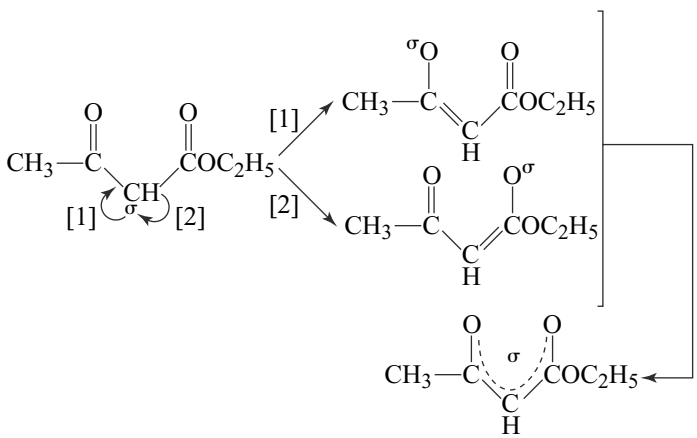


Formation of such ester anions is used in many important synthetic reactions in which C–C bonds are formed.

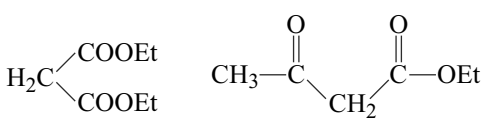
Where the α-position of the ester has a second strongly electron-attracting group, the acidity of an α-hydrogen is greatly increased. Such a CH_2 group is called active methylene group (CH_2 is methylene).



Anions of the above esters are stabilized by both the electron-attracting groups.



Malonic ester and ethyl aceto acetate have active methylene group and are used for the synthesis of variety of organic compounds.



PROBLEMS

Objective-Type Questions

1. If a carbanion is bonded to a hydrogen or an alkyl group, the shape of the methyl carbanion is likely to be

(a) tetrahedral (b) linear
(c) planar (d) pyramidal

2. Which of the following is the most stable carbonium ion?

(a) $C_6H_5\overset{\rho}{C}H_2$ (b) $(CH_3)_3\overset{\rho}{C}$

(c) $(CH_3)_2\overset{\rho}{C}H$ (d) $CH_3\overset{\rho}{C}H_2$

3. Which of the following is the most stable carbanion?

(a) $C_6H_5\overset{\sigma}{C}H_2$ (b) $(CH_3)_3\overset{\sigma}{C}$

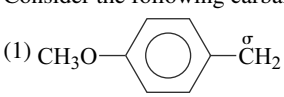
(c) $(CH_3)_2\overset{\sigma}{C}H$ (d) $CH_3\overset{\sigma}{C}H_2$

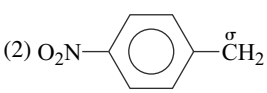
4. Which of the following is the stable free radical?

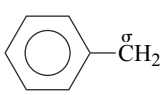
(a) $(CH_3)_3\overset{X}{C}$ (b) $(CH_3)_2\overset{X}{C}H$

(c) $CH_3\overset{X}{C}H_2$ (d) $\overset{X}{C}H_3$

5. Consider the following carbanions:

(1) 

(2) 

(3) 

The correct sequence of the increasing order of stabilities of carbanion is

(a) 1, 2, 3 (b) 3, 2, 1
(c) 2, 3, 1 (d) 1, 3, 2

6. Which of the following is the most stable carbocation?

(a) $C_6H_5\overset{+}{C}H_2$ (b) $C_6H_5\overset{+}{C}HCH_3$

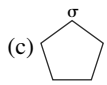
(c) $(C_6H_5)_2\overset{+}{C}H$ (d) $(C_6H_5)_3\overset{+}{C}$

7. In the acid-catalysed dehydration of alcohol to alkene, the reactive intermediate is a

(a) free radical (b) carbanion
(c) carbocation (d) hydronium ion

8. The most stable carbocation is

(a) (b)

(c)  (d)

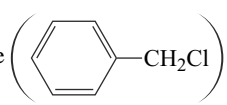
9. A neutral divalent carbon intermediate produced by the removal of two attached atoms is called

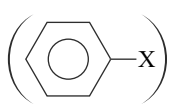
(a) carbanion (b) carbene
(c) free radical (d) benzyne

10. Which of the following are generally unreactive towards S_N2 reaction?

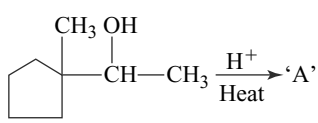
(a) Vinylic halide (>C = C<$_X$)

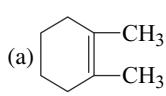
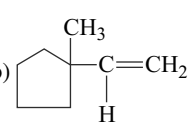
(b) Allyl chloride (CH_2═CH—CH_2Cl)

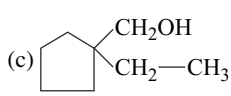
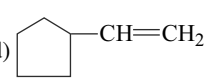
(c) Benzyl chloride 

(d) Phenyl chloride 

11. Consider the following reaction and predict 'A'.



(a)  (b) 

(c)  (d) 

12. When 1,3-butadiene reacts with one equivalent of Br_2 at higher temperature, the major product is

(a) $CH_2{=}CH{-}\underset{\displaystyle Br}{\underset{|}{CH}}{-}\underset{\displaystyle Br}{\underset{|}{CH_2}}$

(b) $\underset{\displaystyle Br}{\underset{|}{CH_2}}{-}\underset{\displaystyle Br}{\underset{|}{C}}{=}\underset{\displaystyle H}{\underset{|}{C}}{-}CH{=}CH_2$

(c) $Br{-}CH_2{-}CH{=}CH{-}CH_2Br$

(d) $BrCH{=}CH{-}CH_2{-}CH_2Br$

13. Mark the correct order of the reactivity of the following substances towards nucleophilic addition reaction.

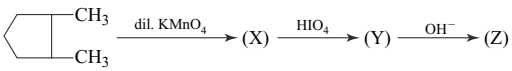
1. HCHO 2. CH_3CHO
3. $CH_3CH_2COCH_3$ 4. $CH_3CH_2COCH_2CH_3$

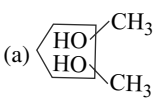
(a) 1 > 2 > 3 > 4 (b) 1 > 2 > 4 > 3
(c) 1 > 4 > 2 > 3 (d) 1 > 3 > 2 > 4

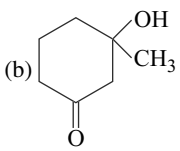
14. Which of the following does not undergo aldol condensation?

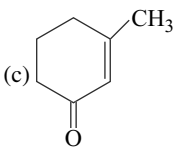
(a) 2,5-hexa dione (b) 2,7-octane dione
(c) 2,8-nonane dione (d) 2,4-pentane dione

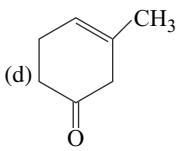
15. Identify the final product (Z) in the following sequence of reactions.



(a) 

(b) 

(c) 

(d) 

16. Which is the strongest nucleophile among the following?

(a) C_2H_5SH (b) CH_3COO^{σ}
(c) $\overset{\oplus}{N}H_3NH_2$ (d) $NCCH_2{}^{\sigma}$

17. Which one among the following does not act as an intermediate in Hofmann rearrangement?

(a) RNCO (b) $RCO\ddot{\ddot{N}}$
(c) $RCO\ddot{\ddot{N}}HBr$ (d) RNC

18. Which of the following undergoes nucleophilic substitution exclusively by S_N1 mechansim?

(a) Ethyl chloride (b) Isopropyl chloride
(c) Chlorobenzene (d) Benzyl chloride

19. Tertiary alkyl halides are practically inert to substitution by S_N2 mechanism because of

(a) insolubility (b) instability
(c) inductive effect (d) steric hindrance

20. Elimination of bromine from 2-bromobutane results in the formation of

(a) equimolar mixture of 1 and 2 butene
(b) predominantly 2-butene
(c) predominantly 1-butene
(d) predominantly 2-butyne

21. Which of the following is least reactive in a nucleophilic substitution reaction?

(a) $(CH_3)_3CCl$ (b) $CH_2{=}CH{-}Cl$
(b) $CH_3{-}CH_2Cl$ (d) $CH_2{=}CH{-}CH_2Cl$

22. The ease of dehydrohalogenation of alkyl halide with alcoholic KOH is

(a) 3° > 2° > 1° (b) 3° < 2° < 1°
(c) 3° > 2° < 1° (d) 3° < 2° > 1°

23. The electrophilic addition of 1,3-butadiene produces

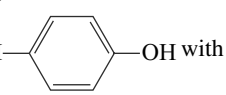
(a) 1,2-addition product only
(b) 1,4-addition product
(c) both 1,2- and 1,4-addition products which are not at equilibrium with each other
(d) both 1,2- and 1,4-addition products which are at equilibrium with each other

24. The intermediate during the addition of HCl to propene in the presence of peroxide is

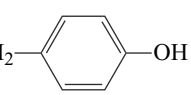
(a) $CH_3\dot{C}HCH_2Cl$ (b) $CH_3\overset{+}{C}HCH_3$
(c) $CH_3CH_2\dot{C}H_2$ (d) $CH_3CH_2\overset{+}{C}H_2$

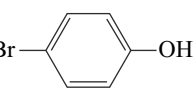
25. During debrominaton of meso-dibromobutane, the major compound formed is

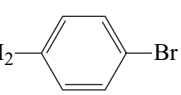
(a) *n*-butane (b) 1-butene
(c) *cis.*-2-butene (d) *trans*-2-butane

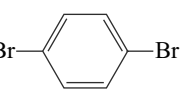
26. The reaction of 

with HBr gives

(a) 

(b) 

(c) 

(d) 

27. Which of the following compounds will react with ethanolic KCN?
(a) Ethyl chloride (b) Acetyl chloride
(c) Chlorobenzene (d) Benzaldehyde

28. The relative order of esterification in alcohols is
(a) $1° < 2° < 3°$ (b) $1° > 2° > 3°$
(c) $1° > 3° > 2°$ (d) $1° < 3° < 2°$

29. The relative order of esterification of acids is
(a) $RCH_2COOH > R_2CHCOOH > R_3CCOOH$
(b) $RCH_2COOH < R_2CHCOOH < R_3CCOOH$
(c) $RCH_2COOH < R_3CCOOH < R_2CHCOOH$
(d) $R_3CCOOH > RCH_2COOH > R_2CHCOOH$

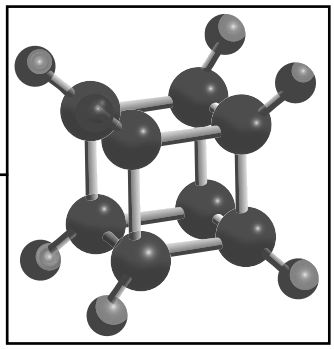
30. The order of stability of allyl, 3° and vinyl radicals is
(a) allyl > 3° > vinyl (b) 3° > allyl > vinyl
(c) 3° > vinyl > allyl (d) vinyl > 3° > allyl

31. Which of the following has the highest nucleophilicity?
(a) F^- (b) OH^-
(c) $\overline{CH_3}$ (d) $\overline{NH_2}$

Answers

1. (d)	2. (a)	3. (a)	4. (a)	5. (d)
6. (d)	7. (c)	8. (d)	9. (b)	10. (a, d)
11. (a)	12. (c)	13. (a)	14. (d)	15. (b)
16. (d)	17. (d)	18. (d)	19. (d)	20. (b)
21. (b)	22. (a)	23. (c)	24. (b)	25. (d)
26. (d)	27. (a, d)	28. (b)	29. (a)	30. (a)
31. (c)				

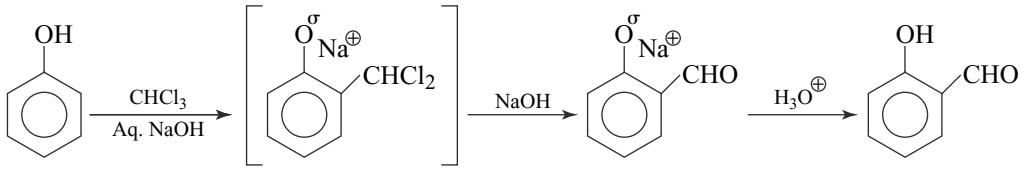
CHAPTER 6



Name Reactions

REIMER–TIEMANN REACTION

Phenols when heated with chloroform and NaOH (or KOH) undergo formylation. The product is mainly *o*-aldehyde (with a small amount of the para-isomer). This reaction is known as Reimer–Tiemann reaction.



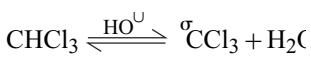
Intermediate [A]

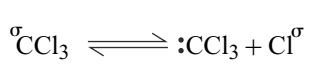
Salicylaldehyde

Mechanism

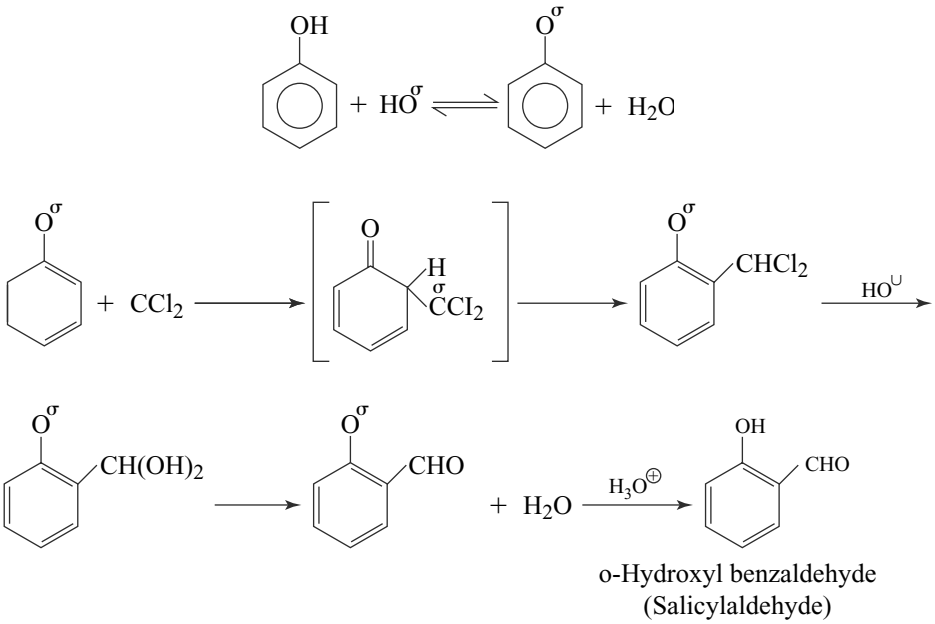
The reaction is aromatic electrophilic substitution.

Electrophile in the reaction is dichloro carbine (:CCl_2). It is formed from $CHCl_3$ as follows:



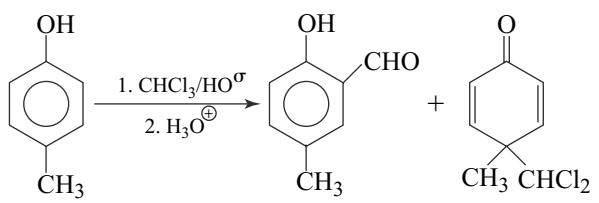


Dichlorocarbene has only a sextet of electrons to carbon, which makes it a strong electrophile. The reaction proceeds as follows:



o-Hydroxyl benzaldehyde
(Salicylaldehyde)

The intermediacy of dichlorocarbene is shown by the reaction given below:



p-Cresol [B]

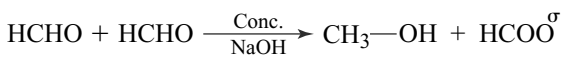
The abnormal compound (that is not the aldehyde) like B proves the intermediacy of CCl_2 in the reaction. The compound B has no H atom at the reaction site that can be lost as H^+ to re-aromatize the ring. It (B) is formed by simply taking up a proton in the final step of acidification.

The compound B is not hydrolyzed partly due to the following reasons:

1. Its insolubility in aq. base.
2. Sterically hindered chlorine atoms.

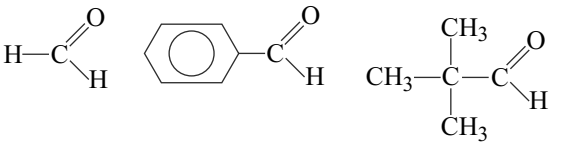
CANNIZZARO REACTION

Aldehydes without α-H atom(s) undergo self-oxidation–reduction (i.e., disproportionation) in the presence of a strong base. It is known as Cannizzaro reaction.



Normally, alcohol and acid are formed in equal amounts.

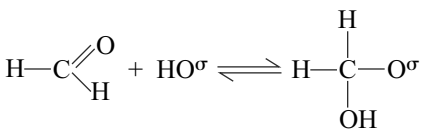
ALDEHYDES WITHOUT α-H ATOMS



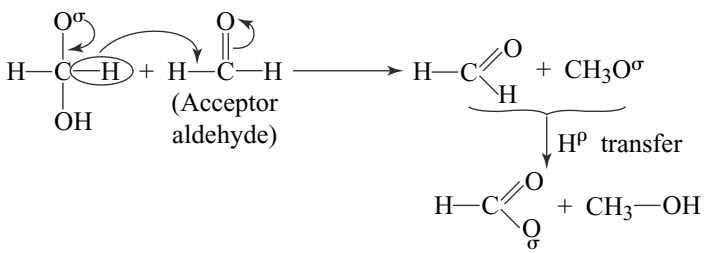
Formaldehyde Benzaldehyde 2,2-Dimethyl propanal

Mechanism

It is a hydride (H^-)-transfer reaction. It becomes possible due to electron-donating nature of O^-. The reaction is outlined below:



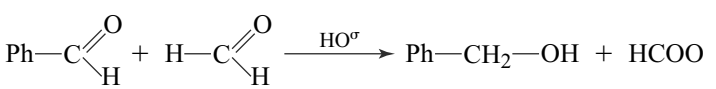
Aldehyde anion



When the reaction is carried out in D_2O, no D is incorporated in the alcohol. It proves direct hydride transfer from the aldehyde anion to the acceptor aldehyde.

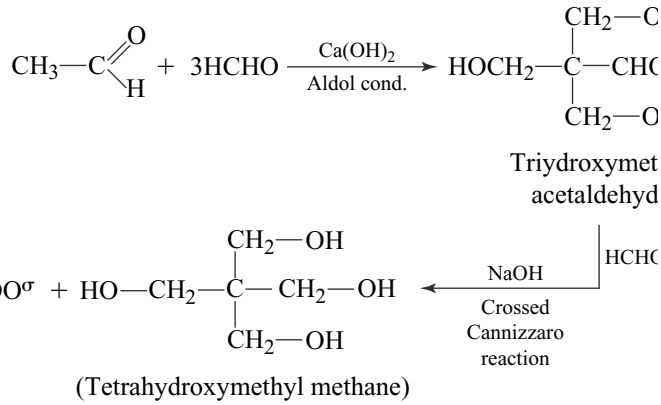
CROSSED CANNIZZARO REACTION

The reaction between two different aldehydes is known as crossed Cannizzaro reaction.



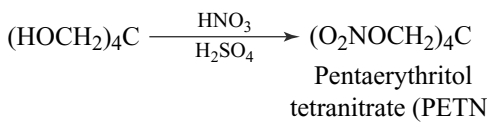
When formaldehyde is involved in crossed Cannizzaro reaction, it is exclusively oxidized and the other one is reduced. It is due to high reactivity of HCHO that adds HO^- easily (over the other aldehyde) and is hydride (H^s) donor.

This reaction is used to prepare pentaerythritol (tetrahydroxymethyl methane). This synthesis is a combination of aldol condensation and crossed Cannizzaro reaction.



(Tetrahydroxymethyl methane)

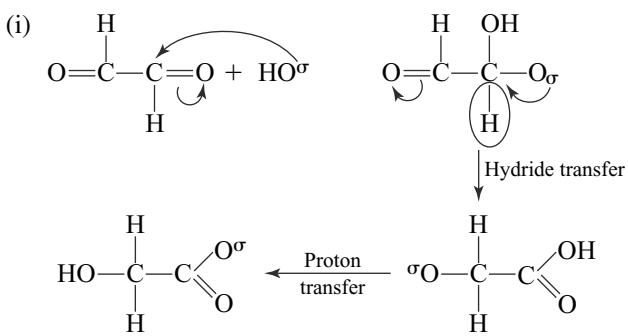
Pentaerythritol forms resin polymers with polybasic acids that are used for surface coating. Its tetranitro derivative is a useful explosive.



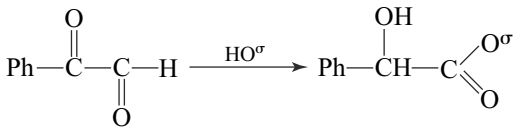
INTRAMOLECULAR CANNIZZARO REACTION

Carbonyl compounds like 1,2-dialdehydes (or α-ketoaldehydes) can transfer H^- ion within the same molecule in the presence of a strong base. Such reactions are called intramolecular Cannizzaro reaction. For example,

(i) glyoxal and (ii) phenyl glyoxal.

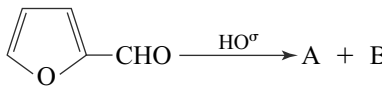


(Glycollate anion)

(ii) 

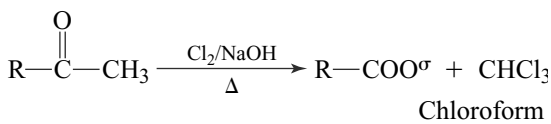
(Mandelic acid anion)

Problem: In the reaction given below find the products A and B. Also write the mechanism of the reaction.



HALOFORM REACTION

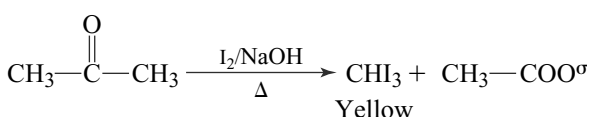
Methyl ketones (and acetaldehyde, the only aldehyde) when heated with X_2 (X = Cl, Br or I) and NaOH (a base), trihalomethane, CHX_3 (haloform) is formed. This reaction is known as *haloform reaction*.



Chloroform

The halogen may be bromine or iodine also.

The formation of iodoform (CHI_3) is used to detect methyl ketones because iodoform is a highly insoluble bright yellow solid.



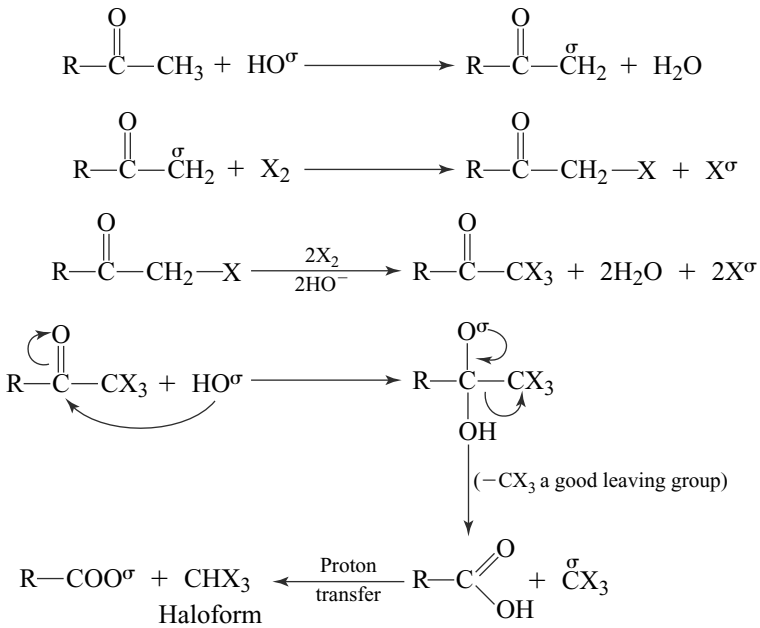
Yellow

Mechanism

This reaction is a combination of two reactions:

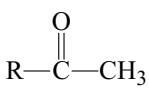
1. Halogenation of ketone in the presence of a base.
2. The cleavage of trihaloketone by base to give haloform and acid anion.

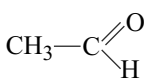
First, base-catalysed halogenation takes place. Each halogen introduced increases the acidity of the rest H atoms. Consequently, a trihaloketone is formed. It is cleaved by HO^- to haloform and $R–COO^-$.

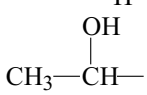


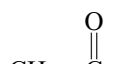
Scope

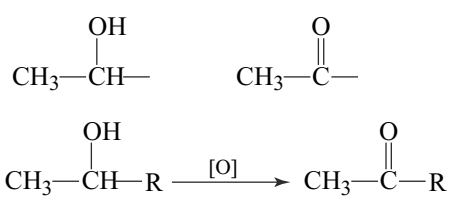
The haloform reaction is given by

(a) methyl ketones 

(b) methyl ketones 

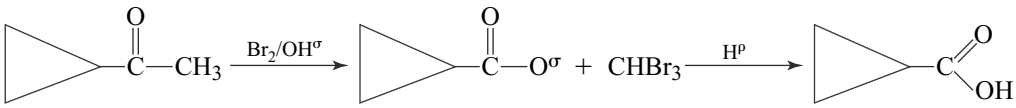
(c) methyl ketones 

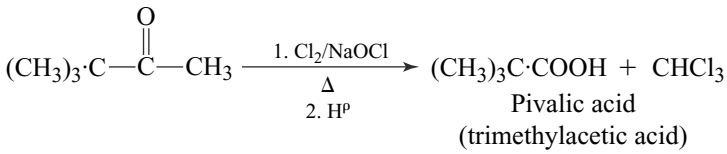
Such alcohols are oxidized under reaction condition to give  group



Uses

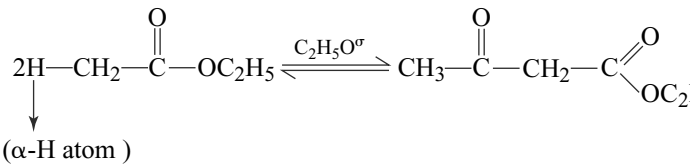
To prepare carboxylic acids:





CLAISEN CONDENSATION

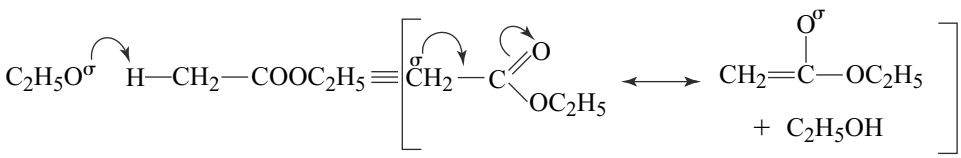
Esters containing α-H atoms when treated with a strong base (EtO^-), β-ketoesters are formed. This is known as *Claisen condensation*.

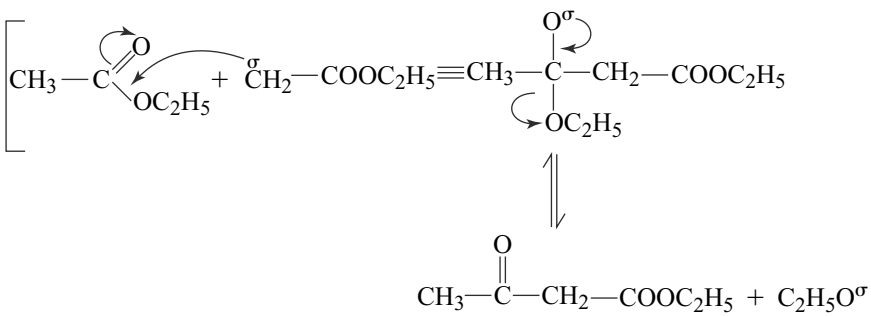


Mechanism

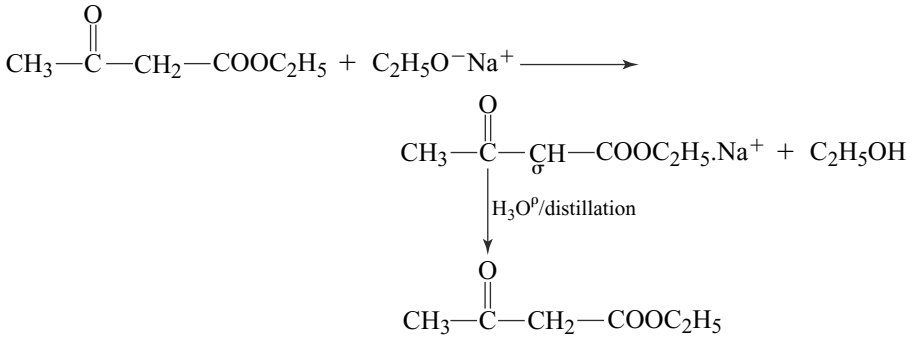
This reaction involves carbanion nucleophile. It is formed due to acidic nature in the α-H atom of the ester. In the second step, this nucleophile attacks the carbonyl carbon of another ester molecule.

Elimination of –OR group completes the reaction (–OR is a good-leaving group).



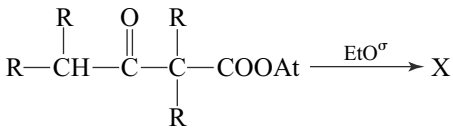


This reaction is reversible. Therefore, to get good yield of the product, more sodium ethoxide is used that forces the equilibrium to the right by converting the β-ketoester into its sodium salt. Free ester is then obtained by acidification followed by distillation.

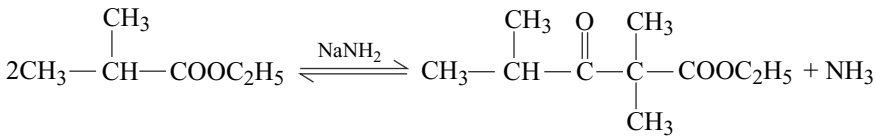


CONDENSATION OF ESTERS HAVING ONLY ONE α-H ATOM

Esters of this class do not give condensation reactions with sodium ethoxide (C_2H_5ONa). It is because the product β-ketoesters are not capable of converting into its sodium salt (as there is no α-H atom) that is essential to force the equilibrium to the right.

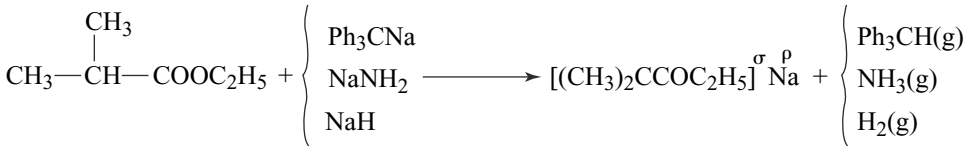


However, very strong bases like $NaNH_2$, NaH or sodium triphenylmethidecan cause Claisen condensation of esters that have only one α-H atom.



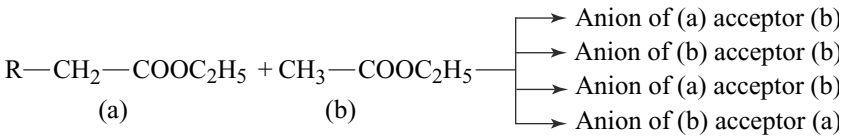
Ethyl 2,2,4-trimethyl-3-keto pentanoate

The reasons are (i) the first step may be irreversible or (ii) the second product of acid–base reaction escapes as a gas (making it irreversible).



CROSSED CLAISEN CONDENSATION

The condensation between two different esters, both having α-H atoms is known as crossed Claisen condensation. It gives four β-ketoesters. Therefore, it has little synthetic utility.

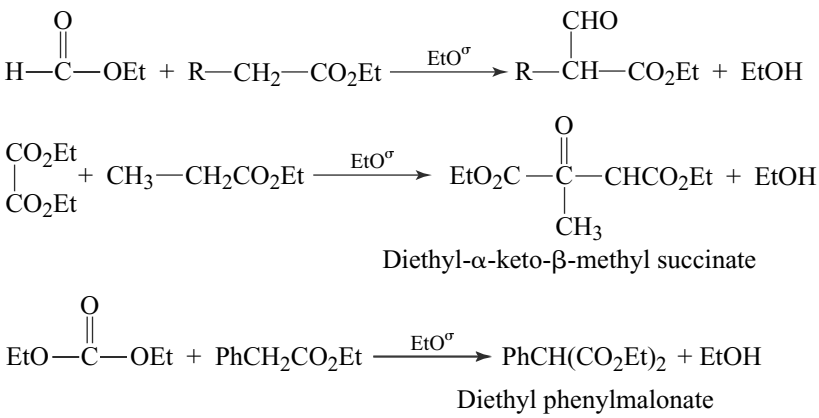


Crossed Claisen condensation in which one ester has no α-H atom

This type of condensations gives single β-ketoester. It is because

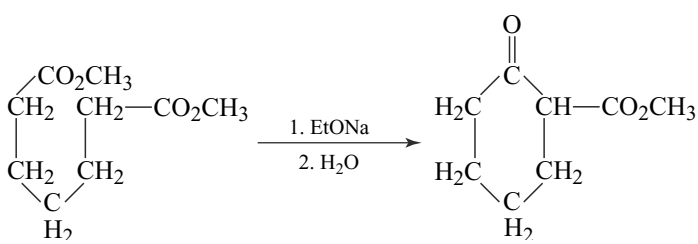
(i) the ester having α-H atom forms nucleophilic reagent and

(ii) the ester having no α-H atom is a good acceptor as it possesses high carbonyl reactivity.



DIECKMANN REACTION

Intramolecular Claisen condensation of esters of dicarboxylic acids forms cyclic β-ketoesters. This reaction is known as *Dieckmann reaction*.

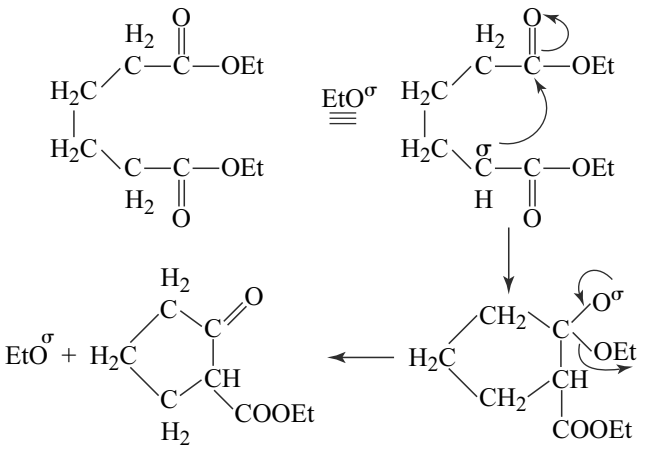


This reaction gives good yield with dicarboxylic acids containing five, six, seven or eight carbon atoms.

Mechanism

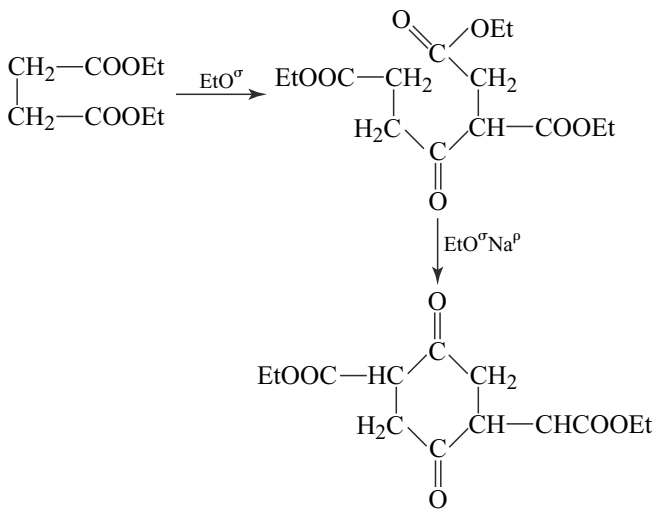
The reaction proceeds as follows:

1. Nucleophilic centre is generated by acid–base reaction between the ester and the base (EtO^-).
2. In the second step, nucleophile attacks the carbon of the second ester group in the same molecule.
3. In the last step, RO^- is expelled to complete the reaction.

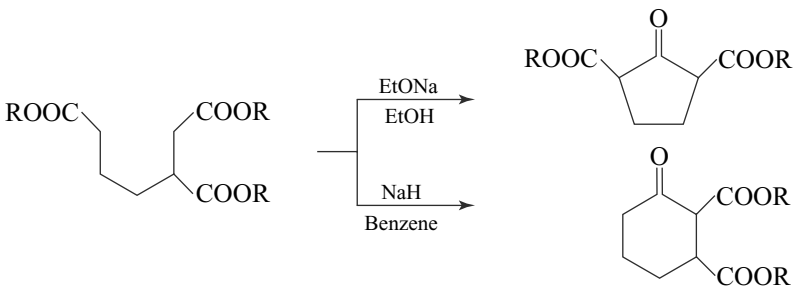


Important points

1. Ester of acids containing C atoms less than six undergo intermolecular condensation (Claisen condensation) followed with intramolecular condensation (Dieckmann reaction), example diethyl succinate gives cyclohexane derivative.



2. In some cases, the reaction condition has effect on the ring size.



ALDOL CONDENSATION

Aldehydes (or ketones) having α-H atoms condense under the influence of mild bases (or acids) to give β-hydroxyaldehydes (aldols). This reaction is known as aldol condensation.

$$2CH_3CHO \xrightarrow{Ba(HO)_2} CH_3{-}\underset{\displaystyle OH}{\underset{|}{C}}H{-}CH_2{-}CHO$$

(Acetaldol)

Bases: $Ba(OH_2)$, dil. NaOH and K_2CO_3 solution.

Mechanism

Base–catalysed aldol condensation

It is a reaction of the enolate anion (carbanion). The α-H atom (acidic) is removed by the base to form the enolate anion. This carbanion then attacks the carbonyl carbon of the second aldehyde. The reaction proceeds as

$$HO^{\sigma} + H{-}CH_2{-}C(=O){-}H \rightleftharpoons \left[{}^{\sigma}CH_2{-}C(=O){-}H \longleftrightarrow CH_2{=}C(-O^{\sigma}){-}H \right] + H_2O$$

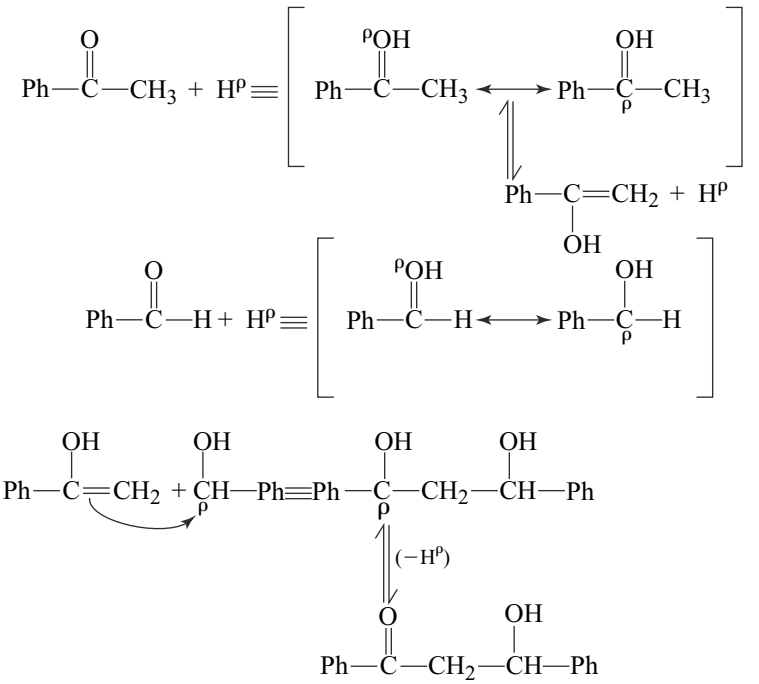
Enolate anion

$$CH_3{-}C(=O){-}H + {}^{\sigma}CH_2{-}CHO \rightleftharpoons CH_3{-}\underset{\displaystyle O^{\sigma}}{\underset{|}{C}}H{-}CH_2{-}CHO \xrightarrow{H_2O} CH_3{-}\underset{\displaystyle OH}{\underset{|}{C}}H{-}CH_2{-}CHO + HO^{\sigma}$$

Aldol

Acid-catalysed aldol condensation

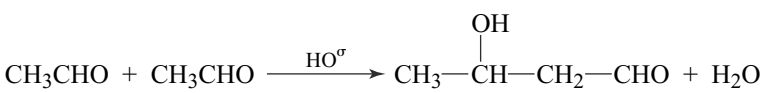
Acid-catalysed condensation proceeds through enol, example condensation involving acetophenone and benzaldehyde



Important points

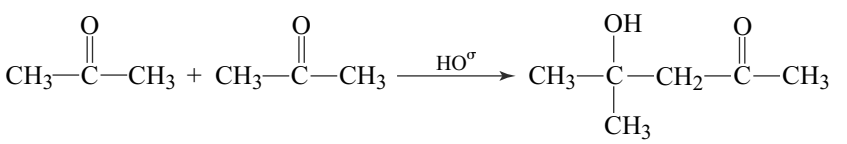
1. The scope of condensation is varied,

(a) Two molecules of the same aldehyde can condense, example



In this case, only one product is formed.

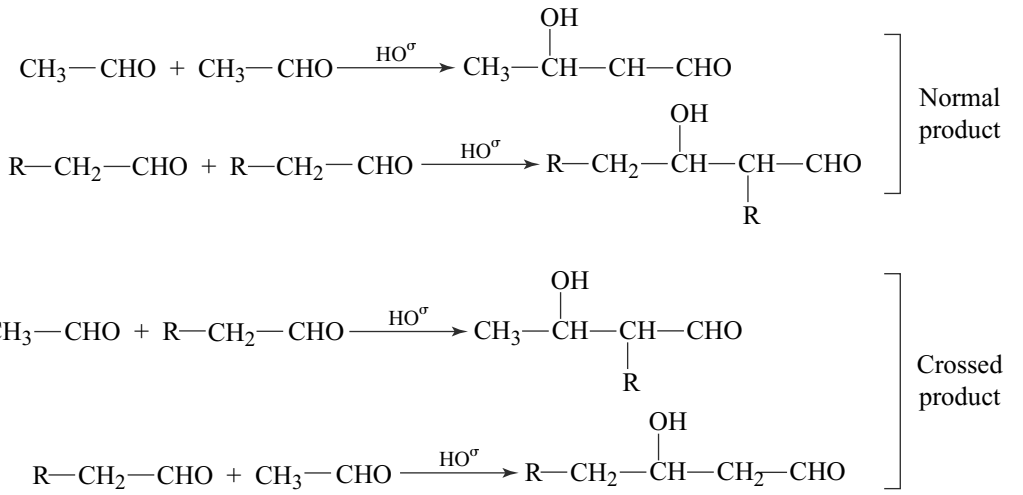
(b) Two molecules of the same ketone may also condense, example CH_3–$COCH_3$ + CH_3COCH_3, which gives only one product.



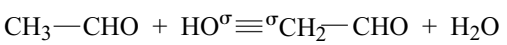
(c) Two molecules of different aldehydes may also condense.

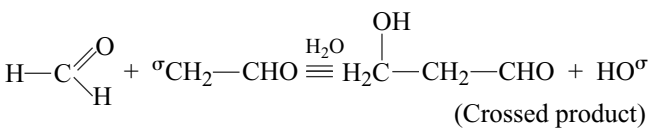
(i) $CH_3CHO + R–CH_2–CHO$

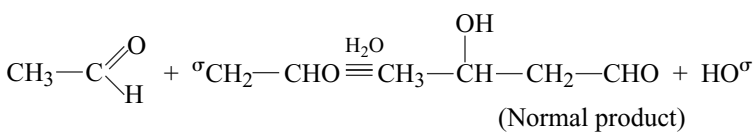
Both these aldehydes can form enolate as they have α-H atom. Therefore, four condensation products are possible. In many cases, crossed product is the main one. It is called *crossed aldol condensation*. (Claisen–Schmidt reaction).



(ii) When one aldehyde has no α-H atom (PhCHO, HCHO), it is enolate acceptor only. The enolate will be formed by the aldehyde having α-H atom, CH_3CHO. In this case, only two products are formed, the normal and the crossed one.







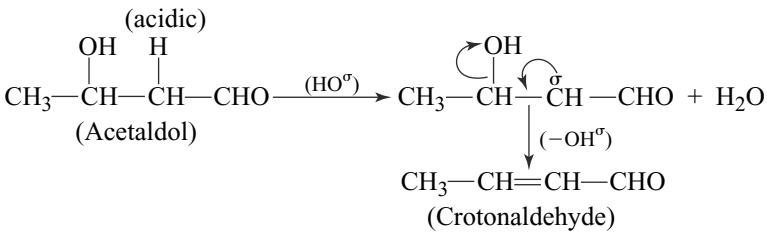
(d) Two different ketones may condense.

(e) An aldehyde and a ketone may also condense.

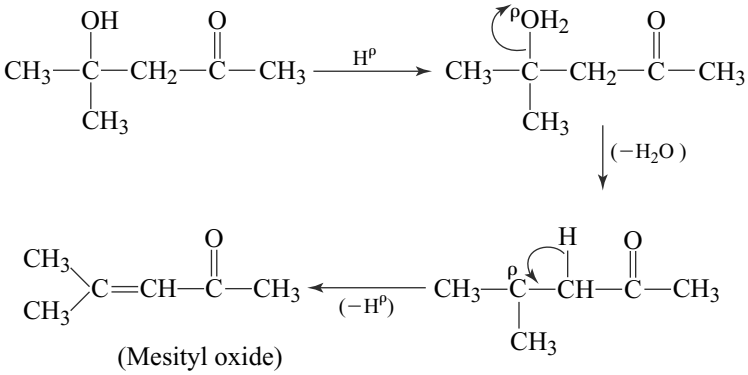
Dehydration of condensation product

The condensation products may be dehydrated either (i) by heating the basic reaction mixture or (ii) by a separate acid-catalysed reaction.

The base-catalysed dehydration takes place only when the product contains acidic hydrogen.

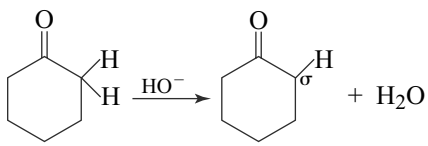


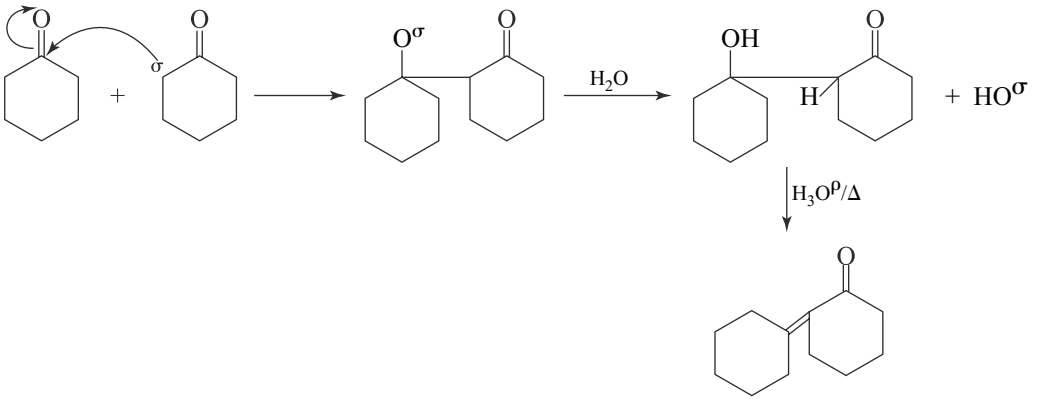
Acid-catalysed dehydration



CONDENSATION OF CYCLIC KETONES

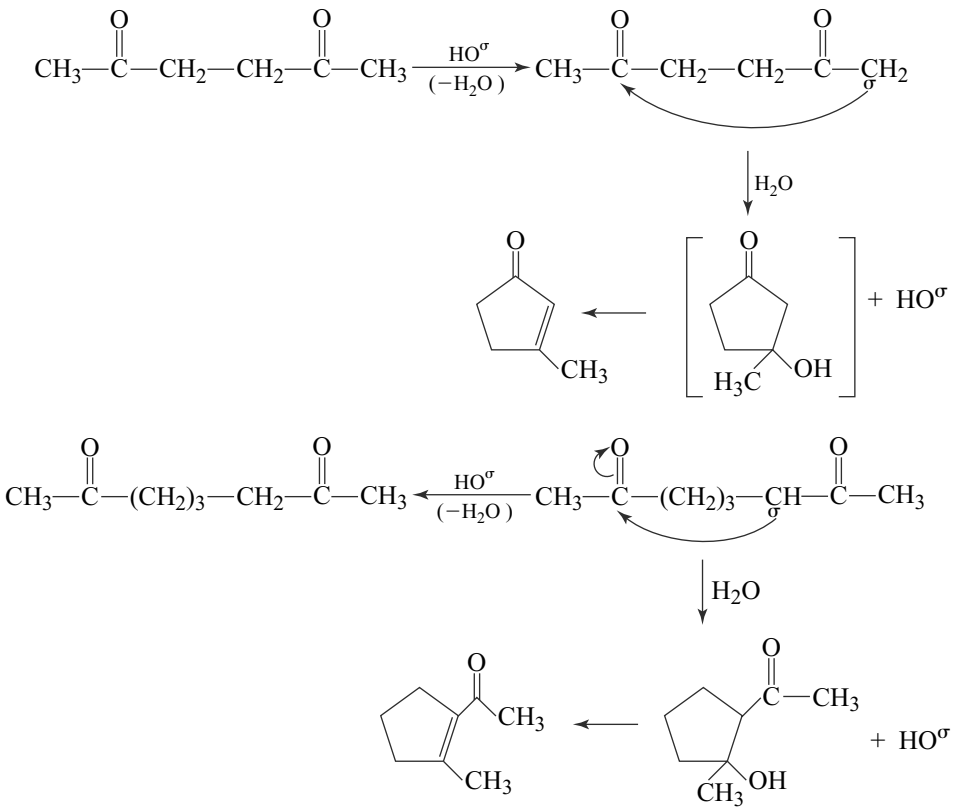
Cyclic ketones having α-H atom are good acceptors also because of much less steric hindrance. For example, cyclohexanone reacts as follows:



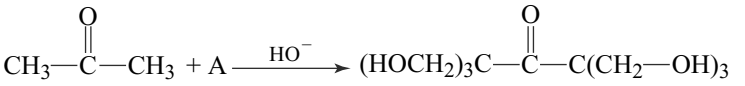


INTRAMOLECULAR ALDOL CONDENSATION

Properly constituted diketones undergo intramolecular aldol condensation to give cyclic product, example

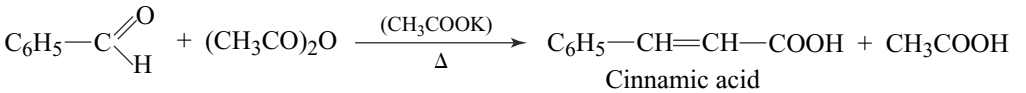


Problem: What is A in the reaction given below?



PERKIN REACTION

The condensation of an aromatic aldehyde with an acid anhydride in the presence of a base is called Perkin reaction. The base is generally the sodium or K salt of the acid corresponding to the anhydride. The product is β-substituted acrylic acid.



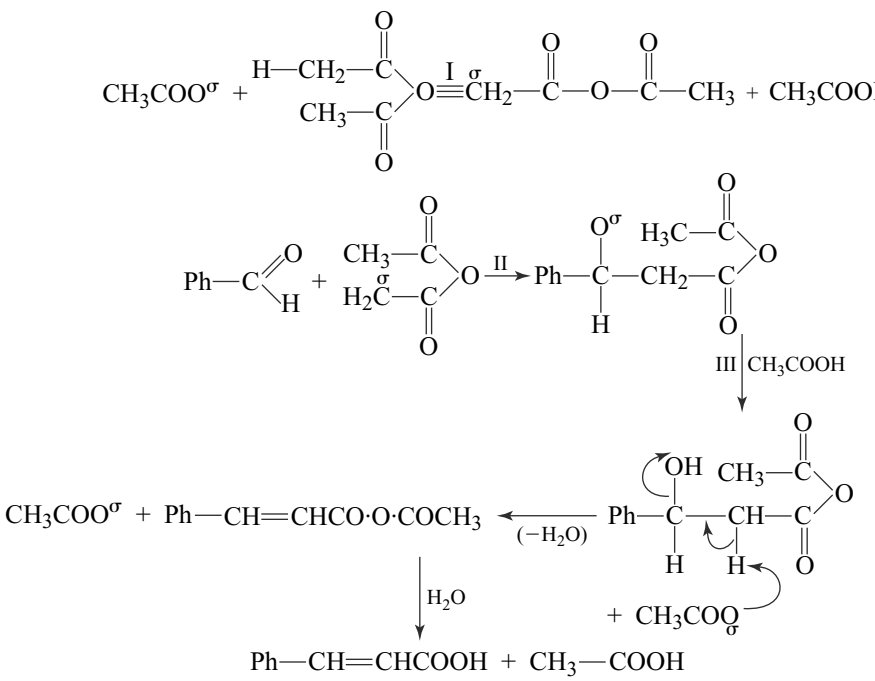
Cinnamic acid

Other bases may also be used, such as Na_2CO_3, pyridine and triethylamine.

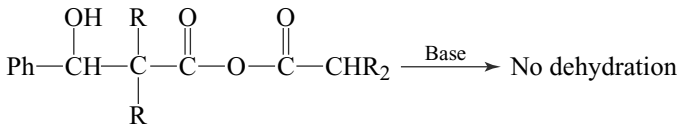
This reaction requires high temperature as a weak base is used with a weak acidic reagent.

Mechanism

The base removes an α-H atom from the anhydride to generate a carbanion. It attacks the aldehyde. The reaction proceeds as follows:

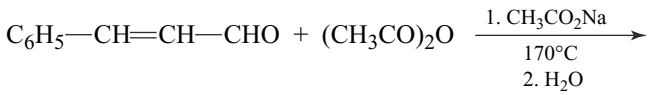


When the anhydride has two α-H atoms, dehydration (i.e., step IV) always occurs. With anhydride of the type $(R_2CHCO)_2O$, hydroxy compound is the product as dehydration cannot take place.



VINYLOGS OF CINNAMIC ACID

Vinylogs are related by the introduction of –CH=CH– units in a chain. Thus, a vinylog of cinnamic acid is produced when cinnamaldehyde is used as a substrate in the Perkin reaction.

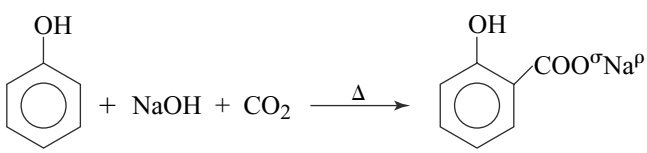


C_6H_5—CH=CH—CH=CHCOOH

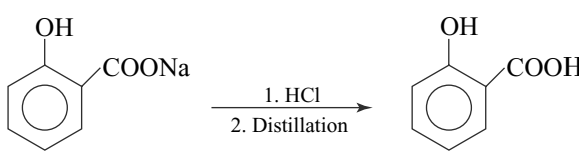
5-Phenyl-2,4-pentAdienoic acid

KOLBE REACTION

When phenol is heated with NaOH and CO_2, sodium salt of *o*-hydroxybenzoic acid (salicylic acid) is formed. This is known as *Kolbe reaction*.



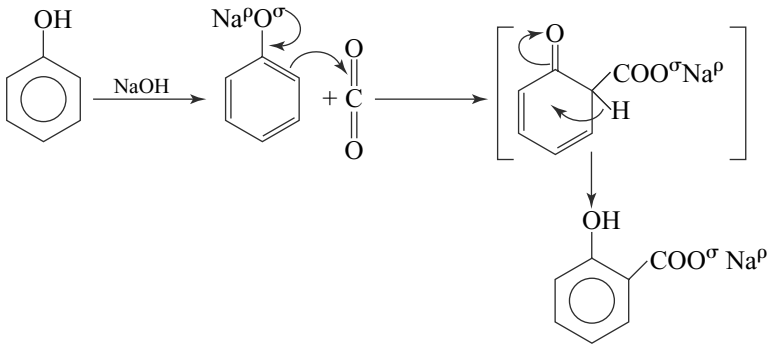
Acidification followed with distillation gives salicylic acid.



Salicylic acid

Mechanism

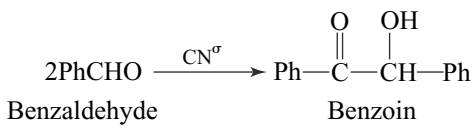
This is an electrophilic-substitution reaction and CO_2 is an electrophile.



In the temperature range 120–140°C and under high pressure (5–7 atm.), phenol is entirely converted into the product. This modification is known as *Kolbe–Schmidt reaction*.

BENZOIN CONDENSATION

The dimerization of benzaldehyde under the catalytic effect of cyanide ion gives benzoin. It is known as benzoin condensation.

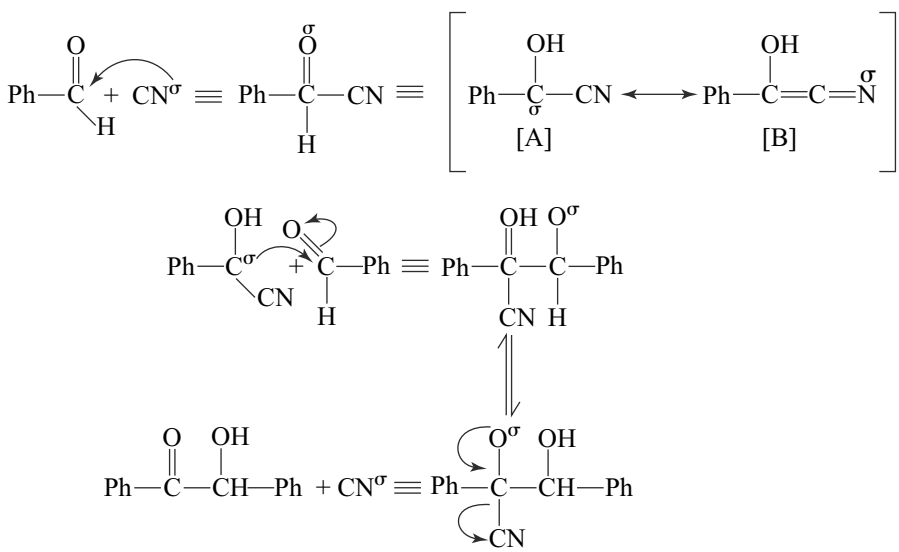


Benzaldehyde Benzoin

Ph is phenyl, C_6H_5

Mechanism

The reaction is reversible, and the accepted mechanism (Lapworth, 1903) is the following:

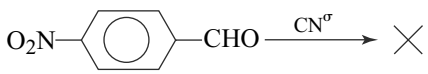


The CN^{s} ion is the specific catalyst for this reaction. It is not catalysed by HO^{s} or other bases, in general. The specific effect of CN^{s} may be due to the following facts:

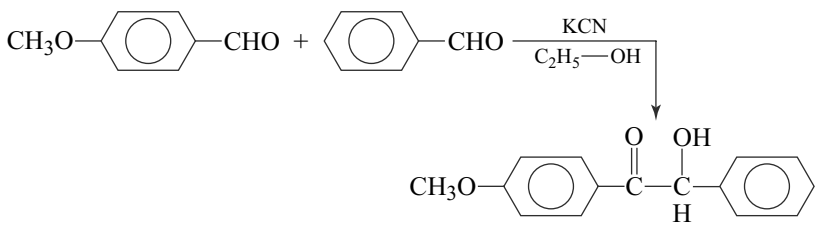
1. CN^{s} is a good nucleophile (so adds easily).
2. It is electron attracting, which increases acidity of the C–H hydrogen, leading to the formation of carbanion [A], which is resonance stabilized (structure B).
3. CN is a good-leaving group, so it easily departs in the last step.

Important Points

1. Substrates having electron-withdrawing group fail this reaction. Thus, *p*-nitrobenzaldehyde does not give benzoin condensation.

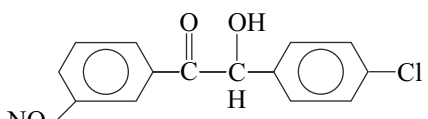


2. Electron-donating groups, such as *p*-$N(CH_3)_2$ and *p*-OCH_3 retard the reaction.
3. Mixed benzoins may be obtained in good yield from two different aldehydes.



4-Methoxybenzoin

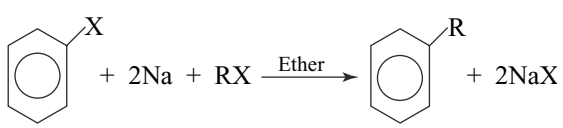
In naming mixed benzoins, substituents in the ring joined to the carbonyl group are numbered in the general way, but primes are used to locate substituents in the ring attached to –CH(OH) group.



3-nitro-4-chlorobenzoin

WURTZ–FITTIG REACTION

When alkyl and aryl halides are heated with metallic sodium in ether, alkyl benzene is formed. It is known as Wurtz–Fittig reaction.



Diaryl and dialkyl derivatives are also formed in this reaction. The three products, obtained in this reaction are easily separable. Therefore, the reaction has synthetic utility.

Mechanism

Available evidences show that this reaction follows ionic mechanism. It proceeds through the intermediate formation of organometallic compound.

$$C_6H_5X + 2Na \longrightarrow C_6H_5^{\sigma}Na^{\rho} + NaX$$

$$C_6H_5^{\sigma} + R{-}X \longrightarrow C_6H_5{-}R + X^{\sigma}$$

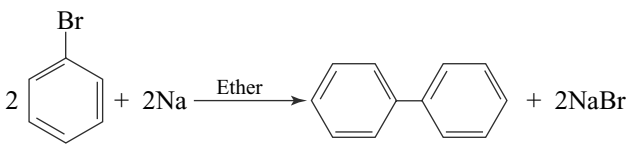
Similarly, other products can be formed.

$$R{-}X + 2Na \longrightarrow R^{\sigma}Na^{\rho} + NaX$$

$$R^{\sigma} + R{-}X \longrightarrow R{-}R + X^{\sigma}$$

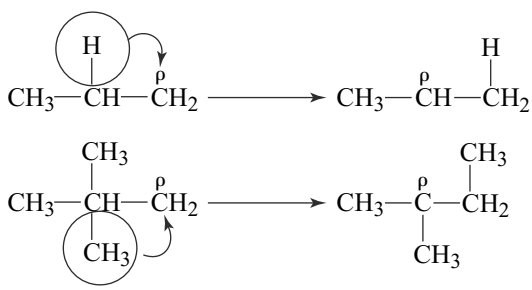
$$C_6H_5^{\sigma} + C_6H_5{-}X \longrightarrow \underset{\text{Biphenyl}}{C_6H_5{-}C_6H_5} + X^{\sigma}$$

When only phenyl halide is used, biphenyl is the product. This is called Fittig reaction.



MOLECULAR REARRANGEMENTS

A reaction in which a group moves from one atom to another in the same molecule is called rearrangement.



Most of the migrations are from an atom to an adjacent atom. They are known as 1,2-shifts. Majority of molecular rearrangements involve migration of a group to

(i) a carbonium ion centre or

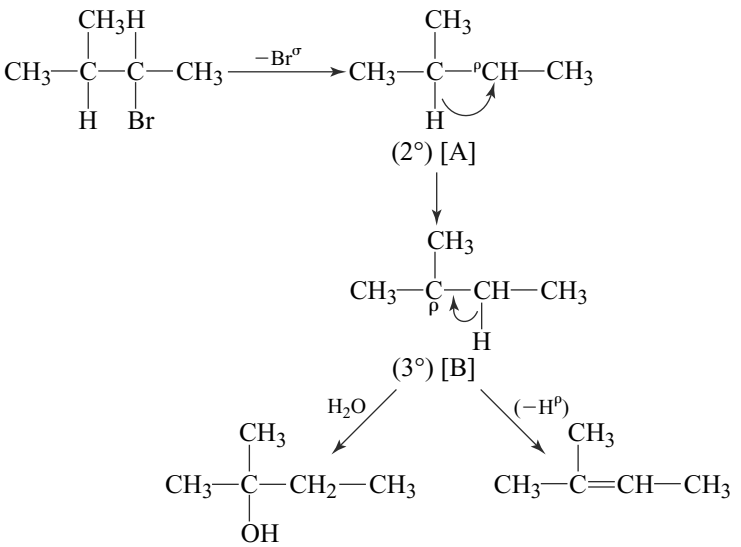
(ii) an electron-deficient N atom or O atom.

Carbonium ion rearrangements

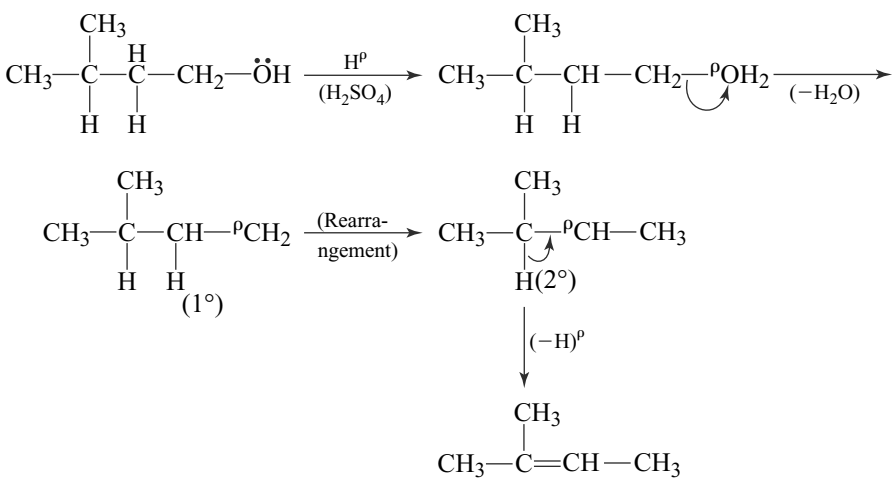
Rearrangement in carbonium ions is a common feature if by doing so a more stable ion results. The hydride shift, cleavage of C–C bond and isomerization are common reactions.

Hydride Shift Reaction

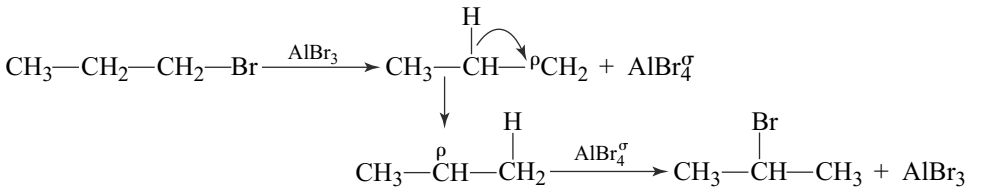
Rearrangements involving shift of hydrogen with bond pair (i.e., as hydride ion, H^-) may occur if a more stable carbonium ion results. For example,



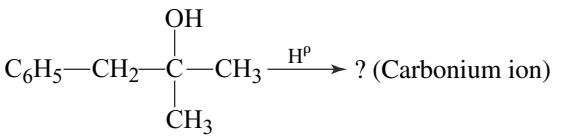
This rearrangement shows greater stability of a tertiary (B) than a secondary (A) carbonium ion. Such rearrangements are very common in the dehydration of alcohols in the presence of H_2SO_4.



This rearrangement takes place as 2° carbonium ion is more stable than 1° carbonium ion.
A similar rearrangement is isomerization of n-propyl bromide to isopropyl bromide in the presence of $AlBr_3$. It is also a H^s shift reaction.



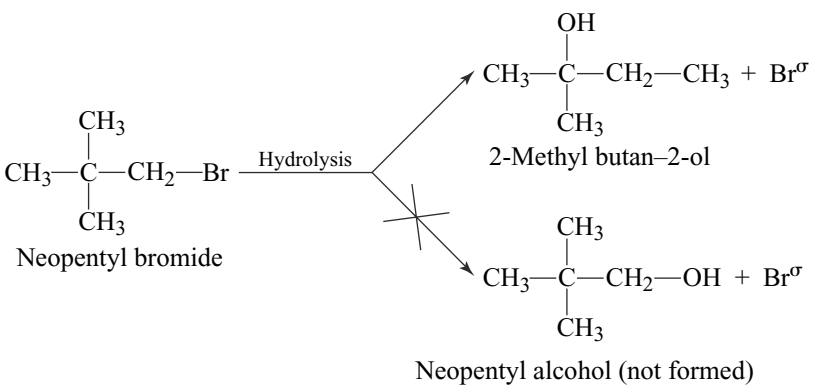
Problem



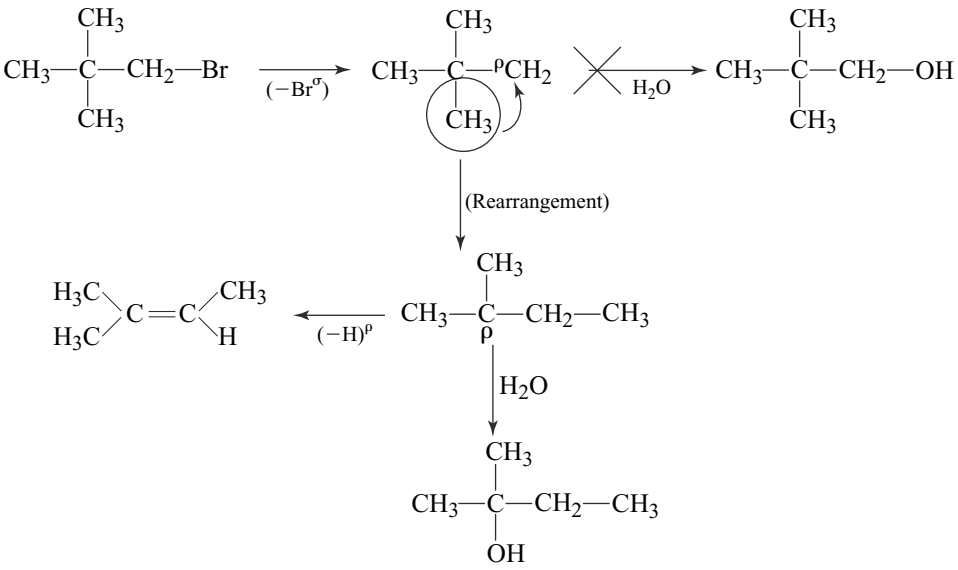
(Hint : Benzylic carbonium ion is more stable)

Rearrangements involving cleavage of C–C bonds Wagner–Meerwein rearrangement (neopentyl rearrangement)

Rearrangements involving C–C bond-breaking which leads to change in carbon skeleton are known as *Wagner–Meerwein* rearrangements.

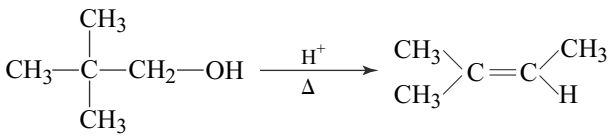


Mechanism

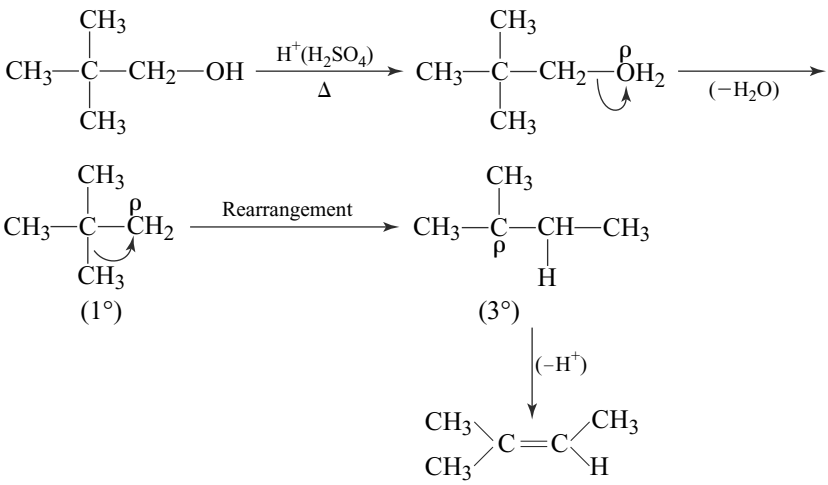


This rearrangement occurs as 1° carbonium ion is less stable than 3° carbonium ion. (This stability difference causes C–C bond cleavage.)

Dehydration of neopentyl alcohol to alkene also proceeds through rearrangement.

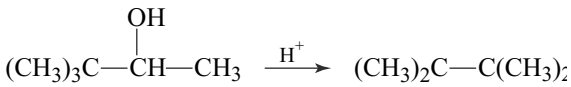


Mechanism

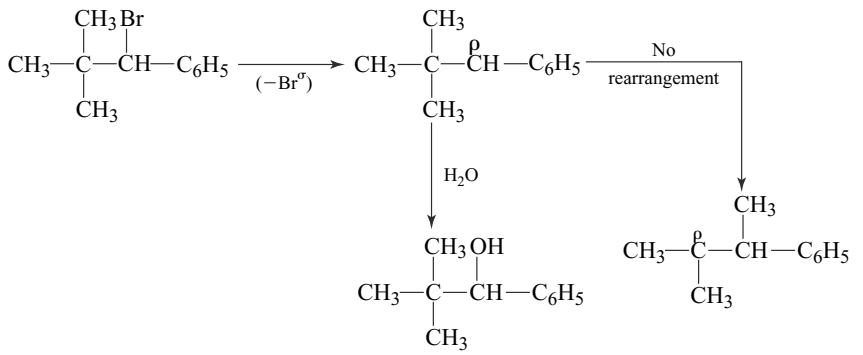


This rearrangement takes place as 1° carbonium ion is less stable than 3° carbonium ion. (This stability difference causes C–C bond cleavage.)

Problem Write the mechanism for the rearrangement given below.



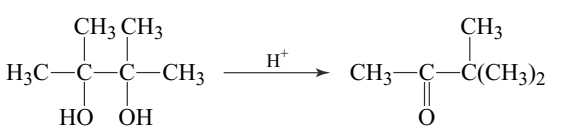
Rearrangement in neopentyl type halide or alcohol is common. But phenyl derivative of neopentyl skeleton does not undergo rearrangement. It is because of the fact that benzylic cation ($-\overset{\oplus}{C}H-Ph$) is more stable compared to tertiary carbocation. The phenyl group ensures delocalization of positive charge over the benzene ring.



Therefore, rearrangement does not take place in benzylic type substrates.

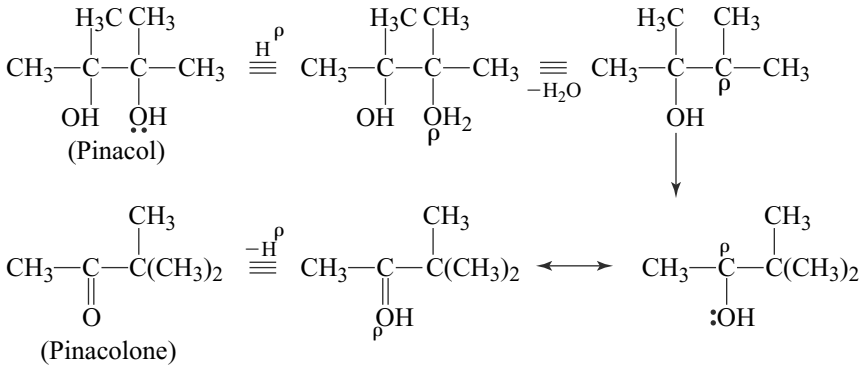
PINACOL–PINACOLONE REARRANGEMENT

Acid catalyzed rearrangement of 1,2-glycols gives carbonyl compounds. For example,



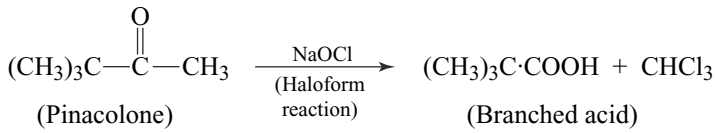
Mechanism

The –OH group is protonated, H_2O departs and carbonium ion is formed. Then rearrangement (intramolecular) takes place. Here, a tertiary carbonium ion undergoes rearrangement because of extra resonance stabilization by the oxygen atom.

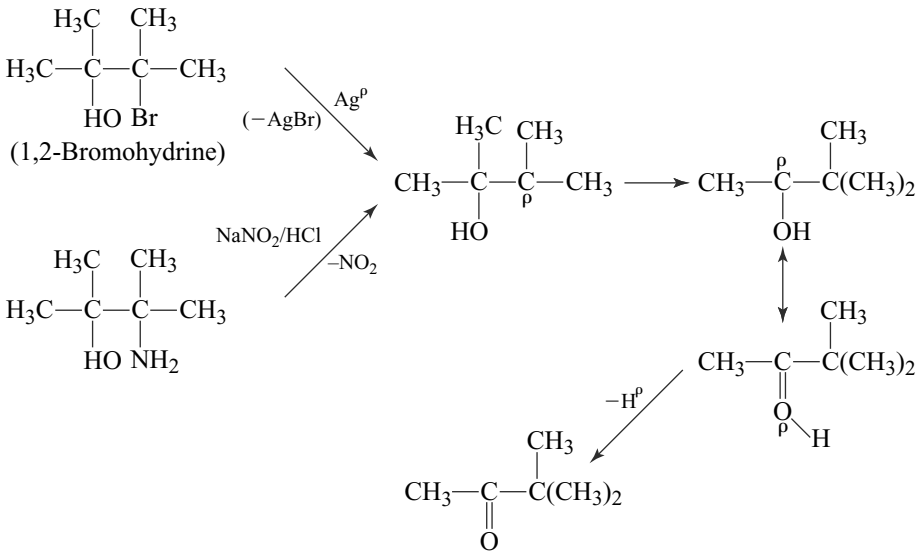


Some important points

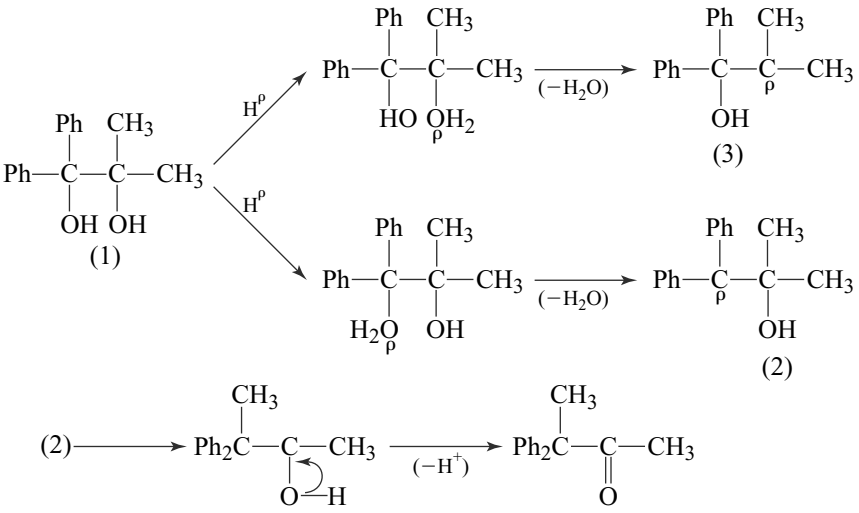
1. As the highly branched structures of the products are not easily constructed, the rearrangement is important in synthesis.



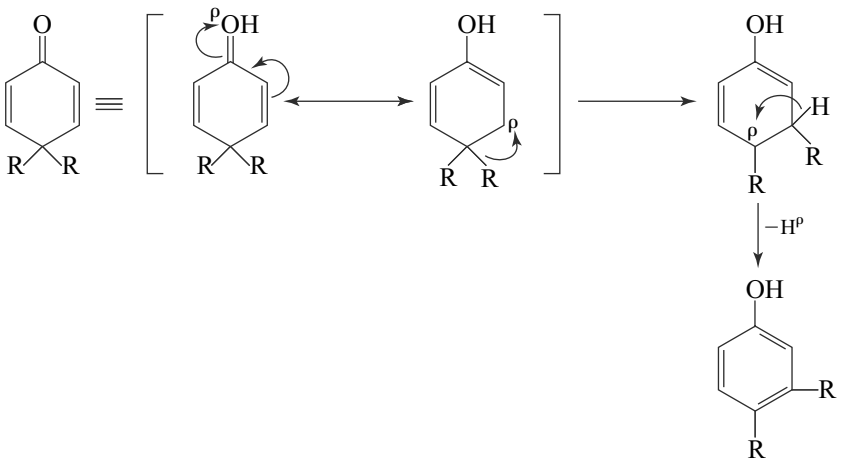
2. Any other reaction that can produce the same carbonium ion gives pinacolone.



3. In unsymmetrically substituted glycols, the positive charge is generated on that carbon which can neutralize it the most. Therefore, in the glycol (I) the –OH group present at the carbon that bears the phenyl group (C_6H_5–) is protonated preferentially. It is because the resulting carbonium ion (II) is more stabilized by phenyl groups rather than methyl groups (III).



4. Rearrangement opposite to pinacol–pinacolone is the dienone–phenol change.



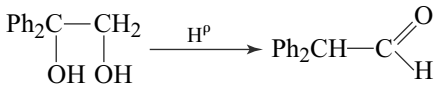
5. The relative tendency of different groups to migrate (that is migratory aptitude) in pinacol–pinacolone rearrangement is not the same. The following orders are found:

(a) $C_6H_5- > (CH_3)_3C > CH_3–CH_2 > CH_3$

(b) p–$CH_3OC_6H_4- > p$–$CH_3C_6H_4- > C_6H_5- > p$–$ClC_6H_4$

The above orders show that a better nucleophile (i.e., stronger electron-pair donor to carbon) migrates easily.

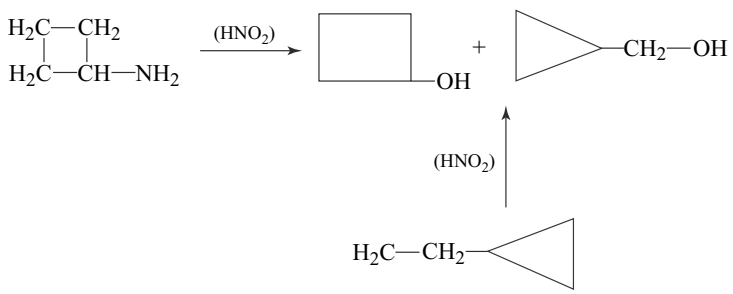
Problem Write mechanism of the reaction given below.



[Hint : OH is protonated and leaves that gives more stable carbocation].

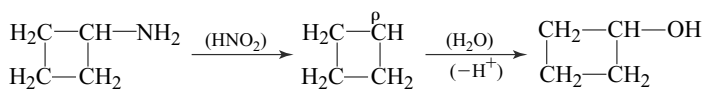
DEMJANOV REARRANGEMENT (EXPANSION AND CONTRACTION OF RINGS)

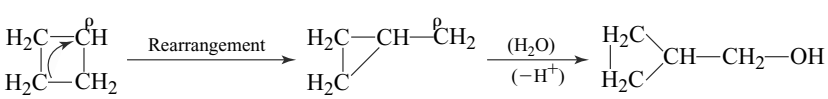
Expansion and contraction of alicyclic rings can take place through carbocation intermediate. It is known as *Demjanov rearrangement.*



Mechanism

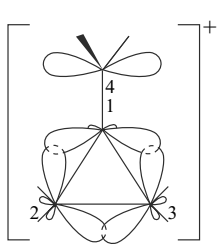
Diazotization of amine gives carbocation. When the positive charge is present on an alicyclic carbon, rearrangement results into ring contraction.



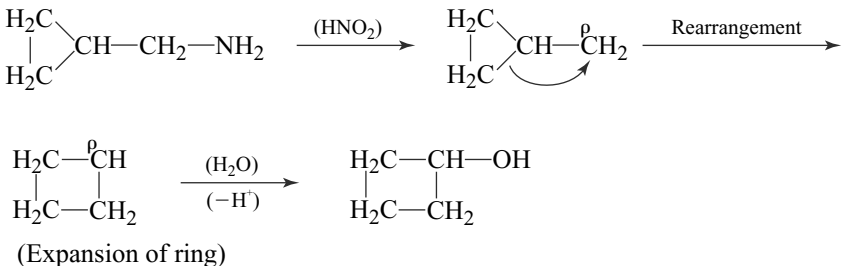


(Contraction)

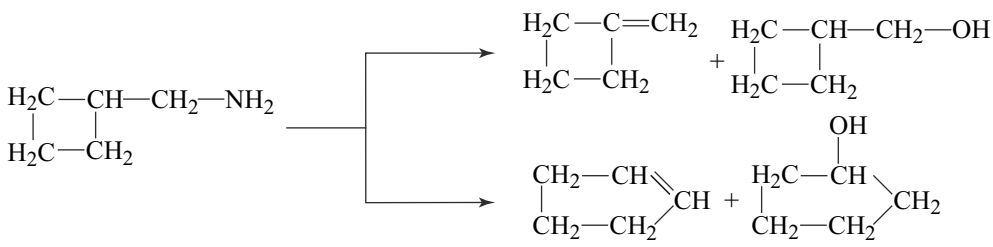
It is a conversion of secondary (2°) to a primary (1°) carbocation, but it becomes possible due to conjugation between the bent orbitals of the eyclopropyl ring and the vacant *p* orbital of the positive carbon.



When the positive charge is present on a carbon α to an alicyclic ring, ring expansion can take place.

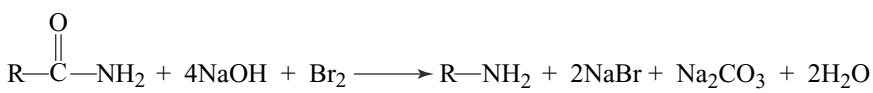


Problem Write the mechanisms for the following changes.

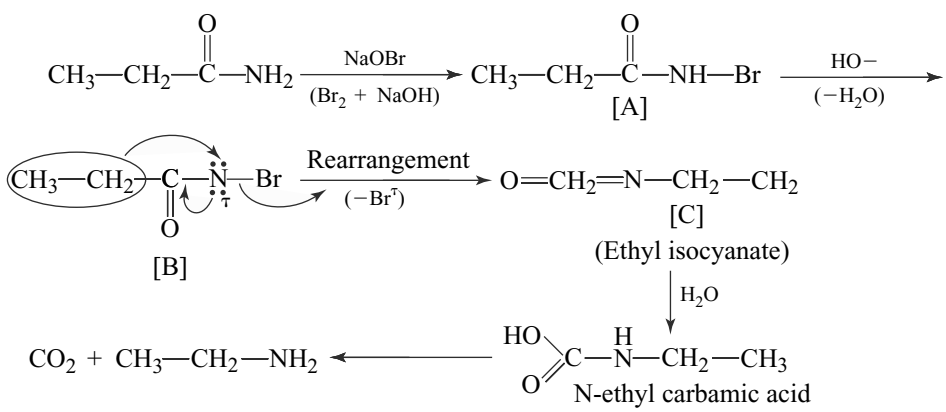


HOFFMANN REARRANGEMENT OR (HOFFMANN BROMAMIDE REACTION)

An unsubstituted amide when treated with sodium hypobromite (or $NaOH + Br_2$), a primary amine is formed which has one carbon less than the amide. It is *Hoffmann rearrangement*.



Mechanism



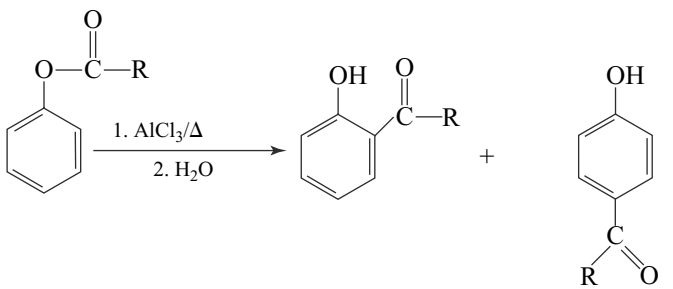
N-ethylcarbamic acid is not stable and decarboxylates immediately.

Important Points

1. In this reaction, N-bromoamide [A], the anion [B] and isocyanate [C] have been isolated.
2. Evidences available to ascertain mechanisms favour the concerted reaction, that is the removal of Br and migration of alkyl group take place in one step.
3. N-substituted amides do not give Hofmann rearrangement.

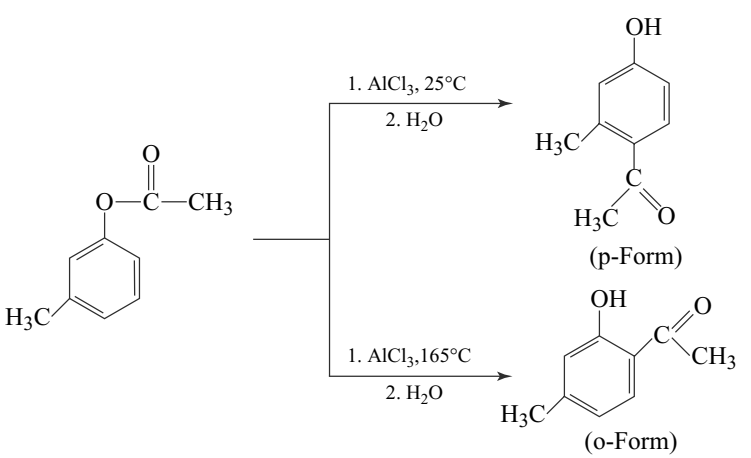
FRIES REARRANGEMENT

Esters of phenol give phenolic ketones on heating with $AlCl_3$ (anhydrous). Both *o*- and *p*- acylphenols may be formed. It is self-acylation and is known as *Fries rearrangement*.



R may be aliphatic or aromatic.

One of the factors that control product ratio is the temperature. At low temperature, *p*- isomer dominates whereas at high temperature, *o*- isomer is formed more.



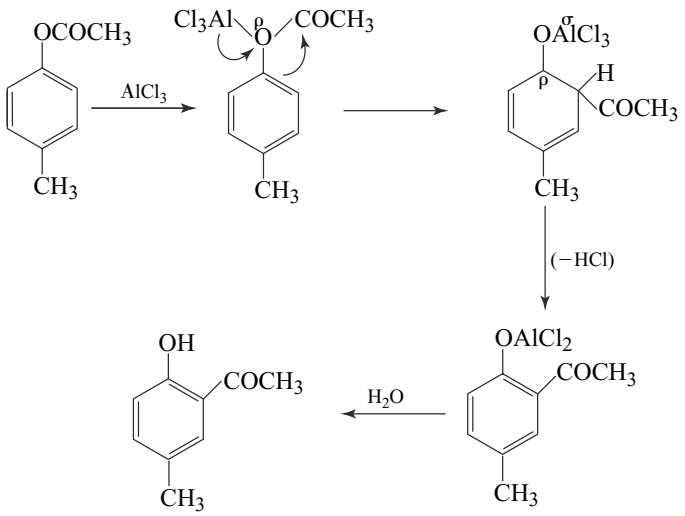
Mechanism

The study of reaction product suggest

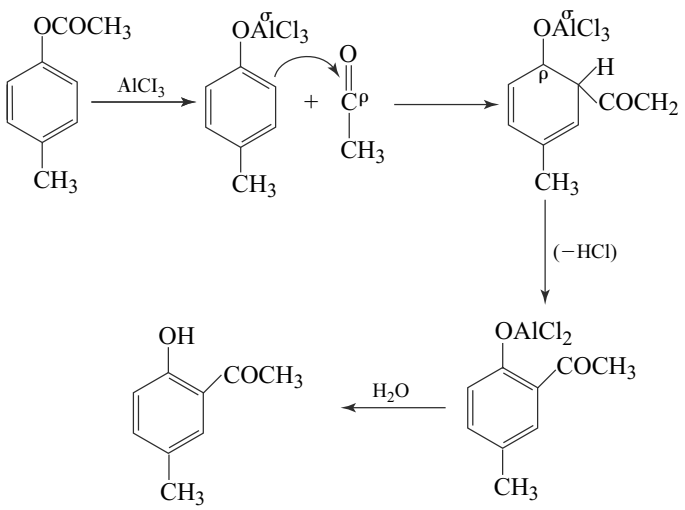
(i) a one-step mechanism and

(ii) a two-step mechanism.

One-step mechanism



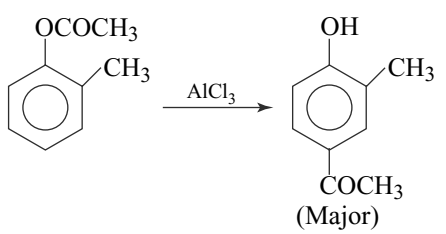
Two-step mechanism



An important application of this reaction is the synthesis of aromatic hydroxyketones (acylation of phenol gives poor yield).

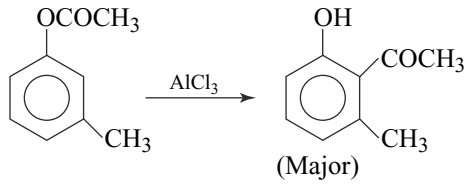
(a)

(i)



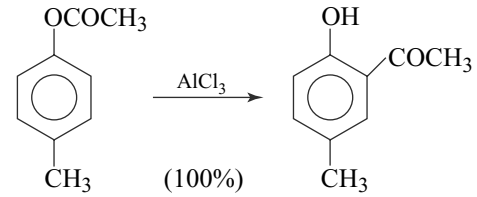
(Major)

(ii)



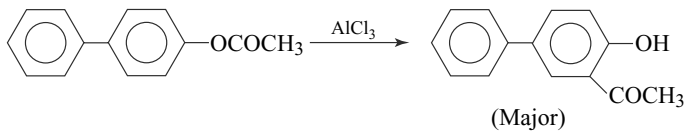
(Major)

(iii)

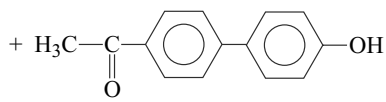


(100%)

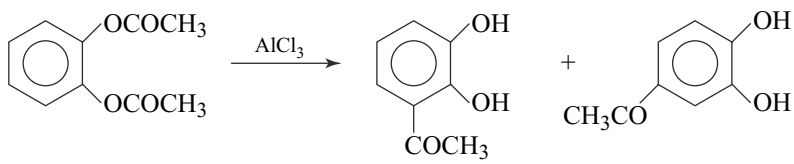
(b)



(Major)



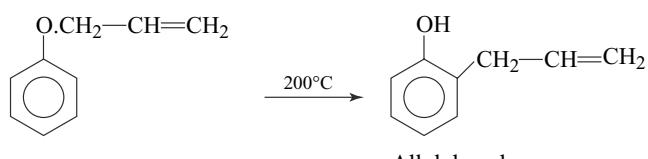
(c)



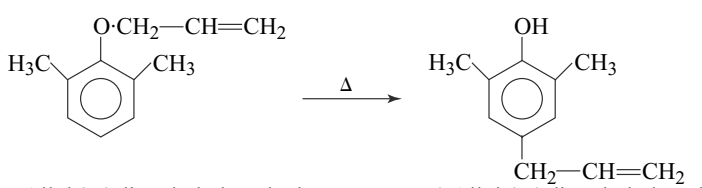
(Minor) (Major)

CLAISEN REARRANGEMENT

Allyl aryl ethers, when heated, give *o*-allylphenols. It is known as *Claisen rearrangement*. If both ortho positions are blocked, the allyl group migrates to the *p* position.



o-Allylphenol



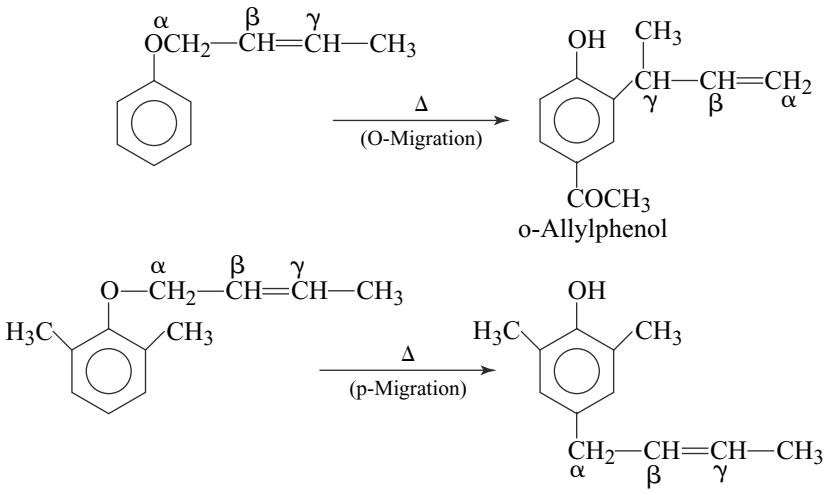
Allyl 2,6-dimethyl phenyl ether 4-Allyl-2,6-dimethyl phenol

Mechanism

This rearrangement proceeds through a cyclic transition state (that is a pericyclic reaction). Studies with allylic groups labelled with substituents (or ^{14}C) show that

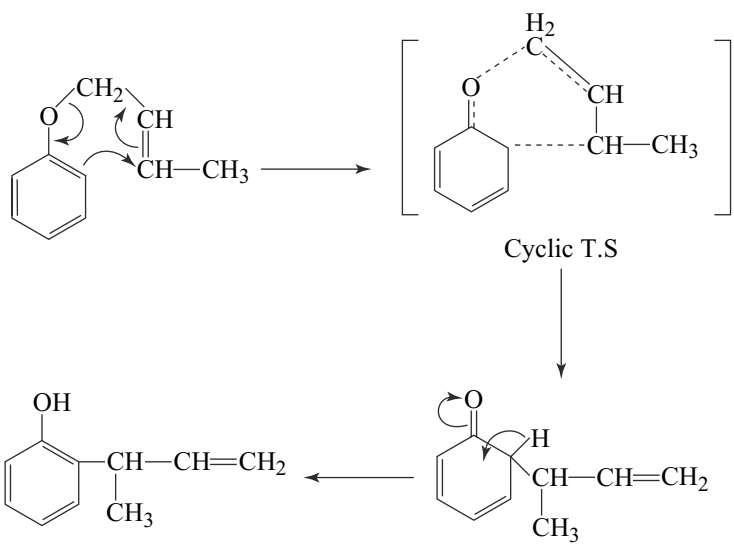
(i) in *o* migration, the γ carbon of the allyl group attaches to the ring carbon, but

(ii) in *p* migration, the α carbon of the allyl group attaches to the ring carbon.



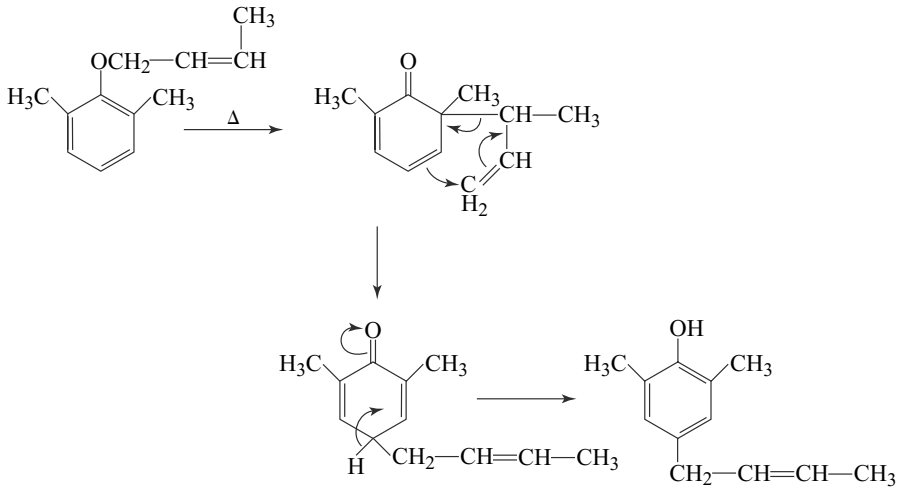
Mechanism of the rearrangement is outlined below:

***o* migration**



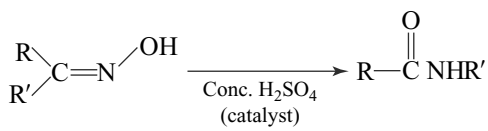
***p* migration**

This reaction takes place in two stages, first the *o* migration occurs then the *p* migration. As there is no H at the *o* position, no aromatization of the ring is possible. Therefore, another isomerization takes place leading to *p* migration of the allyl group.



BECKMANN REARRANGEMENT

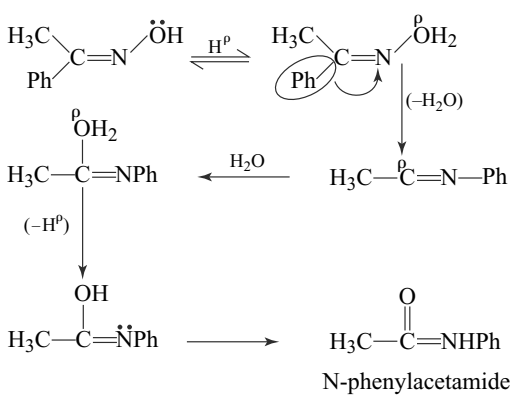
The acid-catalysed conversion of a ketoxime to an N-substituted amide is known as Beckmann rearrangement.



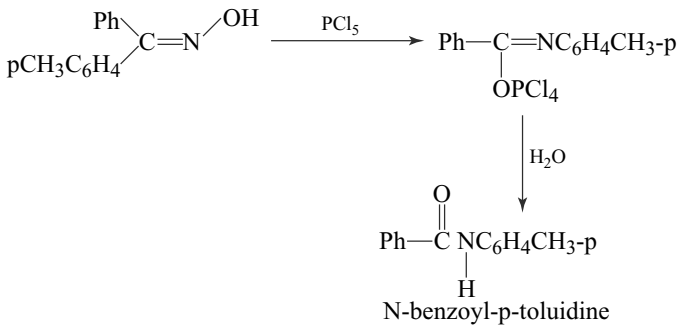
Many other acidic reagents, such as H_3PO_2, P_2O_5, $SOCl_2$ and PCl_5 may also catalyse this rearrangement.

Mechanism

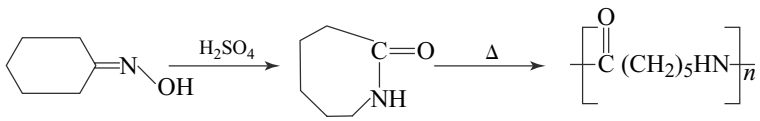
The reaction is highly stereospecific. The group anti (*trans*) to the –OH group of the oxime always migrates.



The reaction with PCl_5 may proceed as



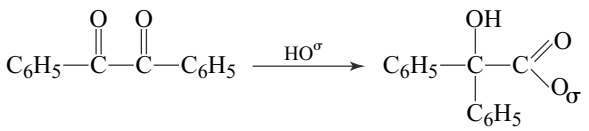
This rearrangement may also be used to enlarge a ring, example synthesis of <art> ∈-caprolactam, which is used for the production of Nylon-6.



∈-Caprolactam Nylon-6

BENZILIC ACID REARRANGEMENT (MIGRATION TO CARBONYL CARBON)

Benzil (an α-diketone) undergoes base catalysed rearrangement to give the anion of benzilic acid (an α-hydroxy acid). It is called benzilic acid rearrangement.

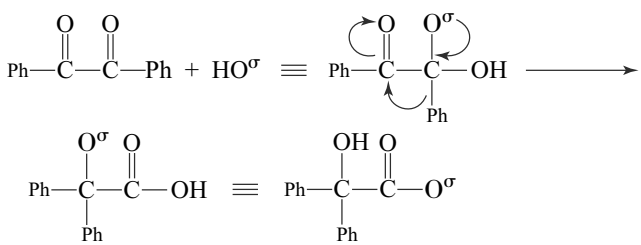


(Benzil) (Benzilate anion)

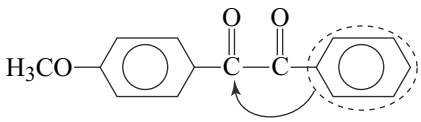
(C_6H_5– is phenyl group, Ph–)

Mechanism

It is a migration to carbonyl carbon.



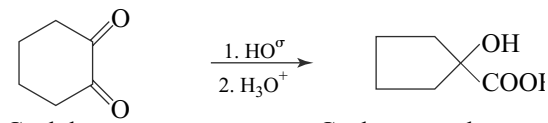
It is found that phenyl group with the lower electron-donating abillity usually migrates. For example, in [A] unsubstituted phenyl group migrates.



[A]

The reaction is similar to the intramolecular Cannizzaro reaction of phenyl glyoxal.

The reaction is general and can take place with aliphatic, alicyclic, aromatic and hetrocyclic 1,2-diketones. For example,



Cyclohexane-1,2-dione

Cyclopentanol-1-carboxylic acid

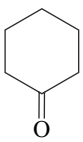
PROBLEMS

Objective-Type Questions

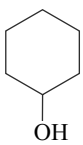
1. Which of the following can undergo aldol condensation fast?

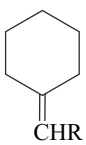
(a) CH_3CHO (b) CH_3CH_2CHO

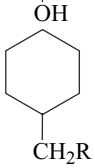
(c) $CH_3CH(OH)CHO$ (d) $CH_3-CH(C_2H_5)-CHO$

2. When  reacts with $Ph_3\overset{\oplus}{P}-\overset{\ominus}{C}HR$, the product is

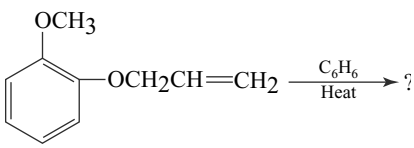
(a)

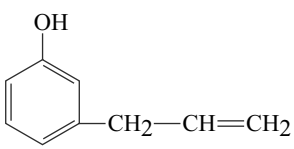
(b) 

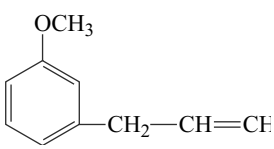
(c) 

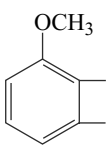
(d) 

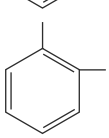
3. What is the product of the following reaction?



(a) 

(b) 

(c) 

(d) 

4. Which of the following would give the iodoform test?

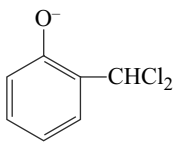
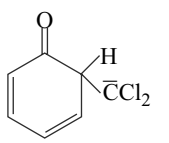
(a) $CH_2(OH)CH_2(OH)$

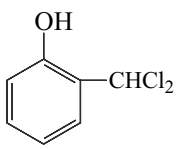
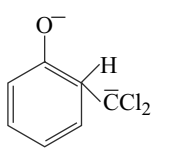
(b) $(CH_3)_3C(OH)$

(c) $CH_3CH_2CH_2CH_2OH$

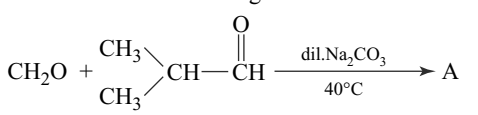
(d) $CH_3CH(OH)CH_2CH_3$

5. When phenol is treated with $CHCl_3$ and NaOH, followed by acidification, salicylaldehyde is obtained. Which of the following species are involved in the above-mentioned reactions as intermediates?

(a)  (b) 

(c)  (d) 

6. What is A in the following reaction?

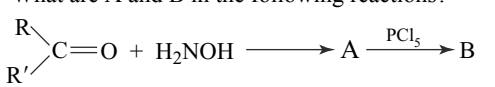


(a) (b)

(c) $CH_3-C(CH_2OH)(CHO)$

(d) $CH_3-CH(CH_2-CH_2-OH)-CHO$

7. What are A and B in the following reactions?



(a) RNHCOR'; $R-C(R')=NOH$

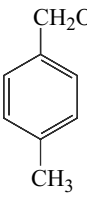
(b) $R-C(R')=NOH$; RNHCOR'

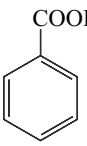
(c) $R-C(R')=NOH$; RNH_2

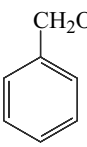
(d) $R-C(R')=NOH$; RCOOH

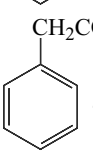
8. What are A and B in the following reaction?

$$p\text{–}MeC_6H_4CHO + HCHO \xrightarrow{KOH} A + B$$

(a)  & HCOOK

(b)  & CH_3OH

(c)  & HCOOK

(d)  & CH_3OH

9. Self condensation of 2 moles of ethyl acetate in presence of sodium ethoxide yields
(a) acetoacetic ester (b) methyl acetoacetate
(c) ethyl propionate (d) ethyl butyrate

10. The Cannizzaro reaction is not given by
(a) trimethylactaldehyde
(b) benzaldehyde
(c) acetaldehyde
(d) formaldehyde

11. Which of the following compounds will give a yellow precipitate with iodine and alkali?
(a) 2-Hydroxypropane (b) Acetophenone
(c) Methylacetate (d) Acetamide

12. The compound that does not give iodoform on treatment with alkali and iodine is
(a) acetone (b) ethanol
(c) diethyl ketone (d) isopropyl alcohol

13. Which of the following compounds does not undergo aldol condensation?
(a) $C_6H_5CH_2CHO$ (b) C_6H_5CHO
(c) CH_3COCH_3 (d) CH_3CH_2CHO

14. Phenol gives salicylaldehyde on heating with $CHCl_3$ and NaOH. It is known as
(a) Cannizzaro reaction
(b) Claisen reaction
(c) Reimer–Tiemann reaction
(d) Hell–Volhard–Zelinsky reaction

15. Given below is the Cannizzaro reaction.

$$2Ph\text{—}CHO \xrightarrow{OH} 2Ph\text{—}CH_2OH + PhCO_2$$

The slowest step in the reaction is
(a) the attack of OH at the carbonyl group
(b) the transfer of hydride to the carbonyl group
(c) the abstraction of proton from the carboxylic acid
(d) the deprotonation of Ph–CH(OH)

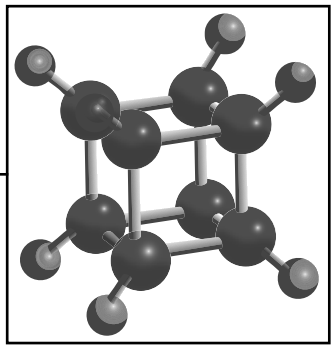
16. A new carbon–carbon bond formation is possible in
(a) Cannizzaro reaction
(b) Friedel–Crafts alkylation
(c) Clemmensen reduction
(d) Reimer–Tiemann reaction

17. Which of the following will undergo aldol condensation?
(a) Acetaldehyde (b) Propanaldehyde
(c) Benzaldehyde (d) Benzene

Answers

1. (a)	2. (c)	3. (c)	4. (b)	5. (a,b,c)
6. (a)	7. (b)	8. (a)	9. (a)	10. (c)
11. (a,b)	12. (c)	13. (b)	14. (c)	15. (b)
16. (b,d)	17. (a,b,d)			

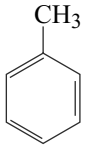
CHAPTER 7



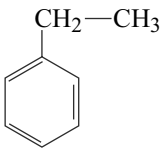
Benzene

Benzene is a hydrocarbon. It is unsaturated and has a ring-like structure. This structural unit is present in a very large number of organic compounds. Many compounds of this class have characteristic odour (smell). Therefore, benzenoid compounds are referred to as 'aromatic' (in Greek 'aroma' means fragrant smell).

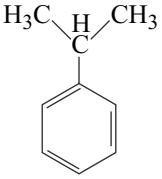
There are a very large number of organic compounds that have properties similar to benzene. They are either benzene derivatives or contain two or more benzene rings.



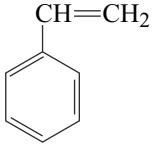
Toluene
(Methyl benzene)



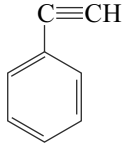
Ethyl benzene



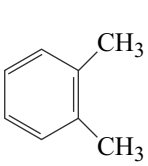
Cumene
(Isopropyl benzene)



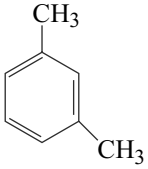
Styrene
(Vinyl benzene)



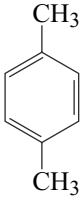
Phenylacetylene
(Ethynyl benzene)



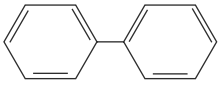
o-Xylene



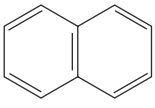
m-Xylene



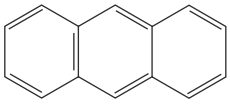
p-Xylene



Biphenyl
(phenyl benzene)



Naphthalene

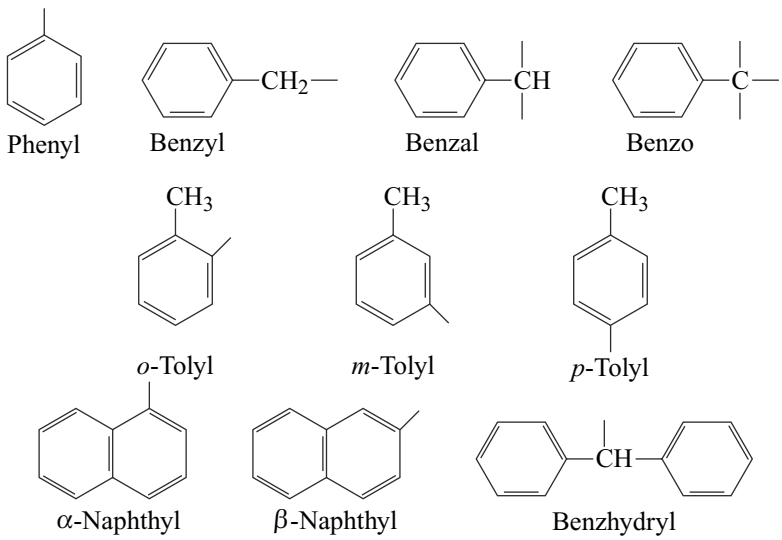


Anthracene

NAMING

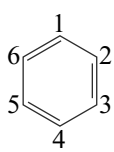
Hydrocarbons of this group are named as alkyl, alkenyl or arylbenzene. But trivial names are more common. The hydrocarbon group, C_6H_5–, is called a *phenyl group* and is abbreviated as the symbol Ph or as ϕ. Aryl groups, in general, are denoted as Ar.

Common aryl groups



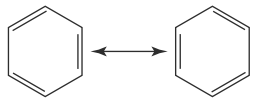
Structure of Benzene

1. It is a liquid hydrocarbon having the molecular formula C_6H_6.
2. It is unsaturated, as the corresponding saturated hydrocarbon is C_6H_{14} that
   (a) adds six halogen atoms,
   (b) adds six H atoms and
   (c) forms triozonide.
   So, three double bonds exist in this compound.
3. The double bonds present in it are different in nature. So
   (a) decolourization of bromine water or of alkaline $KMnO_4$ in cold is not shown,
   (b) halogens are substituted (in the absence of sunlight and in the presence of halogen carriers) and
   (c) HOCl or HX cannot be added to it.
   So, bonds are not exactly ethylenic.
4. Only one mono-substituted derivative (all H atoms in benzene equivalent) and three disubstitution products, (*o*-, *m*- and *p*-) can be formed.
   So, it represents the Kekule advanced ring structure (I).



[I]

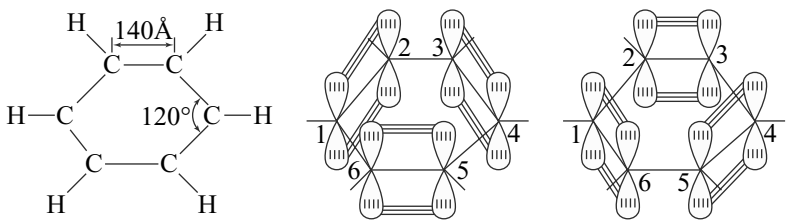
5. Kekule (1872) explained 1:2 and 1:6 difference by proposing oscillating structures (I and II).



[I] [II]

Valence Bond Structure

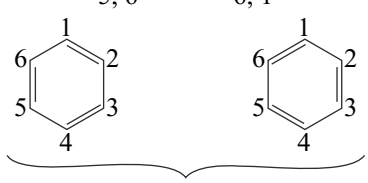
Benzene is a hexagonal planar molecule. Each of the six carbon atoms in benzene are sp^2 hybridized. The sp^2–sp^2-orbital overlap provides six C–C σ bonds. The remaining sp^2 orbital at each carbon overlaps with the s-orbital of an H atom to give six C–H σ bonds. Thus, six p-orbitals, one at each carbon, are oriented parallel to each other but at right angles to the plane having C and H atoms. Now, sidewise overlapping of adjacent pairs of p-orbitals gives π bonds.



(a) (b) (c)

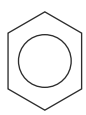
The π-bonds shown above are located between the carbon atoms,

(b)	(c)
1, 2	2, 3
3, 4	4, 5
5, 6	6, 1

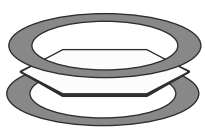


Resonance structures

The bond distance between adjacent carbons is 1.4Å, which is the intermediate between single (1.54Å) and double (1.33Å) C–C bond distance. It means that the C–C bonds in benzene are neither pure single bonds nor pure double bonds. It is actually a resonance hybrid of the above structures and is represented as



The molecular orbital model better represents the benzene structure. It gives the following net picture.



Thus, the hexagonal ring is sandwiched between delocalized π-electron clouds.

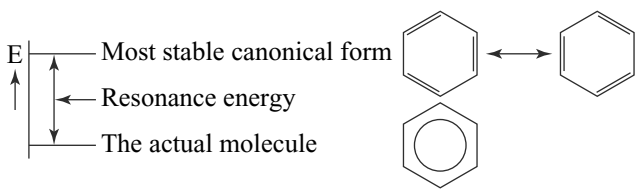
Problem *o*-Xylene is put to ozonolysis. Predict the products.

o-xylene $\xrightarrow{\text{ozonolysis}}$ A + B + C

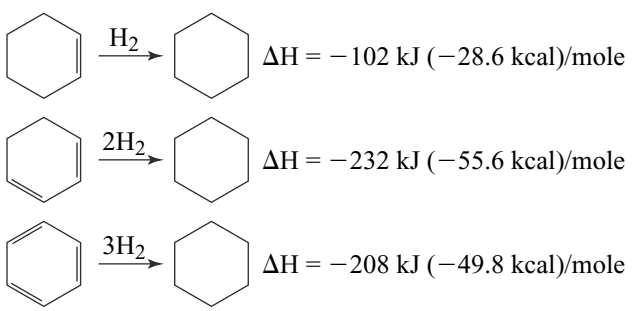
Problem Comment on the C_2–C_3 bond distance in $CH_2{=}CH{-}CH{=}CH_2$ and $CH_2{=}CH{-}CH_2{-}CH{=}CH_2$. In which of the compound, the bond is expected to be smaller.

Resonance Energy of Benzene

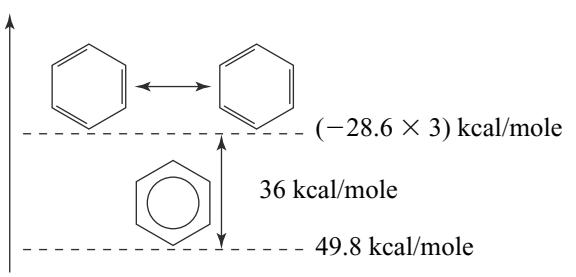
Resonance stabilizes a molecule, that is the resonance hybrid has lower energy as compared even to the most stable resonating structure. The resonance energy is defined as the difference in the energies between the resonance hybrid and the most stable resonating structure.



It is generally calculated from the heat of hydrogenation and the heat of combustion data. For C_6H_6, the resonance energy obtained by either of the methods is close to about 36 kcal/mole.



The heat of hydrogenation of cyclohexene is −28 kcal/mole. For cyclohexadiene, it is −55.6 kcal/mole, that is very near to -28.6×2. Thus, for C_6H_6 it should be $-28.6 \times 3 = 85.8$ kcal/mole but it is only −49.8 kcal/mole. The difference in the heat of hydrogenation is (85.8 − 49.8 = 36 kcal/mole) is the resonance energy of benzene. Thus, benzene is said to be stablized by the resonance to the extent of 36 kcal/mole. Resonance energy is also called the stabilization or delocalization energy.



Resonance energy of fused systems increase as the number of principal canonical forms (Kekule structures) increase.

Aromaticity

Open-chain compounds containing double and triple bonds possess high chemical reactivity, example rapid oxidation, addition reactions and polymerization. But ring compounds like benzene, naphthalene, anthracene, pyridine, pyrrole and thiophene are relatively least reactive towards the above types of reactions. Instead, they undergo substitution reactions. This behaviour of unsaturated ring compounds is associated with a property known as *aromatic character* and this special property of these compounds has been termed as *aromaticity*.

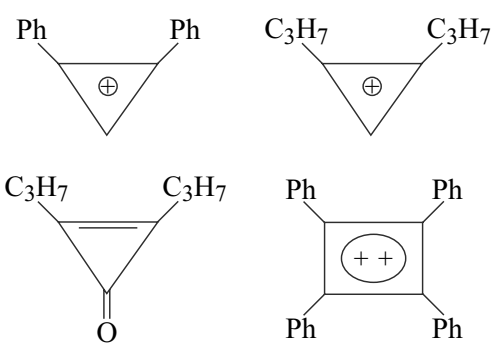
Criteria of aromaticity

A compound is classified as aromatic if the following conditions are fulfilled.

1. It should be a ring compound.
2. The molecular formula of the compound should indicate unsaturation, example presence of double bonds.
3. Atoms constituting the ring should lie in the same plane, that is the ring should be planar.
4. The single and double bonds constituting the ring should occur alternately.
5. The π-electron in the ring should be delocalized, that is the molecule is resonance stabilized.
6. The number of π electrons delocalized over the ring should be given by $(4n + 2)$ where $n = 0, 1, 2, 3$, etc. This is known as *Huckel's* rule. Ring with 2, 6, 10 and 14 electrons may, therefore, be aromatic.
7. As the delocalized electrons constitute a closed ring of electrons, an aromatic compound should be able to sustain an induced ring current. Such currents can be detected by NMR spectroscopy.
8. Aromatic compounds preferentially undergo substitution reaction rather than addition reaction.
9. Aromatic compounds give special absorption bands in the IR spectra.

A vast majority of aromatic compounds have six π electrons in a ring (aromatic sextet). Benzene is the prime example, but there are many others that are mentioned below.

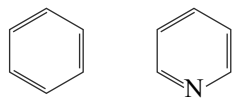
1. **Aromatic duet [$n = 0$ in $(4n + 2)$]**
   The following two π-electron systems are aromatic. They are formed by the loss of proton, which are ionic and obey Huckel's rule.



2. Aromatic sextet [$n = 1$ in $(4n + 2)$]

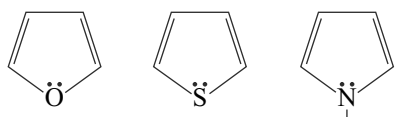
Aromatic compounds containing six π electrons are most common. The examples include the following.

(a) Benzenoid compounds



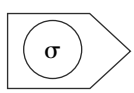
Benzene Pyridine

(b) Non-benzenoid heterocyclic aromatic systems: Here, lone pair at the heteroatom with π electrons forms aromatic sextet.

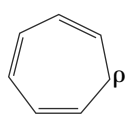


Furan Thiophene Pyrrole

(c) Cyclic systems, which are ionic and obey Huckel's rule.



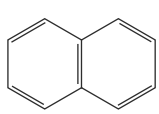
Cyclopentadienyl anion

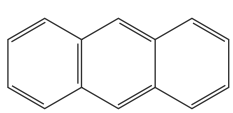


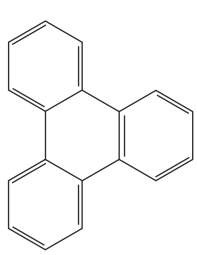
Cycloheptatrienyl cation (tropylium ion)

(d) Tropone is also a six π-electron aromatic system.

3. Fused ring systems

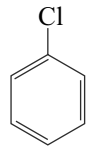
Naphthalene  10 electron ($n = 2$)

Anthracene  14 electron ($n = 3$)

Triphenylene  18 electron ($n = 4$)

Isomerism

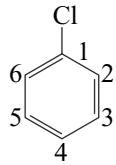
All H atoms in benzene are chemically equivalent. It, therefore, forms only one monosubstitution product.



Chlorobenzene

However, the position (that is C centres) in monosubstituted benzene, do not remain equivalent. Therefore, position isomers arise.

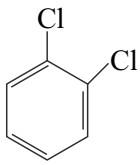
For locating substituents, the C atoms in the benzene ring are numbered.



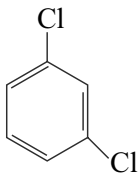
Thus, for a disubstituted (or polysubstituted) benzene, the substituents are located in such a way that they fall at the lowest number.

Isomers of disubstituted benzene

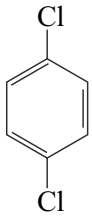
Three isomers are possible for a disubstituted benzene. They are named as 1,2 or 1,3 or 1,4 isomers, which are shown below.



1,2-Dichlorobenzene or ortho-dichlorobenzene
(written as *o*-dichlorobenzene)
(It is equivalent to 1,6-dichlorobenzene.)



1,3-Dichlorobenzene of meta-dichlorobenzene
(written as *m*-dichlorobenzene)
(It is equivalent to 1,5-dichlorobenzene.)

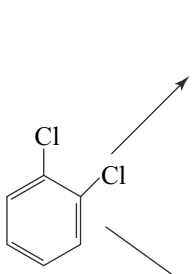
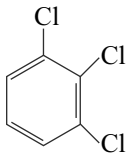
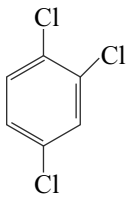
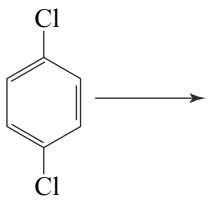
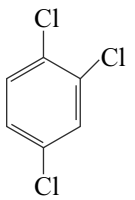
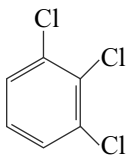
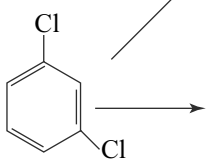
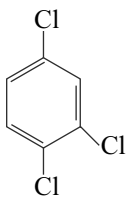
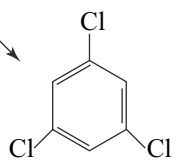


1,4-Dichlorobenzene or para-dichlorobenzene
(written as *p*-dichlorobenzene)

Isomers of trisubstituted benzene

Four isomers of trisubstituted benzene exist for the same substituents. Each of the disubstituted isomers (three) gives rise to a different number of further isomers on trisubstitution. They are shown for a trichlorobenzene ($C_6H_3C_{l3}$) in the table given below.

Table 7.1

Disubstituted	Trisubstituted	Total isomers
	 1,2,3-Trichlorobenzene	1,2,3-Trichlorobenzene
	 1,2,4-Trichlorobenzene	1,2,4-Trichlorobenzene
	 1,2,4-Trichlorobenzene	
	 1,2,3-Trichlorobenzene	
	 1,3,4-Trichlorobenzene	1,3,4-Trichlorobenzene
	 1,3,5-Trichlorobenzene	1,3,5-Trichlorobenzene

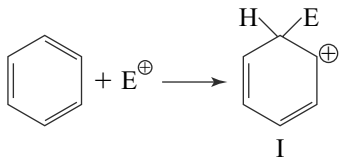
***Notes*:**

1. The four isomers are 1,2,3; 1,2,4; 1,3,4 and 1,3,5 trichlorobenzene.
2. The ortho-isomer produces two trisubstituted isomers, the meta three and the para one.

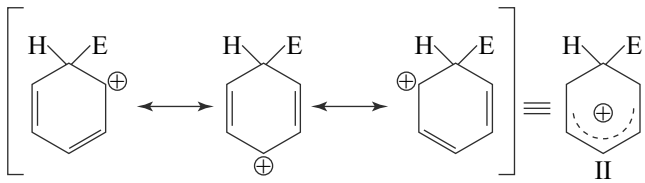
Electrophilic aromatic substitution

Electrophilic aromatic substitution is a two-step reaction.

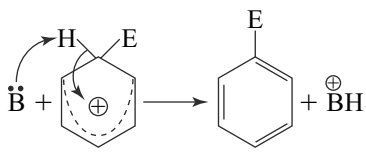
1. First step is the addition of electrophile to the benzene ring. To form a bond between benzene and the electrophile, the susbstrate provides an electron pair.



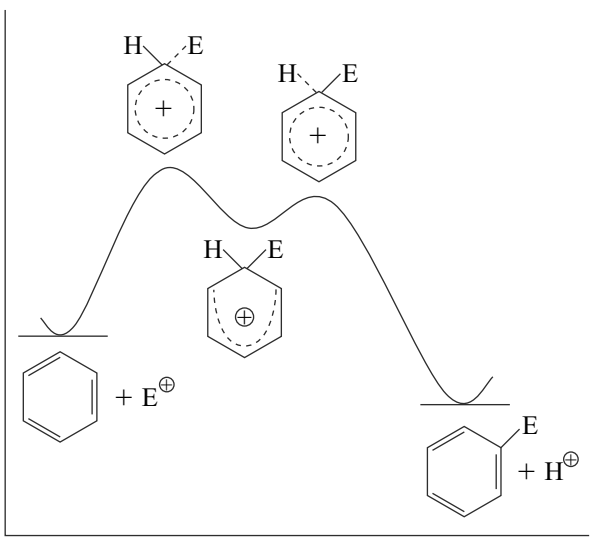
The intermediate (I) has no aromatic structure. It is a cation (arenium ion) with four π electrons that are delocalized over five C atoms, the sixth carbon being a saturated one (sp^3). The cation (I) is known as the *Wheland intermediate*.



2. In the second step, loss of a proton from (II) to a base (B): results in the regeneration of aromatic ring and the substitution product.

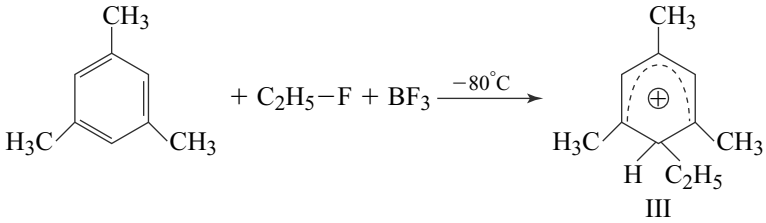


The gain in stabilization due to regeneration of aromatic ring facilitates easy breaking of the C–H bond. The energy diagram for the above process may be represented as given below.



The proof for the mechanism (mentioned in the previous page) comes from (a) the isolation of *Wheland* intermediate of the type (I) (the σ-complex) and (b) the isotope effect.

Intermediate of the type (I) given above has been isolated in many cases. One such example is the type (III) (an orange crystalline solid).

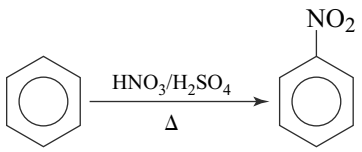


III

If a bond breaks in the rate-determining step, it will show isotope effect. But isotope effect is absent in most of the substitution reactions of benzene. Thus, the first step and not the proton elimination is the rate-determining step. This proves the two-step reaction.

NITRATION

Nitration is the introduction of the nitro group ($-NO_2$) in the benzene ring.



Reagents

1. Conc. HNO_3 + conc. H_2SO_4 (the nitrating mixture)
2. Fuming HNO_3
3. Nitration in anhydrous condition is carried out with N_2O_5 in CCl_4 in the presence of P_2O_5 (it removes H_2O).

$$N_2O_5 \equiv NO_2^{\rho} + NO_3^{\sigma}$$

4. Nitronium salts

$$NO_2^{\rho}.\,ClO_4^{\sigma},\quad NO_2^{\rho}.\,BF_4^{\sigma},\quad NO_2^{\rho}.\,SbF_6^{\sigma}$$

Mechanism

The active electrophile in nitration is nitronium ion ($NO_2^{\oplus}$). The most common nitrating agent is the mixture of conc. HNO_3 and conc. H_2SO_4. It produces nitronium ion as shown in the reaction given below.

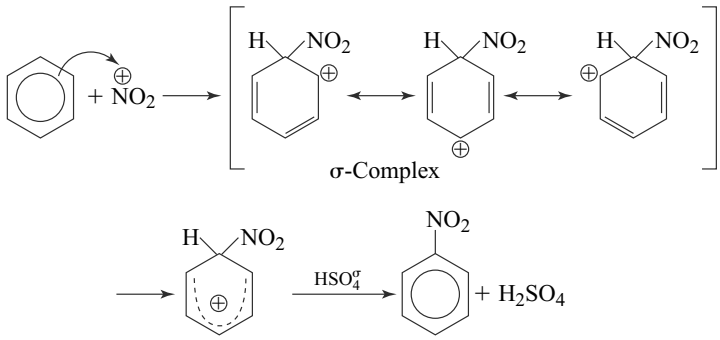
$$HO{-}NO_2 + H_2SO_4 \equiv H{-}\overset{H}{\underset{\rho}{O}}{-}NO_2 + HSO_4^{\sigma}$$

$$H{-}\overset{H}{\underset{\rho}{O}}{-}NO_2 + \equiv H_2O + NO_2^{\rho}$$

$$H_2SO_4 + H_2O \equiv H_3O^{\rho} + HSO_4^{\sigma}$$

$$HNO_3 + 2H_2SO_4 \equiv NO_2^{\rho} + H_3O^{\rho} + 2HSO_4^{\sigma}$$

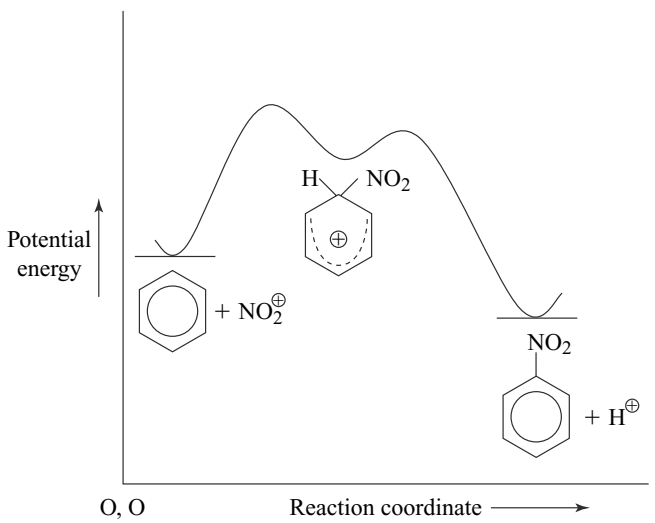
Such equilibrium in the mixture is confirmed by fourfold depression in the molecular freezing point [Van't Hoff factor, $i = 4$ (four ions are there)]. Raman spectrum also confirms the presence of nitronium ion ($NO_2^{\oplus}$). The reaction proceeds as



The intermediate carbonium ion (σ-complex) is resonance stabilized but lacks aromaticity. Aromaticity is regained at the loss of a proton (by a base, here, HSO_4^-), which results in the substitution product.

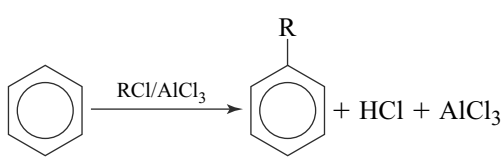
$$\text{Rate} = K\,[C_6H_6]\,[NO_2^+]$$

Addition of $NO_2^{\oplus}$ is a rate-determining step (no isotope effect is observed). The potential energy diagram of nitration may be represented as given below.



ALKYLATION

When an alkyl group (R–) is introduced into the benzene ring, the reaction is known as alkylation.



The active electrophile in the reaction is the polarized alkyl group or free carbocation.

Reagents

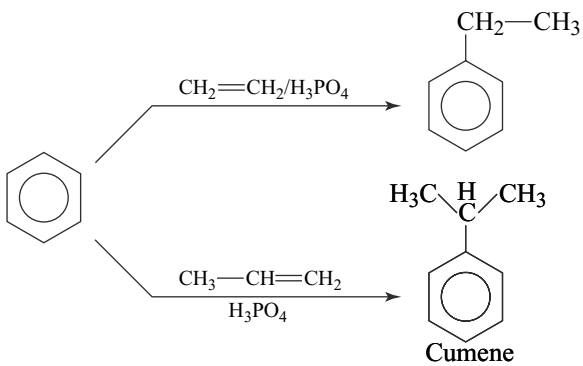
1. Alkyl halide with a Lewis acid ($AlCl_3$, $FeCl_3$, BF_3, $ZnCl_2$, etc.). This reaction is known as *Friedel–Crafts alkylation*.
2. Alkenes and alcohols in the presence of acidic catalyst (H_3PO_4, H_2SO_4, HF, etc.).

Under acidic conditions alkenes and alcohols produce carbocation by protonation, which is the active substituting agent.

$$CH_3—CH{=}CH_2 + H^+ \longrightarrow CH_3\overset{\oplus}{C}HCH_3$$

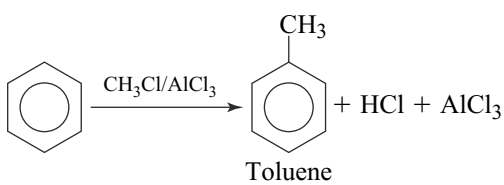
$$CH_3—CH_2—\ddot{O}H + H^+ \equiv CH_3\overset{\oplus}{C}H_2 + H_2O$$

Ethylbenzene is made commercially from benzene and ethylene using H_3PO_4 as the catalyst. Similarly, isopropyl benzene (cumene) is made from benzene and propene.



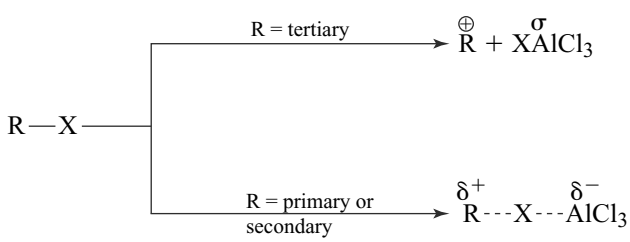
Friedel–Crafts Alkylation

Alkylation of benzene using alkyl halide and a Lewis acid is called *Friedel–Crafts alkylation*.

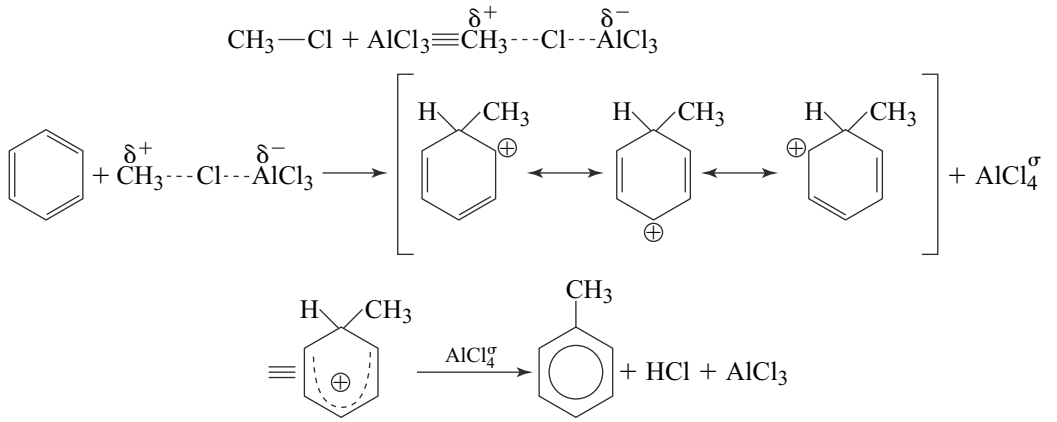


Mechanism

In alkylation, the active electrophile is carbocation or polarized complex. The function of the catalyst is to increase the polarity of the C–Cl bond in the alkyl halide by complexing with it.

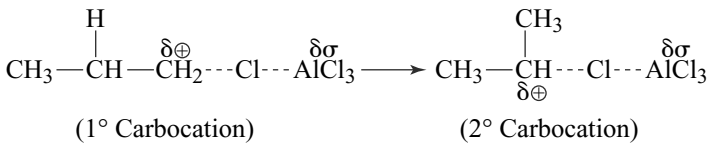


The reaction proceeds as



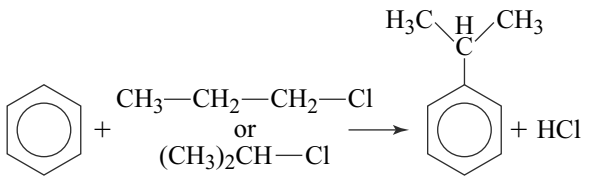
Important points

1. Friedel–Crafts alkylation may proceed with the rearrangement in the alkylating group (due to the conversion of a less stable to a more stable carbocation).

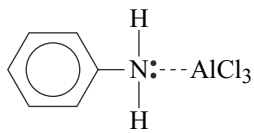


(1° Carbocation) (2° Carbocation)

Thus, alkylation with *n*-propyl chloride (or isopropyl chloride) gives isopropyl benzene, not *n*-propylbenzene.

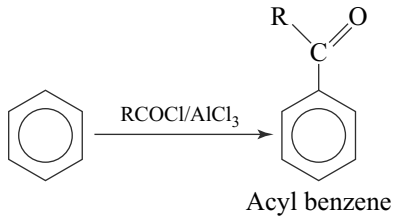


2. A serious drawback to Friedel–Crafts alkylation is the tendency to polyalkylation as the R group activates the benzene ring. But excess of arene favours monosubstitution.
3. Electron-attracting groups inhibit Friedel–Crafts alkylation (due to the deactivation of the ring). For example, nitrobenzene is often used as solvent in alkylation.
4. Electron-donating groups, such as $-NH_2$, –OR and –OH also do not facilitate the reaction. It is because these basic groups coordinate with the catalyst.



Acylation of Benzene

(Friedel–Crafts acylation)
When an acyl group (R'CO) is introduced into the benzene ring using an acyl halide (RCOCl) and $AlCl_3$ (Lewis acid), it is known as Friedel–Crafts acylation.



Acyl benzene

Reagents

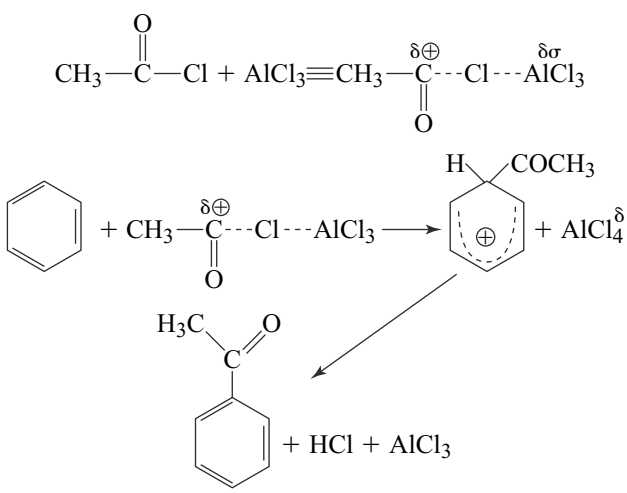
1. Acycl halide (RCOCl) or acid anhydride, $(RCO)_2O$, in the presence of a Lewis acid catalyst ($AlCl_3$).
2. Acylium salts, such as

$$CH_3CO^{\oplus}.\ SbCl_6^{\sigma},\ CH_3CO^{\oplus}.BF_4^{\sigma}$$

(These have been discovered by Olah.)

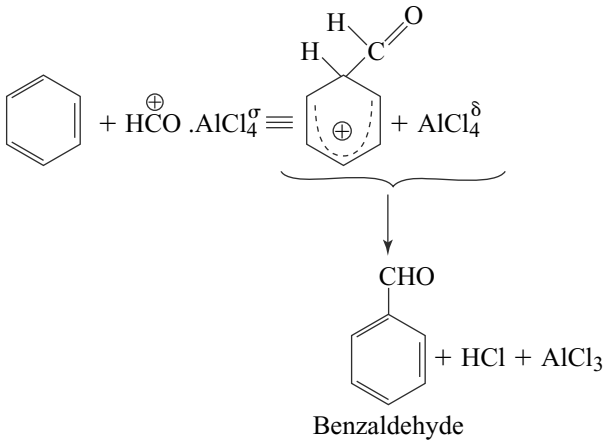
Mechanism

The function of the Lewis acid catalyst is to generate the active electrophile, which, potentially, is an acyl cation.



Formylation (that is introduction of –CHO group) into the benzene ring may be carried out by the use of CO, HCl and $AlCl_3$. This reaction is known as *Gattermann–Koch reaction*.

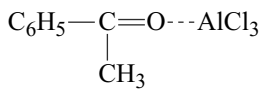
$$CO + HCl + AlCl_3 \equiv \overset{\oplus}{H}CO\ .AlCl_4^{\sigma}$$



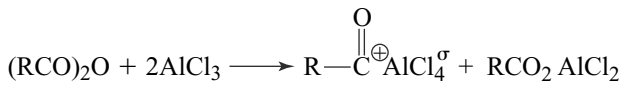
Benzaldehyde

Important points

1. Unlike alkylation, this reaction is carried out in a solvent, example CS_2 or nitrobenzene.
2. Acylation require more catalyst than alkylation because the Lewis acid catalyst complexes with the product ketone.

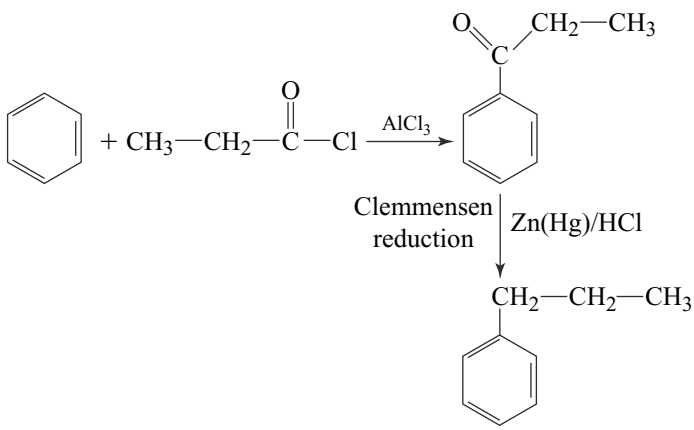


3. With acid anhydride as acylating agent, more catalyst is still required.



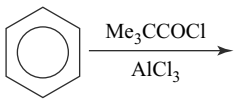
4. Acylation gives monosubstitution product (R—C— group deactivates the aromatic ring).

   For this reason, alkylbenzenes are sometimes prepared by acylation, followed by reduction of >C=O group to $>CH_2$. For example, *n*-propyl benzene is best prepared as



(Alkylation of benzene with *n*-propyl chloride and $AlCl_3$ gives isopropyl benzene and not *n*-propyl benzene.)

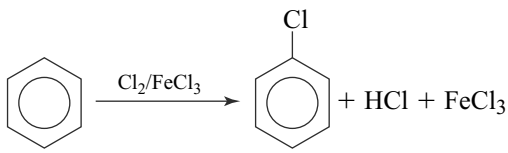
Problem: Write the product and the mechanism of the following reactions.



A [Hint: tert carbocation is very stable, decarboxylation follows (CO is lost)].

HALOGENATION

The reaction to introduce a halogen into the benzene ring is known as halogenation.



Chlorobenzene

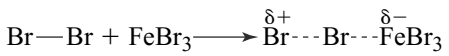
The reactivity order of the halogens towards benzene is $F_2 > Cl_2 > Br_2 > I_2$. Therefore, reaction conditions differ widely.

1. Fluorine is too reactive (many organic compounds inflame in F_2) and indirect methods are used.
2. Chlorination and bromination are usual reactions and they take place in the presence of a Lewis acid ($AlCl_3$, $FeCl_3$, $ZnCl_2$, etc.).
3. Iodine is unreactive but with an oxidising agent (HNO_3) good yields of iodobenzene is obtained.

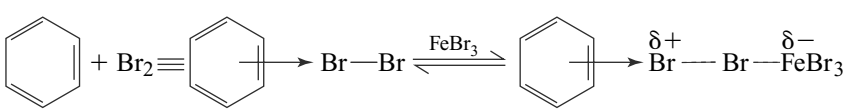
Chlorination and Bromination

Many reagents can be used for these reactions. They are

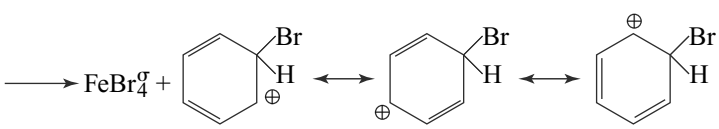
1. Cl_2 and Br_2 with a Lewis acid, $AlCl_3$, $FeCl_3$, $ZnCl_2$, etc. The function of Lewis acid catalyst is to polarize the halogen–halogen bond.

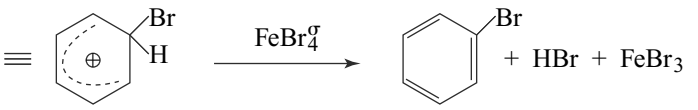


The positive end of the halogen attacks benzene and the negative end complexes with the catalyst. The reaction may be represented as under.

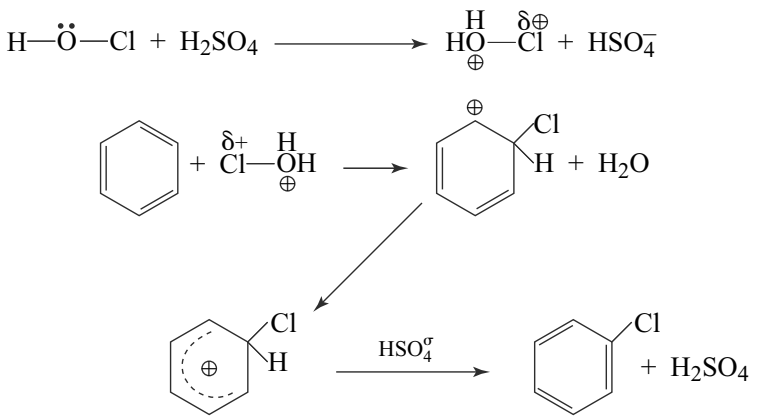


π-Complex

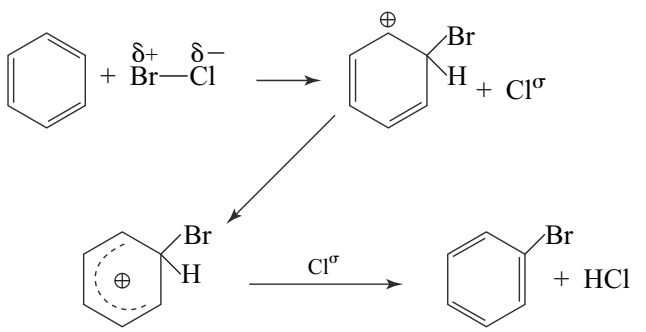




2. HOCl and HOBr in the presence of a strong proton acid (H_2SO_4). The proton acid helps in generating the electrophile.

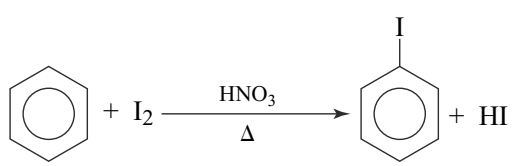


3. Interhalogen compound – In the interhalogen $\overset{\delta+}{Br} - \overset{\delta-}{Cl}$, the less electronegative halogen is electrophilic. Therefore, Br–Cl brominates benzene.

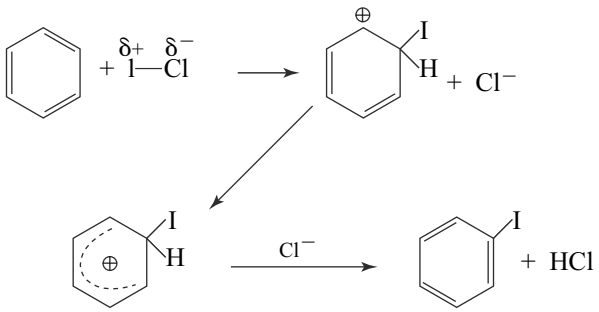


Iodination of Benzene

1. Iodine in the presence of an oxidising agent, HNO_3, converts to an electrophilic reagent (perhaps I^+). It shows kinetic isotope effect, that is the second step is rate controlling.

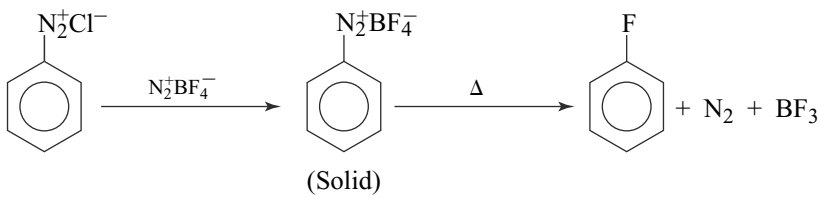


2. The interhalogen I–Cl introduces iodine in benzene. It is because of the iodine that is the electrophilic centre, $\overset{\delta+}{I}-\overset{\delta-}{Cl}$.



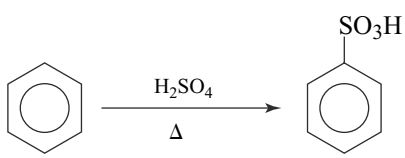
Fluorobenzene

It is obtained by indirect reactions, the Schiemann reaction. Benzene diazonium chloride is treated with $NaBF_4$. It gives a precipitate of benzene diazonium fluoroborate. The carefully dried salt on controlled heating decomposes to fluorobenzene, N_2 and BF_3.



Sulphonation

When the sulphonic acid group ($-SO_3H$) is introduced into the benzene ring, the reaction is known as sulphonation. The product is benzene sulphonic acid.

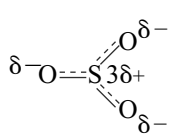


Reagent

The common reagent is oleum (98% H_2SO_4). The active electrophile in oleum is believed to be SO_3.

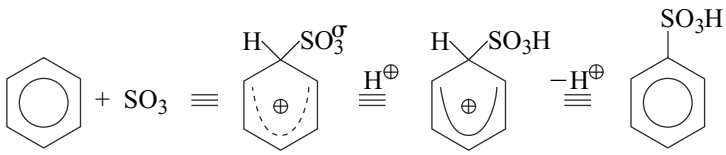
$$2H_2SO_4 \equiv SO_3 + \overset{\oplus}{H_3O} + HSO_4^{\ominus}$$

In SO_3, S–O bonds are highly polar that makes S an electrophilic centre.



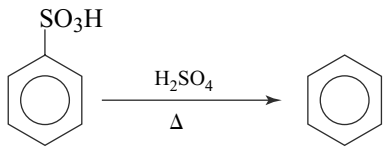
Mechanism

The reaction proceeds as given below.

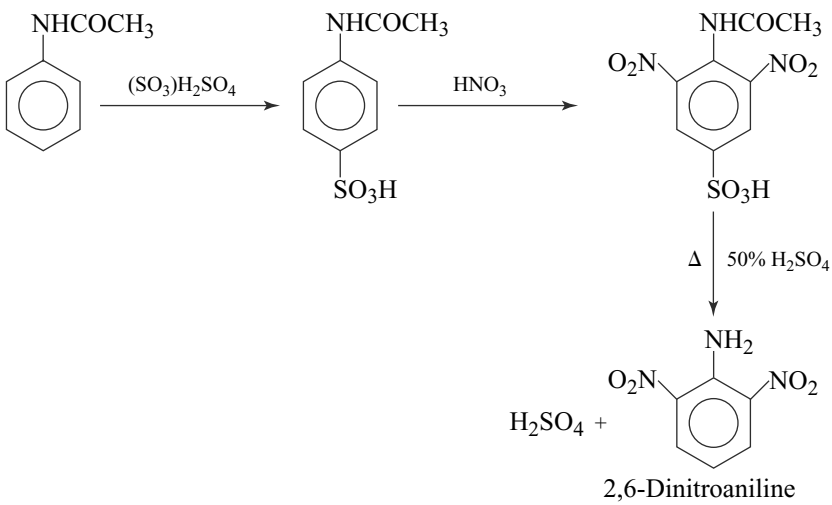


This reaction is (i) reversible and (ii) shows positive isotope effect (deutero benzene is sulphonated slowly than benzene), that is the second step is rate controlling.

Because of the reversible nature, desulphonation takes place when benzene sulphonic acid is heated with ~50% H_2SO_4.



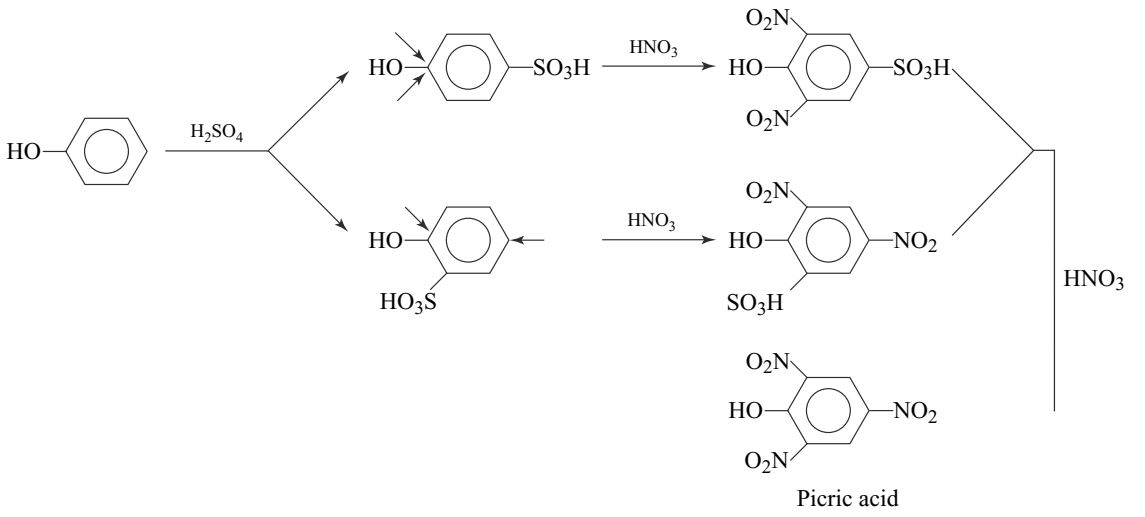
It has practical applications. The $–SO_3H$ group is powerful *m*-directing. Therefore, it is introduced for (i) blocking a site and (ii) orientation purpose. After introduction of the other group, the sulphonic acid group is removed by hydrolysis. For example,



In the above reaction,

1. $–NHCOCH_3$ is *o*-, *p*-directing,
2. $–SO_3H$ is *m*-directing,
3. the *p*-position is blocked by sulphonation,
4. nitration, therefore, gives 2- and 6-dinitro compound and
5. in the last step, desulphonation and hydrolysis of $–NHCOCH_3$ take place to give the final product.

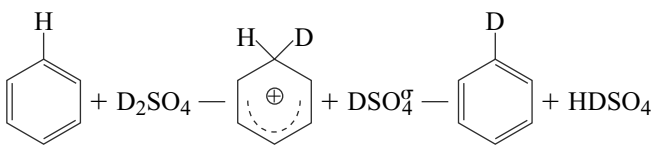
Another application of sulphonation and desulphonation is in the synthesis of picric acid (2,4,6-trinitrophenol). Direct nitration of phenol is a very fast reaction (may be explosive).



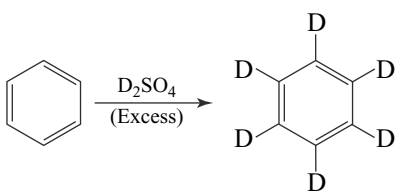
Picric acid

DEUTERATION

The ring hydrogen of benzene (or aromatic compound) may be exchanged with D using deuteriosulphuric acid (D_2SO_4).

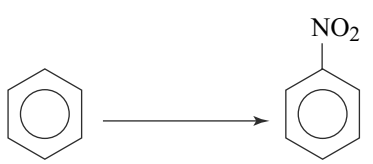


If large excess of D_2SO_4 is used all H atom of benzene can be exchanged for D.

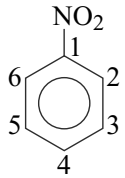


Orientation and Reactivity

Benzene is a symmetric molecule and all H atoms in it are chemically equivalent. It, therefore, forms only one monosubstitution product.



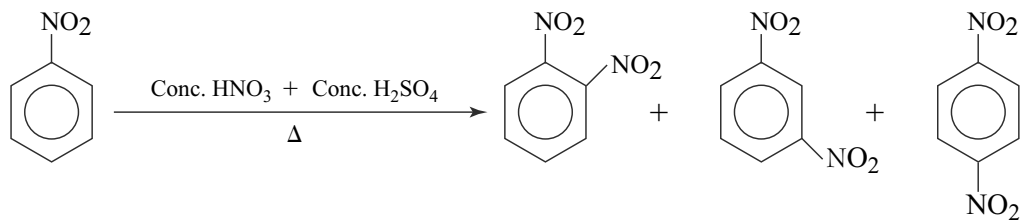
However, the positions (that is C centres) in monosubstituted benzene do not remain equivalent. Three positions are located in the ring. They are as follows:



1,2 (≡ 1,6) ortho (*o*-)
1,3 (≡ 1,5) meta (*m*-)
1,4 para (*p*-)

Therefore, the electrophilic substitution on a monosubstituted benzene may produce ortho-, meta- or para-disubstituted derivative. But the position, the incoming electrophile will occupy on a monosubstituted benzene ring, is directed by the group already present in the ring. It is known as orientation (or directive influence) of a group. The reactivity of the monosubstituted benzene ring also depends on the group already present.

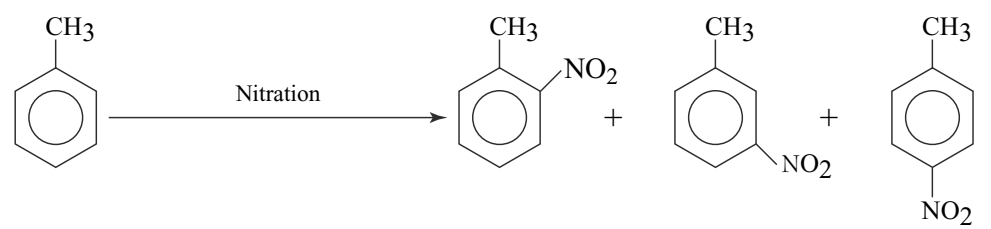
Let us consider some electrophilic substitution on monosubstituted benzene ring.

(a) 

o- 6% *m*- 93% *p*- 1%

In reaction (I), the incoming electrophile ($NO_2^{\oplus}$) mainly occupies *m*-position and in reaction (II), the rate of the reaction is found slower than the nitration of benzene.

Thus, $-NO_2$ group is metadirecting and deactivates benzene ring (all *m*-directing groups are deactivating as well).

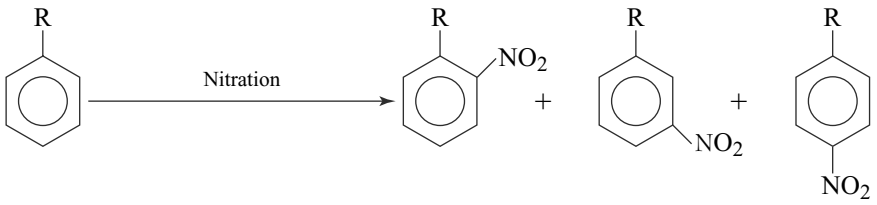
(b) 

o- 56.5% *m*- 3.5% *p*- 40%

In reaction (I), the incoming electrophile ($NO_2^{\oplus}$) mainly occupies ortho- and para-positions and in (II), the reaction is found faster than nitration of benzene. Thus, CH_3- group is ortho- and para-directing and activates benzene ring.

Now, it is observed that orientation and reactivity both are controlled by the group already present on the ring. Groups direct predominantly but not exclusively.

Table 7.2 Orientation and rate data for nitration



ortho meta para

R	Orientation			Relative rate	Conclusion
	o (%)	*m* (%)	*p* (%)		
$-CH_3$	56.5	3.5	40	24	*o*- and *p*-directing and activating
$-C(CH_3)_3$	12.0	8.5	79.5	15.7	
$-CH_2-Cl$	32.0	15.5	52.5	0.302	
$-Cl$	29.6	0.9	68.9	0.033	*o*- and *p*-directing and deactivating
$-NO_2$	6.0	94.0	1.0	$\sim 10^{-7}$	
$-CO_2C_2H_5$	28.3	68.4	3.3	0.0003	
$-CF_3$	–	100	–	Low	*m*-directing and deactivating
$-\overset{\oplus}{N}(CH_3)_3$	–	89	11	Low	

Notes:
1. The rate is relative to benzene.
2. Steric factor has some effect on orientation especially at *o*-position. It is seen in first, second and last examples in the table above.

Inspection of the data in the table above shows that each group falls into one of three categories.

1. **Ortho-, para-orientation with activation of benzene ring**
   The groups that activate all ring positions, relative to benzene but are more activating for the ortho- and para-positions than the meta-position give ortho- and para-orientation with activation.

   $$-OH, -O^{\sigma}, -OR, -OC_6H_5, -NH_2, -NR_2, -NHCOCH_3, -CH_3, -C_6H_5$$

2. **Ortho-, para-orientation with deactivation of benzene ring**
   The groups that deactivate all the ring positions but deactivate ortho- and para-positions less than the meta-position. Thus, ortho- and para-orientation is favoured. These groups are classified as ortho–para-directing with deactivation. They include

   $$-CH_2Cl, -F, -Cl, -Br, -I, -CH{=}CH_2, -CH{=}CHNO_2$$

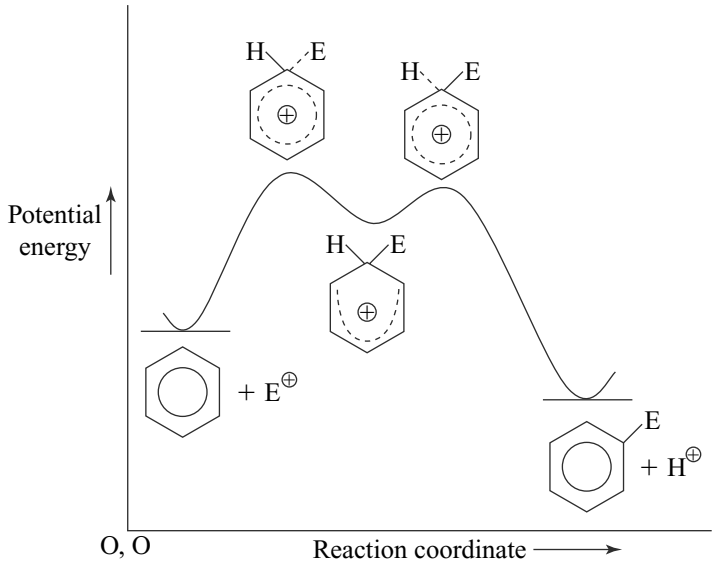
3. **Meta-orientation with deactivation of the ring**
   The groups that deactivate all ring positions but ortho- and para-position more than the meta-position. Thus, meta-isomer is formed. All meta-directing groups are deactivating. They include

   $$-NO_2, -N^{\rho}H_3, -N\,R^{\rho}{}_3, -CF_3, -CCl_3, -SO_3H, -CO_2H, -CO_2R, -CONH_2, -CHO, -COR, -C{\equiv}N$$

Explanation for orientation and reactivity

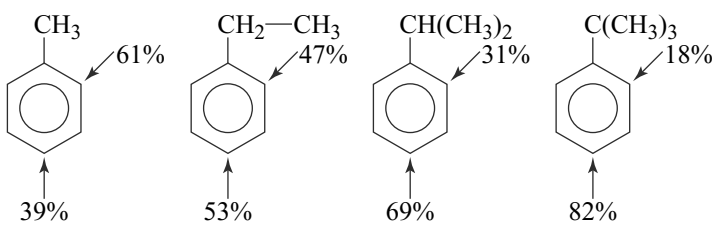
The ratio of products in most electrophilic substitutions of benzene derivatives is determined by the rates at which they are formed and not by their relative stabilities, that is the product is kinetically and not thermodynamically controlled.

In most of the aromatic electrophilic substitutions, formation of σ-complex (or Wheland intermediate) is a rate-controlling step as it compares in energy to the transition state.



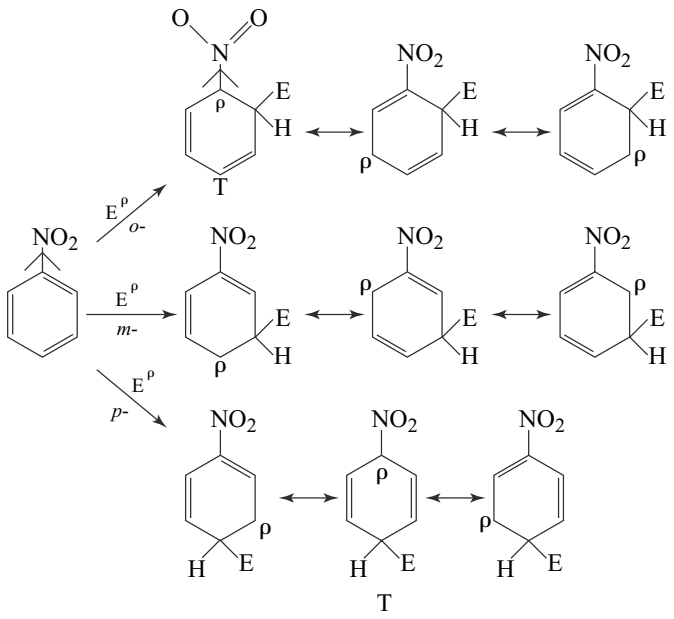
Thus, any effect due to the substitutent that stabilizes the σ-complex will increase the rate of substitution. The effect that controls orientation and reactivity are (i) inductive effect and (ii) resonance. Steric factor is limited to *o*-position only.

Nitration (as well as other electrophilic substitutions) is subject to steric hindrance. Substitution of ortho to a large group is difficult. The isomer distribution in the mononitration, of alkylbenzenes, is shown below.



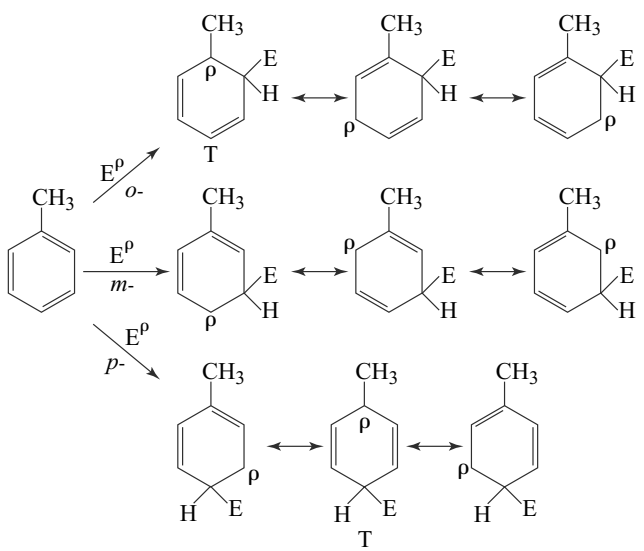
Inductive effect orientation and reactivity

1. Groups having electron-attracting inductive effect (–I effect) deactivates benzene ring and are *m*-directing, such as $-NO_2$, –CN, $-SO_3H$, etc.

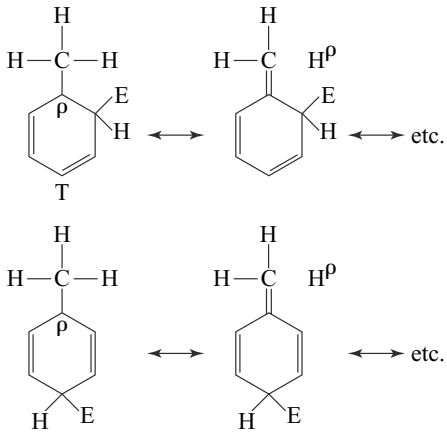


Nitro groups are electron-attracting that create positive charge on the ring. So, it deactivates the ring towards an electrophile. Also, attack at *o*- and *p*-positions places positive charge at the carbon that is joined with NO_2 group (structures marked 'T'). Thus, *o*- and *p*-attack is not favoured. Attack at the *m*-position has no structure like 'T'. It is, thus, preferred. Thus, $-NO_2$ group is deactivating and *m*-directing.

2. Groups having electron-donating inductive effect (+I effect) activates benzene ring and are *o*-, *p*-directing, such as CH_3.



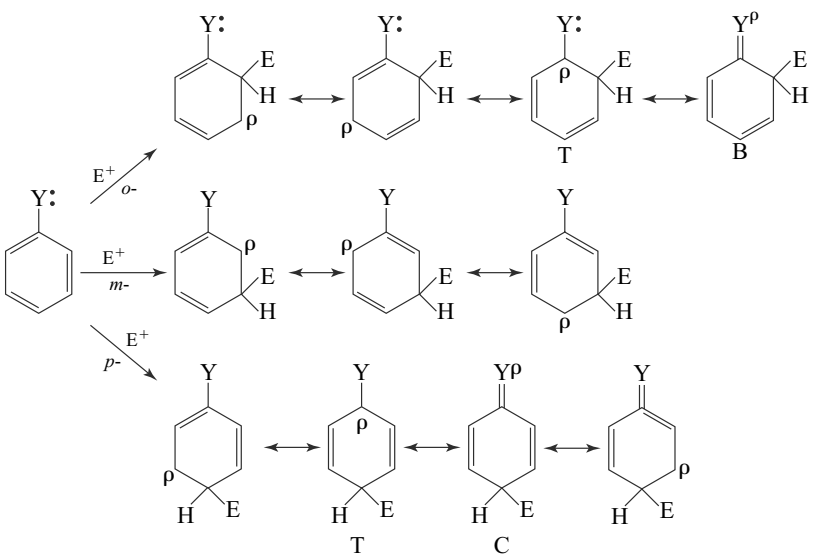
The CH_3 group is electron-donating, so it activates benzene ring towards an electrophile. The T-type structures are stabilized by electron-donating effect of $-CH_3$ group through hyperconjugation.



The σ-complex in the case of *o*-, *p*-substitution is more stabilized compared to *m*-substitution. Thus, $-CH_3$ group is activating and *o*-, *p*-directing.

Resonance, orientation and reactivity

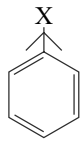
Resonance is another electronic effect that determines orientation and reactivity. Groups, which have a lone pair at the atom, directly joined with ring carbon specifically stabilizes the σ-complex for *o*- and *p*-attack through resonance (using its lone pair).



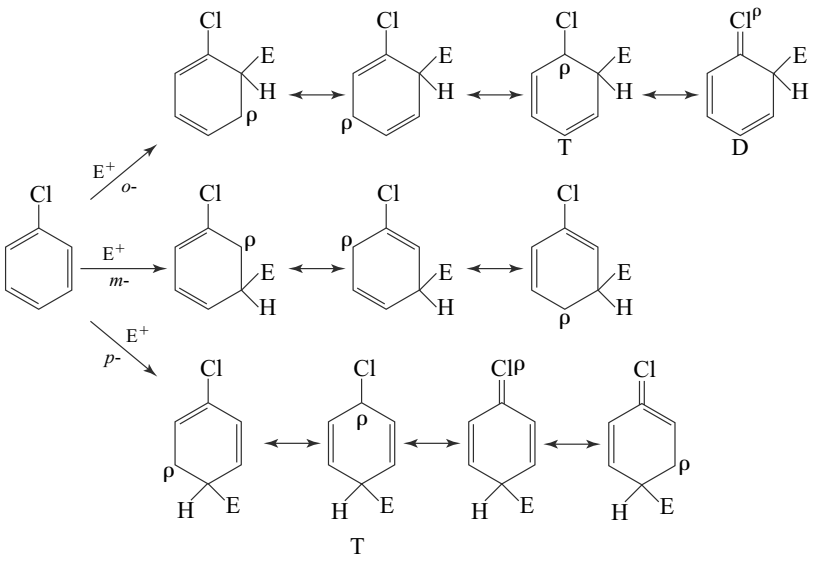
Structures marked T are stabilized by resonance in which Y is using its lone-pair electron. The structures marked B and C are not only extra resonance forms, but also have octet to each carbon. Other structures have only a sextet to one carbon. No structure like B or C is possible for the meta-substitution. Thus, group like Y not only directs electrophile to ortho and para but activates these positions also.

Halogen substituent, orientation and reactivity

Halogens are strongly electronegative. They pull C–X bond-pair electrons towards itself (–I effect), deactivating all ring positions.



In addition to the above, halogens, which have lone pairs, are capable of establishing conjugation with the aromatic ring, especially when the electrophile goes to *o*- and *p*-position (not *m*-position).



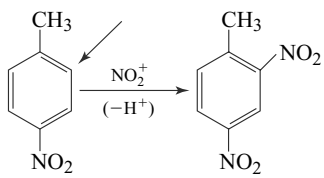
It is seen that no 'T' type structure is produced when electrophile enters into *m*-position. Also, in the structures like D, the positive charge in the ring is shared by halogen producing octet to all C atoms.

Thus, inductive effects of halogens reduce overall reactivity but resonance effect is powerful enough to determine orientation.

Halogens are deactivating with o- and p-orientation. The $-CH_2Cl$ group has similar effect.

Orientation in disubstituted benzenes

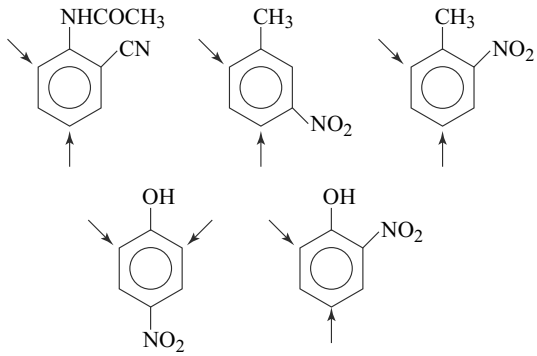
When two (or more) groups are present on the ring, their effects (that is orientation and reactivity), qualitatively, are additive. Thus, *p*-nitrotoluene is less reactive than toluene because of the deactivating $-NO_2$ group. But the third substituent enters ortho to CH_3 group and *m*- to $-NO_2$ group.



The $-CH_3$ group is *o*-, *p*-directing (here *p*-position is blocked).

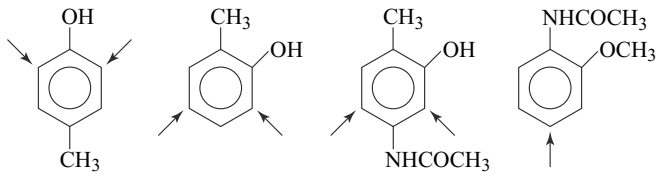
The NO_2 group is meta-directing. Thus, both groups direct third electrophile at the position shown by the arrow. Some generalizations concerning orientation are given below.

1. When two groups having opposite directive influence, the *o*-, *p*-directing group decides site of the third substitution.



($-CH_3$, –Cl, –OH groups are ortho, para and $-NO_2$ group is meta directing).

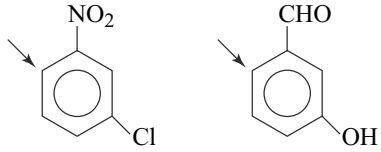
2. When both the substituents are *o*-, *p*-directing, stronger one controls the orientation.



$-CH_3$ group operates through +I effect but $-NHCOCH_3$ group operates through resonance effect. (Resonance dominates over inductive effect with respect to orientation.) Directing power of different groups follow the given order.

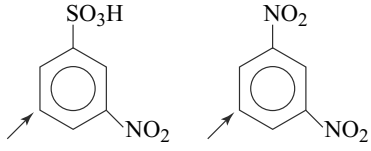
$$-NH_2, -OH, -NR, -O^{\sigma} > OR, OCOR, NHCOR > R > Halogen$$

3. When a meta-directing group is present, meta to an ortho, para group, the third electrophile goes ortho to the *m*-directing, rather than para.



In such species, the third electrophile never occupies ring position ortho to the ortho-, para-directing group. It is called *ortho effect*.

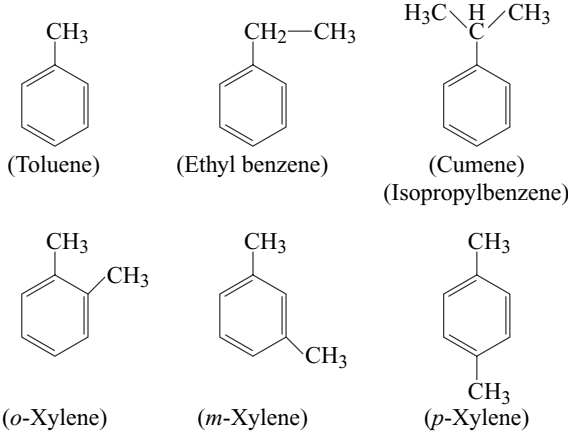
4. When two *m*-directing groups are present *m*- to each other, the third electrophile occupies the site which is *m*- to each one.



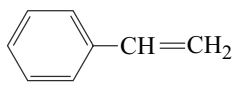
ARENES

Arenes are hydrocarbon derivatives of benzene. They may be the following:

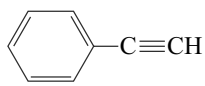
1. Alkylbenzenes



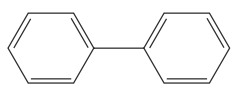
2. Alkenylbenzene



Styrene (Vinyl benzene)



Phenyl acetylene



Biphenyl

3. Alkynylbenzene

4. Arylbenzene

In all of the above compounds, the special stability associated with the benzene ring is retained.

Industrial Source of Alkylbenzene

Coal and petroleum are the two important sources of alkylbenzenes.

$$\text{Coal-tar} \longrightarrow \text{benzene, toluene, xylene}$$

Reactions to Prepare Arenas

1. Friedel–Crafts alkylation (explained in the previous chapter).

2. Reduction of acylbenzene (explained in the previous chapter).

3. Wurtz–Fittig reaction

Alkyl halide and aryl halide in ether react with sodium to give alkylbenzene.

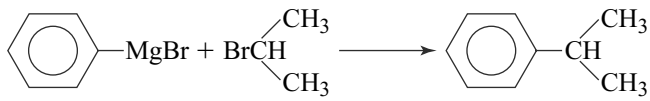
$$C_6H_5Cl + 2Na + CH_3—Cl \longrightarrow C_6H_5—CH_3 + 2NaCl$$

It is not a good synthetic method as many side products are formed.

$$C_6H_5—Cl + 2Na + C_6H_5—Cl \longrightarrow C_6H_5—C_6H_5 + 2NaCl$$

$$CH_3Cl + 2Na + CH_3Cl \longrightarrow CH_3{-}CH_3 + 2NaCl$$

4. Grignard reagent + alkyl halide



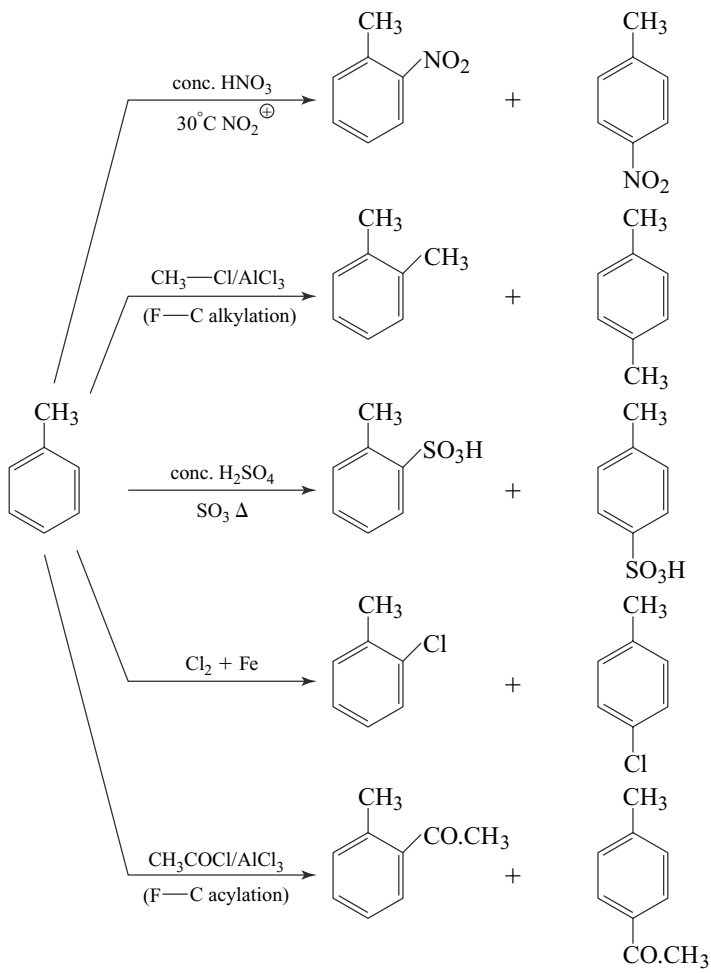
Physical Properties

Alkylbenzenes burn with sooty flame. They are *toxic* and *carcinogenic*.

Chemical Properties

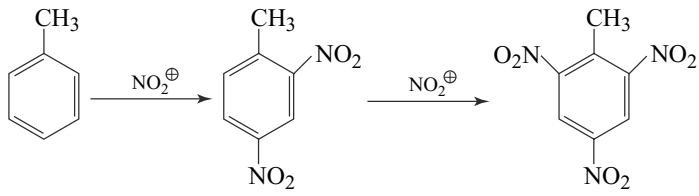
Alkylbenzenes give two types of reactions.

1. **Reactions of the benzene ring**
   Alkyl groups are electron donating. They activate benzene ring and are ortho-, para-directing. Therefore, electrophilic substitutions give both ortho- and para-isomers.



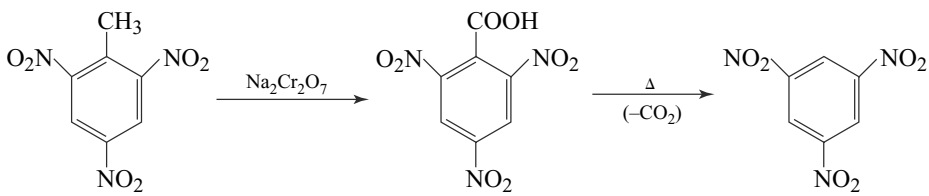
2,4,6-Trinitrotoluene (T.N.T.) (Explosive)

It is prepared by nitrating toluene with fuming HNO_3 and fuming H_2SO_4.



(TNT)

T.N.T. is a good source for 1,3,5-trinitrobenzene. It is prepared as given below.

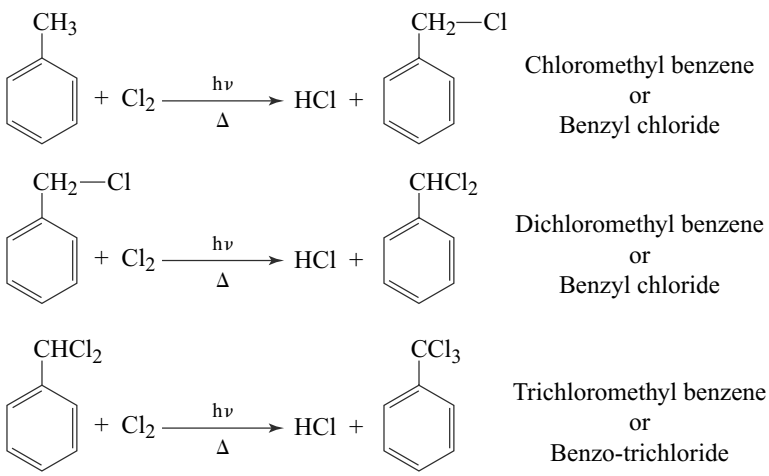


(In acetic acid) (TNB)

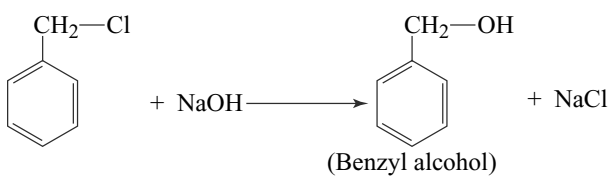
2. Reactions of the side chain

(a) Substitution of H of R

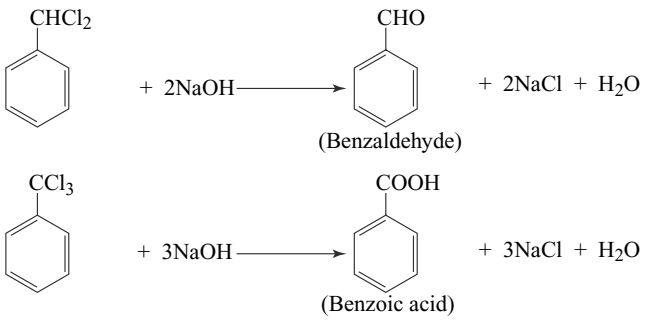
On passing Cl_2 in boiling toluene in sunlight or UV light, hydrogen atoms of the CH_3 group are replaced by Cl.



These chlorides are highly reactive and are readily hydrolyzed by NaOH.

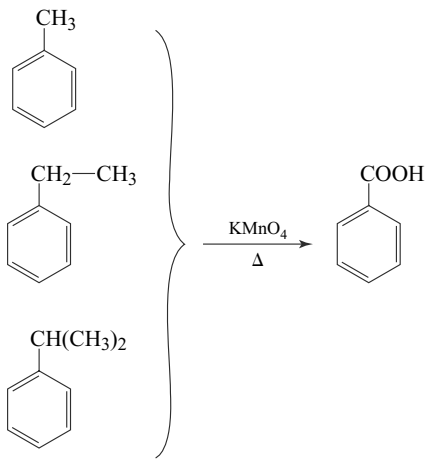


(Benzyl alcohol)



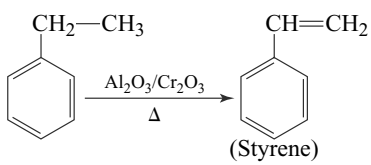
(b) Oxidation of R

The alkyl group (R) is oxidized to —COOH group. The product is always benzoic acid, irrespective of the length and nature of the alkyl group. Common oxidizing agent is $KMnO_4$.



(c) Styrene from ethylbenzene

Ethylbenzene on dehydrogenation over Al_2O_3/Cr_2O_3 forms styrene.



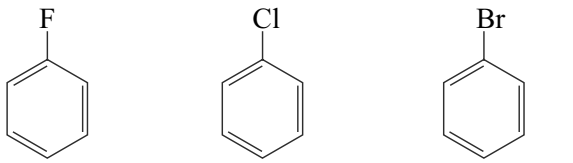
Styrene is industrially important as it forms polymers.

Comparison:

	C_2H_5Cl	C_6H_5Cl	$C_6H_5CH_2Cl$
$AgNO_3$ solution	AgCl Precipitates slowly	No reaction	AgCl Precipitates readily

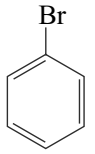
ARYL HALIDES

When halogen is attached to an arene ring, (example, benzene and naphthalene), the class of compound is known as aryl halide.



Fluorobenzene Chlorobenzene Bromobenzene

Aryl halides resemble vinyl halide to some extent as both have their halogen attached to sp^2 carbon.

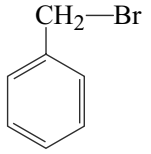


Phenyl bromide (Bromobenzene)

$CH_2{=}CH{-}Br$

Vinyl bromide (Bromoethene)

In contrast to phenyl halides, benzyl halides are quite reactive like allyl halides.

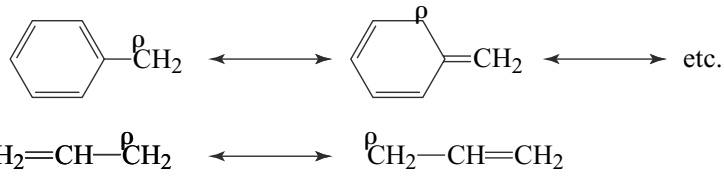


Benzyl bromide

$CH_2{=}CH{-}CH_2{-}Br$

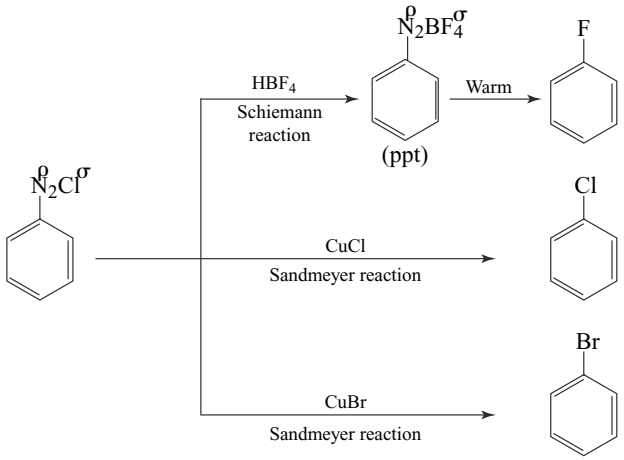
Allyl bromide

High reactivity of these compounds is associated with the stability of their respective carbocations through delocalization of positive charge.

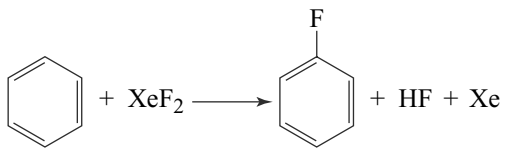


Preparation:

1. Direct halogenations
   Explained and discussed (electrophilic aromatic substitution).
2. From diazonium salts

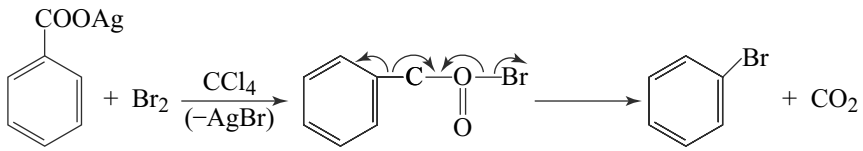


Fluorobenzene can also be prepared by reacting benzene with XeF_2.



3. By Hunsdiecker reaction

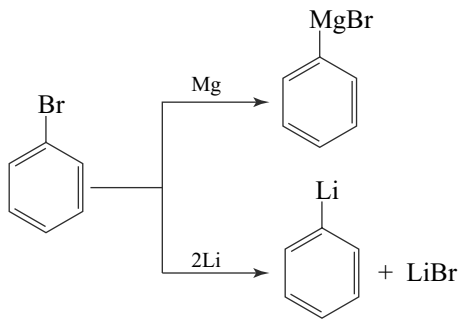
Aryl bromide is obtained when silver salt of aromatic acid is heated with Br_2. Evidence points a hemolytic mechanism for this reaction.



Reactions:

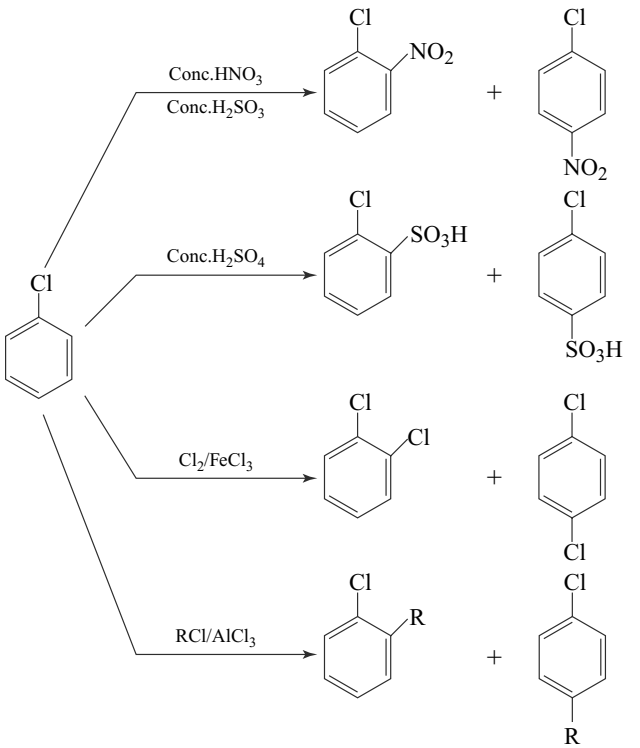
1. Formation of organometallic compound

Aryl halide in ether reacts with Mg to form Grignard reagent and with Li to give aryl lithium



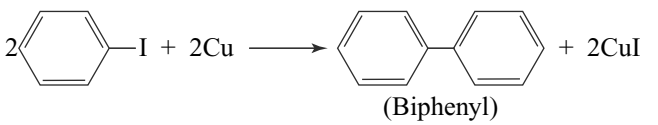
2. Electrophilic reactions of the ring

Halogens are *o*-, *p*-directing with deactivation of the ring. Thus, halobenzenes form *o*-, *p*-derivatives.



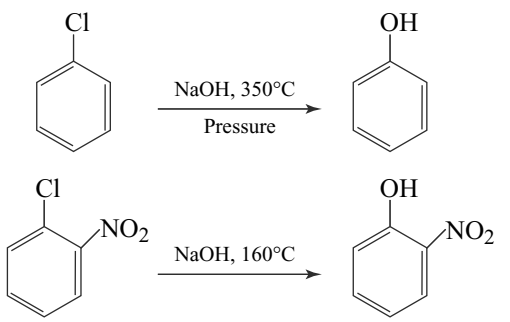
3. Ullmann reaction

Iodobenzene, when heated with Cu powder, forms biphenyl. It is known as Ullmann reaction.



4. Nucleophilic-substitution reactions

Aryl halides (C_6H_5Cl, $CH_3C_6H_4Cl$, etc.) are much less reactive to the usual nucleophiles. But strong electron-attracting groups (—CN, —NO_2, —$N_2^{\oplus}$, etc.) on the ring, especially at the ortho- or para-position or both, activate aryl halides towards a nucleophile.

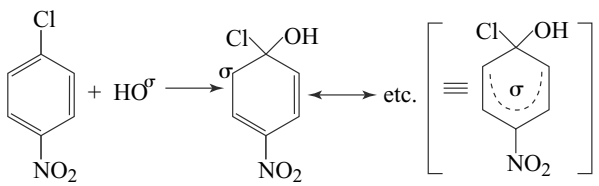


The second reaction requires less forcing condition as $-NO_2$ group activates the ring towards the OH^- nucleophile. The reactions of aryl halides, thus, can be divided into two parts. Nucleophilic reactions of (a) activated aryl halides and (b) simple aryl halides.

Reactions of Activated Aryl Halides

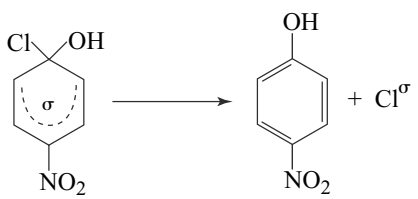
A nucleophilic aromatic substitution may proceed in two steps.

1. Attack of nucleophile at the carbon bearing halogen. It destroys aromatic system (C at the reaction site changes from sp^2 to sp^3).

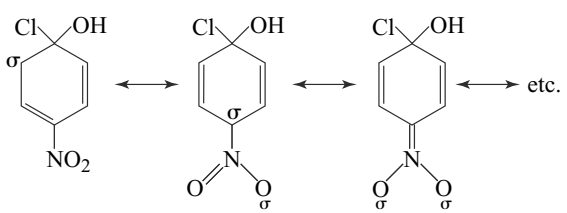


[A]

2. In the second step, loss of an anion regenerates aromatic system leading to the product.

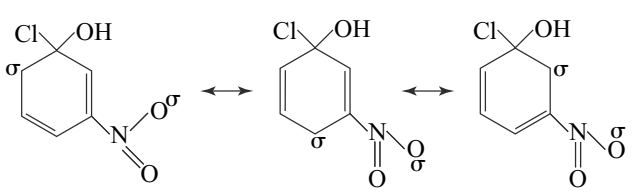


The formation of an intermediate like (A) is highly unfavourable for simple aryl halides. (Ph–Cl) but if electron-attracting groups are present on the ring, formation and stabilization of (A) become facile. It is because the electron-attracting group shares the negative charge generated at the ring through resonance (B).



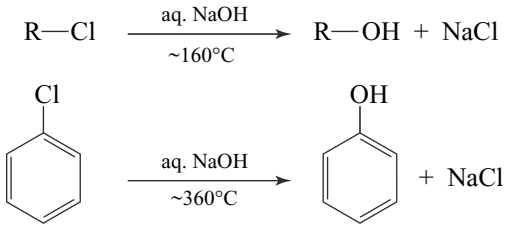
A B

If $-NO_2$ group is at the *m*-position, a structure like (B) is not possible, that is the negative charge is not shared by the $-NO_2$ group.

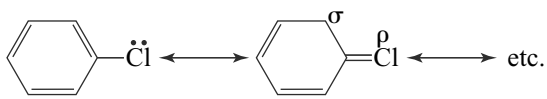


Reactions of Simple Aryl Halides (Benzyne Mechanism)

Unlike alkyl halides, aryl halides are much less reactive to the nucleophiles.

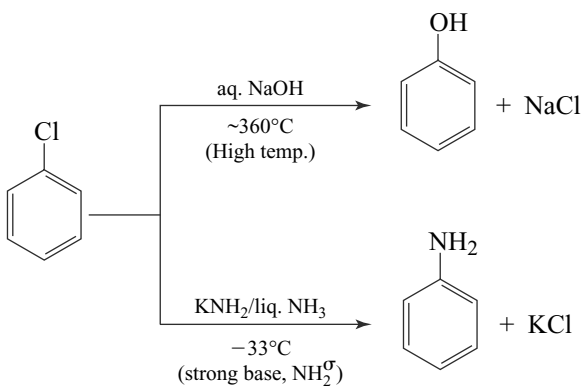


In aryl halides, halogen is attached to sp^2 carbon and the lone pair at halogen is in conjugation with the π electrons of the ring. It makes C–X bond strong and so is less reactive.

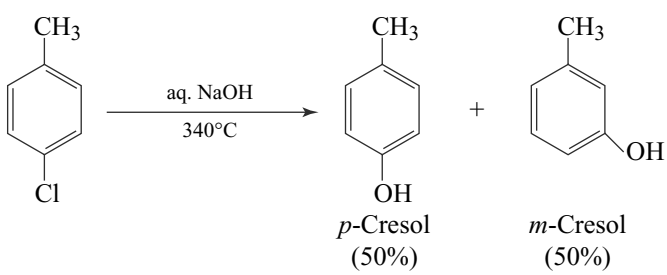


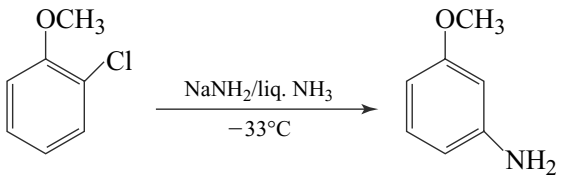
But aryl halides may undergo nucleophilic-substitution reactions under forcing conditions involving the following conditions.

1. Either high temperature or
2. Strong base



Rearrangements are also found in such reactions.





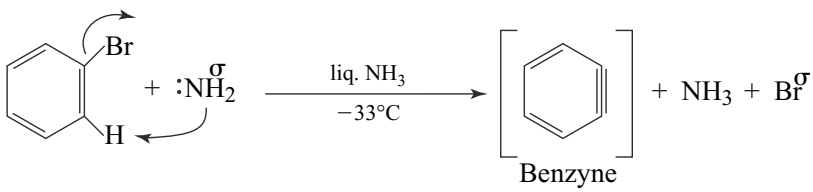
o-Chloroanisole *m*-Chloroanisole (100%)

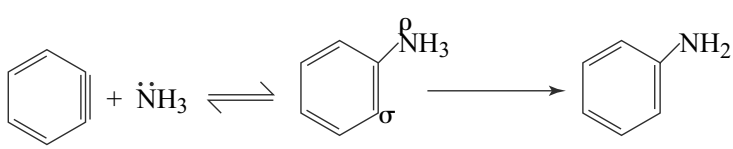
Study of such reactions support a two-step mechanism.

1. A base catalysed elimination and
2. Addition of the nucleophile
   (It is opposite to electrophilic aromatic substitution, which is an addition–elimination reaction.)

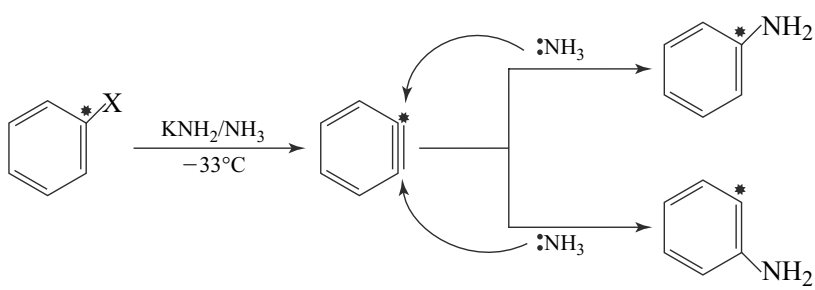
That is, the reaction is elimination–addition process. This mechanism is popularly known as *Benzyne mechanism*. The reaction is illustrated for the amination of bromobenzene.

In the first step, elimination is caused by NH_2^- ion to produce a highly reactive intermediate called benzyne (C_6H_4). It has an extra bond between two ortho carbons. In the second step, benzyne reacts with any available nucleophile (here the solvent NH_3) to give the addition product.





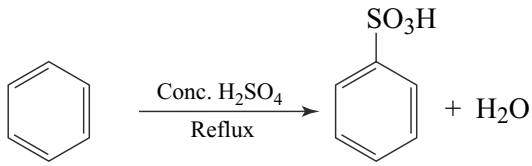
The above mechanism is supported by carrying out the reaction with benzene ring in which one of the ring carbons is labelled with ^{14}C isotope. This substrate produces almost equal amounts of 1- and 2-^{14}C-labelled anilines. It is because, any of the ortho carbon atoms of benzyne can be attacked by the nucleophile.



AROMATIC SULPHONIC ACIDS

Aromatic sulphonic acids are Ar–SO_3H in which Ar is aromatic hydrocarbon maicty. For example, C_6H_5–SO_3H is benzene sulphonic acid. It contains C–S bond.

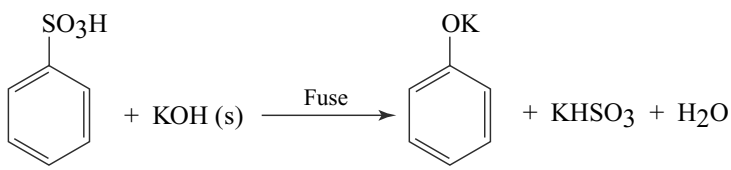
Benzene sulphonic acid is obtained when benzene is refluxed with conc. H_2SO_4.



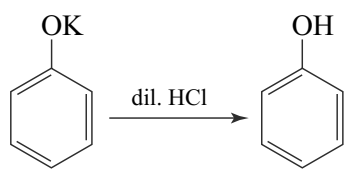
Fuming H_2SO_4 reacts at room temperature.

Properties and Reactions

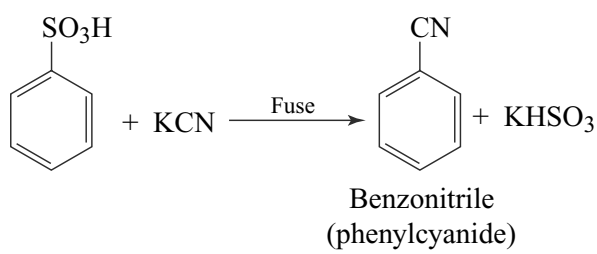
1. C_6H_5–SO_3H is a white crystalline solid.
2. It is strong acid (Ka ≈ 0.5).
3. Replacement of –SO_3H group.
   (a) When fused with NaOH (or KOH), sodium phenoxide is formed.



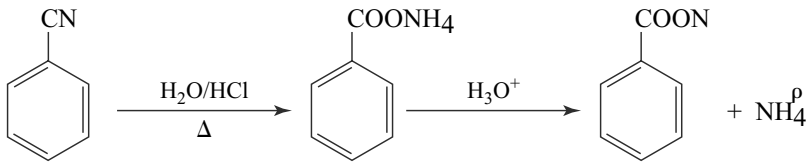
Potassium phenoxide on acidification gives phenol.



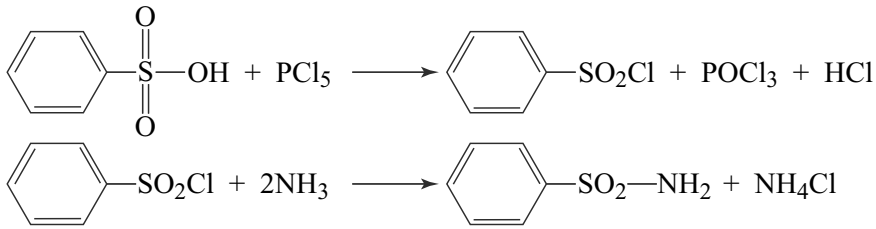
(b) On fusing with KCN, benzonitrite is formed.



Benzonitrile is hydrolyzed by boiling with conc. HCl to benzoic acid.

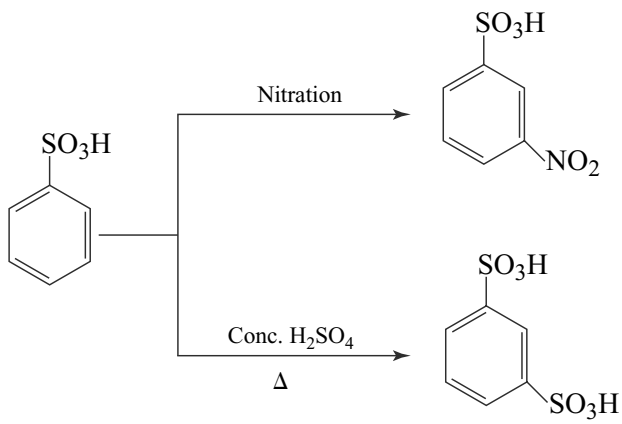


4. Replacement of –OH of $–SO_3H$
The –OH part of $–SO_3H$ is replaced by PCl_5 to give benzene sulphonyl chloride.

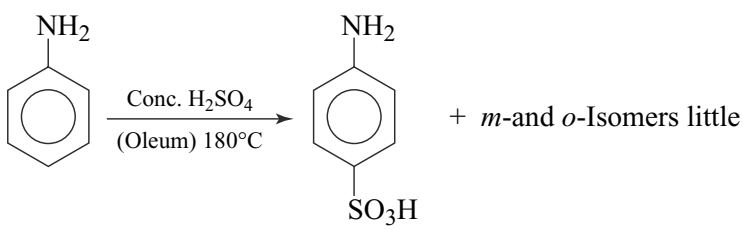


Sulphonyl chloride is Hinsberg's reagent (used in separation of amines).

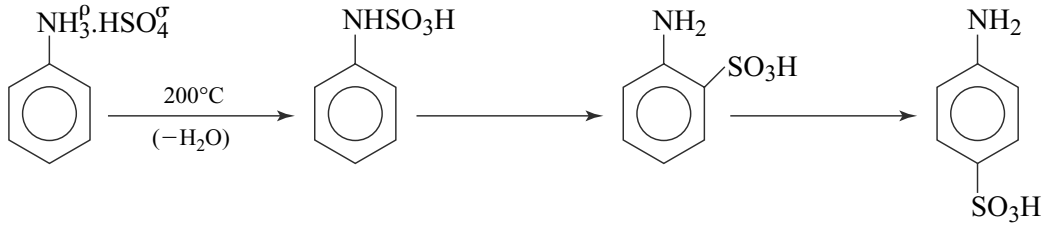
5. Electrophilic substitution
The $–SO_3H$ group is deactivating and *m*-directing.



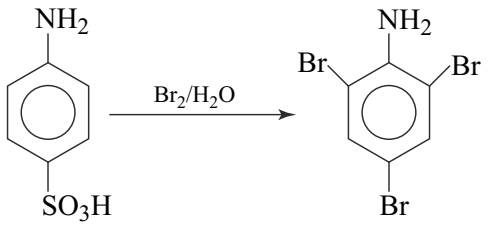
Sulphanilic acid (*p*-aminobenzene sulphonic acid)



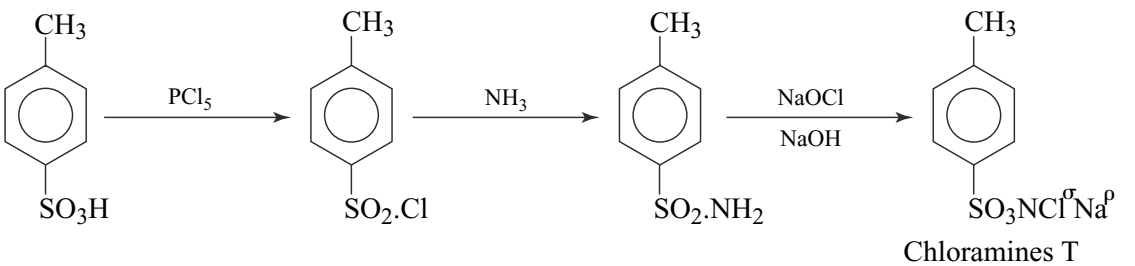
Commercial preparation by 'baking' of aniline hydrogen sulphate.



Sulphanilic acid reacts with bromine water to form 2,4,6-tribromoaniline.

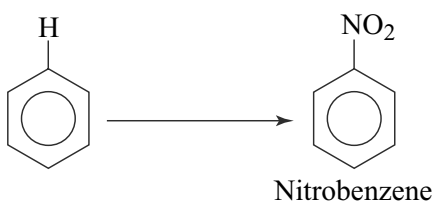


Chloramines T (Na salt of N-chloro-*p*-toluene sulphonamide)



AROMATIC NITRO COMPOUNDS

Replacement of H atom (or atoms) from benzene or an aromatic hydrocarbon by NO_2 group gives aromatic nitro compounds.



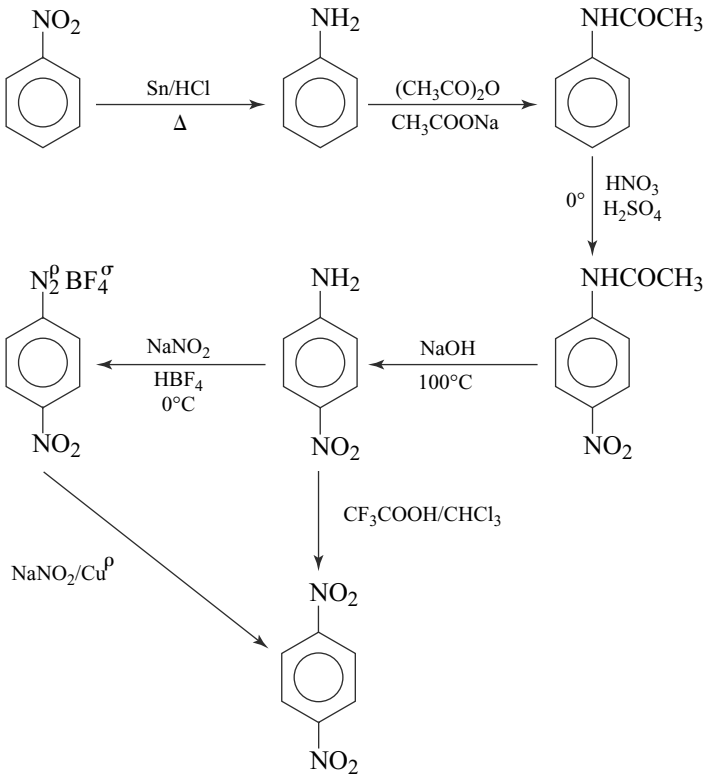
Synthesis

The most general method of introducing $-NO_2$ group into the aromatic ring is the direct nitration. A number of reagents can be used (discussed in aromatic electrophilic substitution).

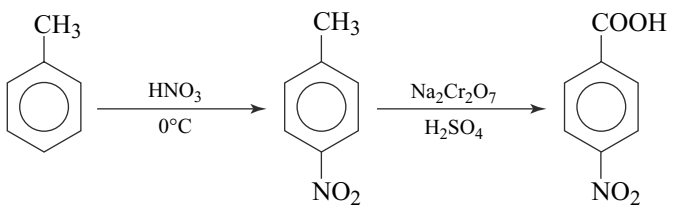
The common reagent is the nitrating mixture, conc. HNO_3 + conc. H_2SO_4. But the direct nitration may not give the desired product because of the orientation effect of the group already present on the ring. For

example, *p*-dinitrobenzene from nitrobenzene and *p*-nitrobenzoic from benzoic acid cannot be obtained by direct nitration of nitrobenzene and benzoic acid, respectively. It is because $-NO_2$ and –COOH groups are *m*-directing.

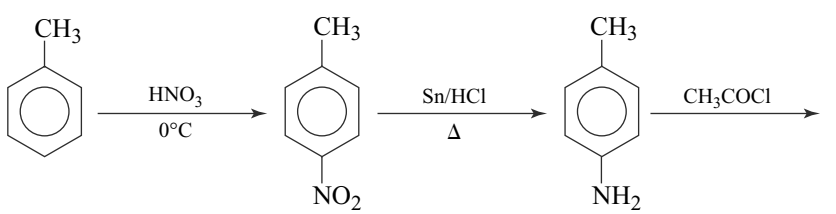
Synthesis of p-dinitrobenzene from nitrobenzene

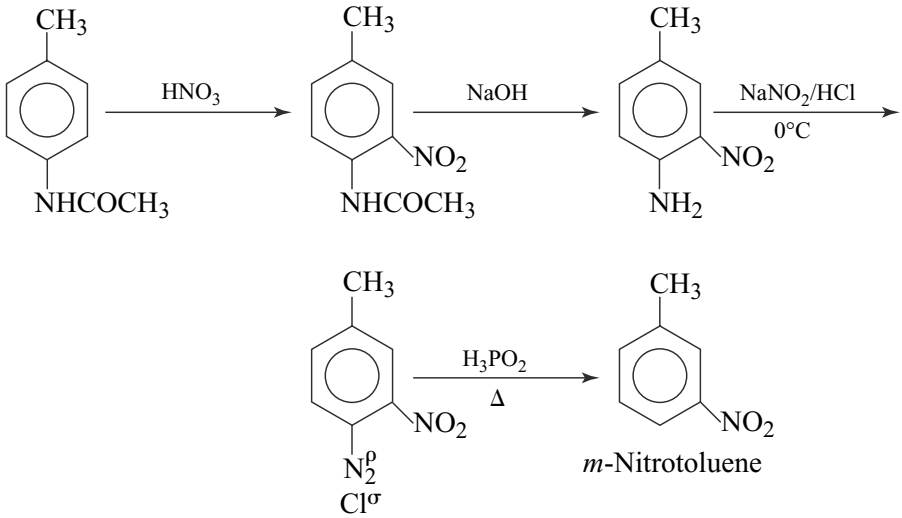


Preparation of p-nitrobenzoic acid



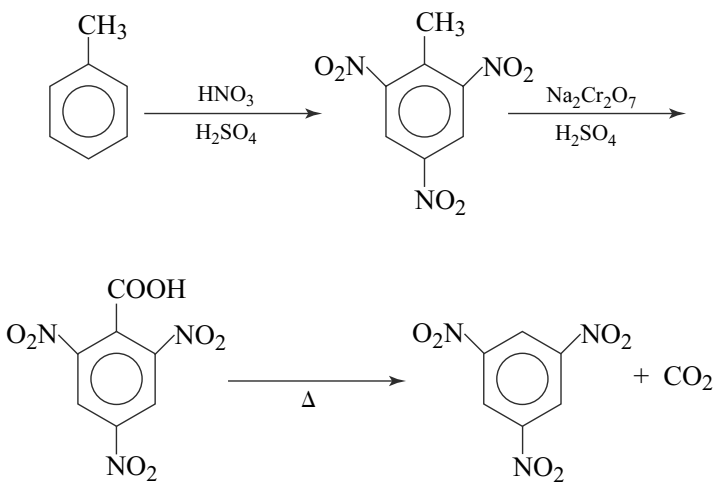
1. *m*-nitrotoluene from toluene





2. 1,3,5-Trinitrobenzene from benzene

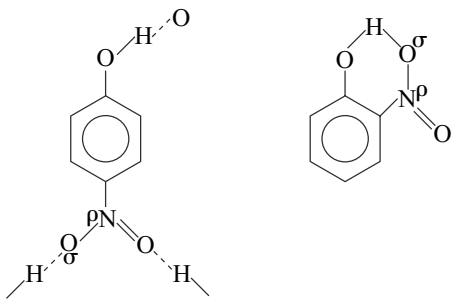
Direct nitration of *m*-dinitrobenzene requires drastic condition, which is a difficult reaction. However, toluene is readily converted into trinitro derivative, which on oxidation and decarboxylation, gives 1,3,5-trinitrobenzene.



Trinitrobenzoic acid easily decarboxylates due to electron-attracting effect of the NO_2 groups.

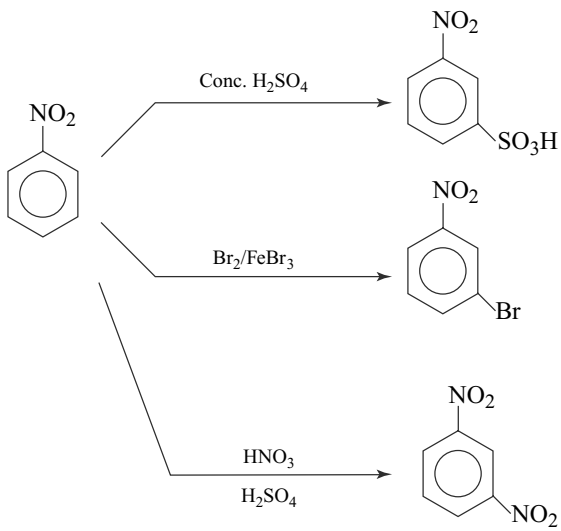
Physical Properties

1. Nitrobenzene is a liquid.
2. Dinitro compounds are yellow crystalline solids. They have high MP and BP, which increase the number of nitro groups. It is because of this fact that increased number of nitro groups increases dipole–dipole attraction.
3. Unlike *p*-nitrophenol, *o*-nitrophenol has low BP. It is because *p*-nitrophenol has intermolecular whereas *o*-nitrophenol has intramolecular H-bonding. Therefore, *o*-nitrophenol is a volatile steam.

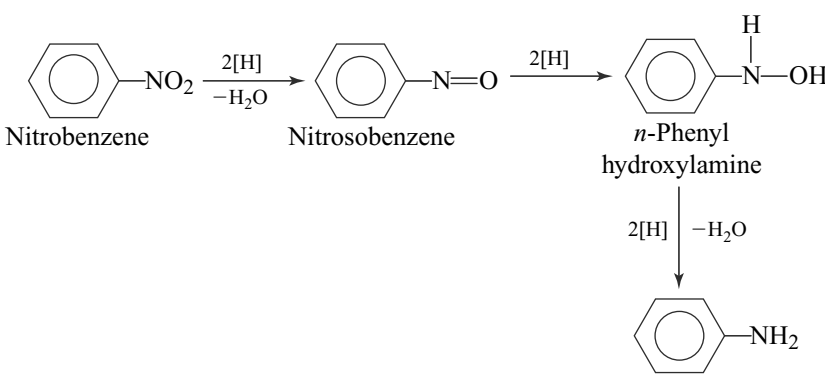


Chemical Properties

1. Electrophilic substitution
The nitro group ($-NO_2$) is *m*-directing and deactivatives benzene ring. Electrophilic-substitution reactions mainly give *m*-isomers.



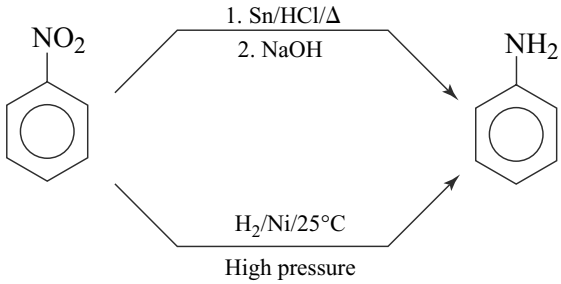
2. Reduction of nitro compounds
The reduction of nitrobenzene to aniline proceeds in the following way.



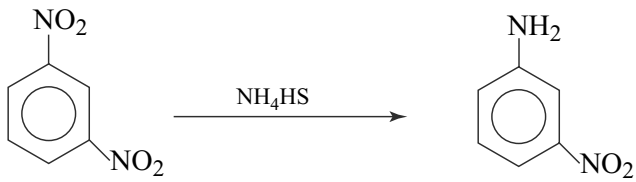
The above reaction shows that six equivalent of reducing agents is required.

Different combination of reducing agents gives different product.

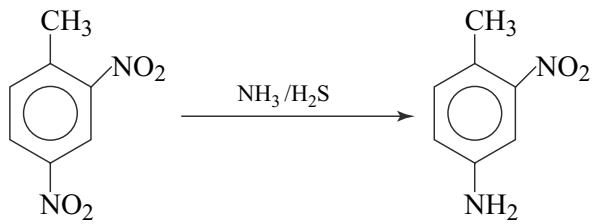
1.



2. Ammonium sulphide (NH_4HS) or Na_2S reduce only one $-NO_2$ in a dinitro compound much faster than the other.

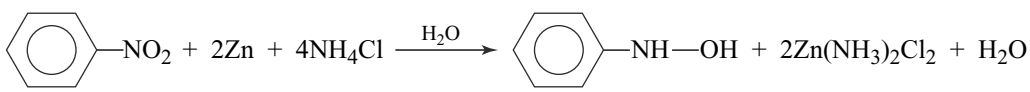


It is not always easy to predict which of the two NO_2 groups is reduced more readily, but reduction of 2,4-dinitrotoluene leads to preferential reduction of the 4-nitro group.



(a) Zinc and NH_4Cl in aq. medium

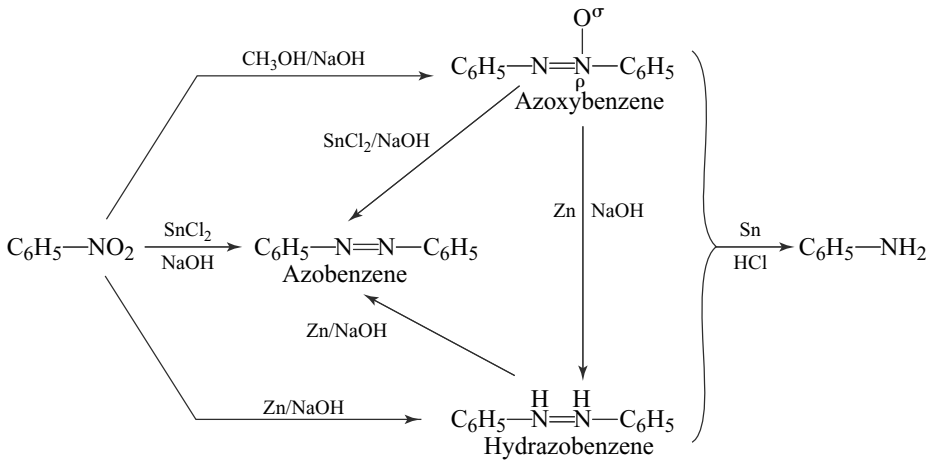
Zinc dust and NH_4Cl in H_2O reduces nitrobenzene to N-phenylhydroxylamine.



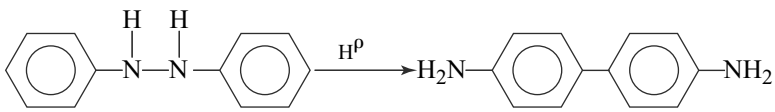
This reaction is the basis of *Mulliken's* test for nitro group. Phenylhydroxylamine gives silver mirror test due to its reducing property.

(b) Reduction of nitrobenzene in alkaline medium

Reduction of nitrobenzene in alkaline medium using different reducing agents gives variety of products. The reactions are summarized below.



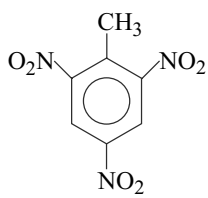
Hydrazobenzene in strong acid solution rearranges to benzidine (4,4′-diaminobiphenyl). It is an important dye intermediate.



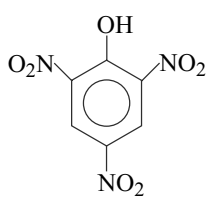
Polynitro Compounds

Aromatic compounds that contain many nitro groups are polynitro compounds. A number of them have explosive property, such as the following:

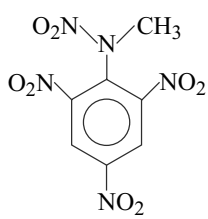
2,4,6-Trinitrotoluene (TNT)



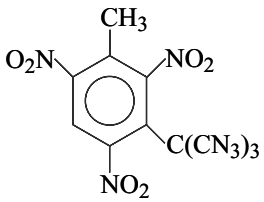
2,4,6-Trinitrophenol (picric acid)



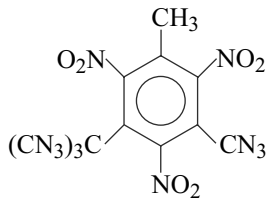
N,2,4,6-tetranitro-N-methyl aniline (tetryl)



Some polynitro derivatives of benzene possess musk-like odour. They are used as ingredients of cheap perfumes and soaps.

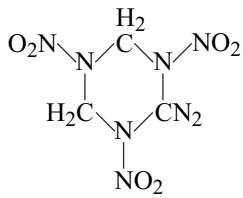


1-Methyl-3-t-butyl-
2,4,6-trinitrobenzene



1,3-Dimethyl-5-t-butyl-
2,4,6-trinitrobenzene

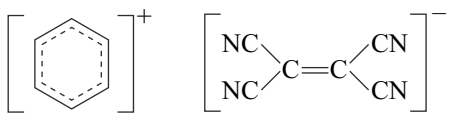
Highly explosive substance like cyclonite (RDX) is also a polynitro compound. But it is a heterocyclic compound.



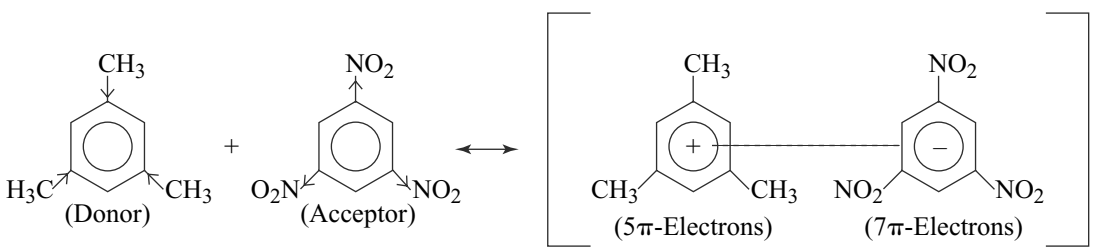
Hexahydro, 1,3,5-trinitro-sym-triazine (RDX or cyclonite)
(RDX-Research developed explosive)

CHARGE-TRANSFER COMPLEXES

Charge-transfer complexes (or π-complex) involve donor and acceptor species in a 1:1 ratio. They are always highly coloured. An example is shown by benzene (donor) and tetracyanoethene (acceptor), each of which separately is colourless, but form a bright orange complex. In the complex, some of the benzene electrons leak into tetracyanoethene.



Polynitro compounds also form charge-transfer complex with hydrocarbons. For example, 1,3,5-trinitrobenzene (acceptor) and 1,3,5-trimethyl benzene (donor) form a charge-transfer complex.



(Donor) (Acceptor) (5π-Electrons) (7π-Electrons)

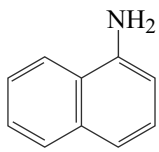
(π-Complex)

Hydrocarbon is electron donor and the polynitrocompound is acceptor due to strong –I effect of NO_2 groups. Charge-transfer complexes are also formed by 2,4,6-trinitrophenol (picric acid) with hydrocarbon (example anthracene), which are called 'picrates'. Picrates are crystalline yellowish solids. This behaviour is used in separation, purification and identification of aromatic hydrocarbons.

AROMATIC AMINES

Aromatic amines are compounds in which amino group is directly linked to the ring. Like aliphatic amines, aromatic amines also constitute three classes namely, primary (1°), secondary (2°) and tertiary (3°) amines.

$C_6H_5—NH_2$	$(C_6H_5)_2NH$	$(C_6H_5)_3N$
(1°)	(2°)	(3°)
Phenylamine (aniline)	diphenylamine	triphenylamine



1-Naphthylamine

Aniline

Common name of phenyl amine is aniline. It is the simplest aromatic amine.

Preparation

1. Nitrobenzene is reduced by metal and acid (Sn/HCl) to aniline.

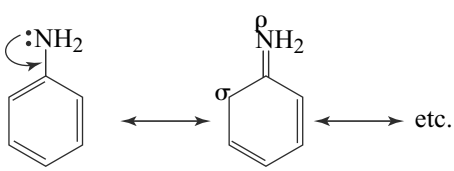
$$2C_6H_5NO_2 + 3Sn + 12HCl \longrightarrow 2C_6H_5NH_2 + 4H_2O + 3SnCl_4$$

2. By Hoffmann bromamide reaction (see name reactions).
   Benzamide on treatment with Br_2 and NaOH produces aniline.

$$C_6H_5 — \underset{\underset{O}{\|}}{C} — NH_2 + Br_2 + 4NaOH \longrightarrow C_6H_5NH_2 + 2NaBr + 2H_2O + Na_2CO_3$$

Physical properties

1. Aniline is musty smelling liquid.
2. Pure aniline is colourless but on exposure to air it turns brown.
3. It is almost insoluble in water.
4. Aromatic amines are toxic.
5. Aniline is a very weak base, weaker than NH_3. It is due to conjugation of lone pair at N with π-electrons of benzene ring.



Base strength has been discussed in detail in Chapter 4, *Organic acids and bases.*

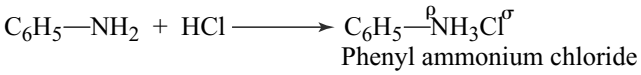
Chemical reactions

Reactions of aniline can be classified into two groups:

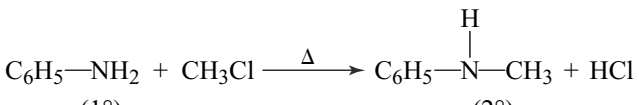
1. Reactions of NH_2 group and
2. Reactions of the benzene ring (that is aromatic nucleus).

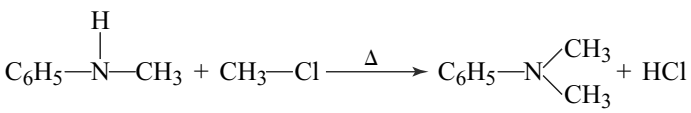
Reactions of $-NH_2$ group

1. **Aniline is basic and forms salts**

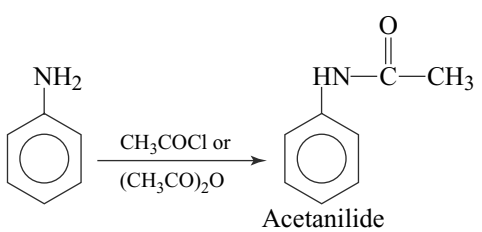


2. **Alkylation**
   When aniline is heated with an alkyl halide (CH_3Cl), N-alkyl derivative are formed.

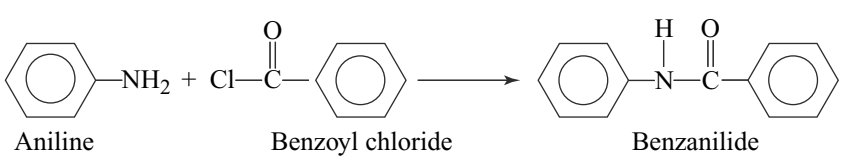




3. **Acylation**
   Aniline reacts with acetyl chloride (acid chloride) or acetic anhydride to form N-acyl phenylamine, that is N-substituted amide. This reaction is known as acetylation.



When acid chloride is benzoyl chloride, the reaction is known as 'Schotten–Baumann' reaction.



4. Carbylamine reaction

Aniline, like other primary amines forms phenyl isocyanide on heating with $CHCl_3$ and KOH. It has very bad odour (nauseating odour).

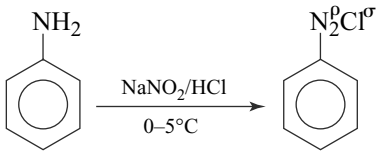
$$C_6H_5—NH_2 + 3KOH + CHCl_3 \longrightarrow C_6H_5NC + 3KCl + 3H_2O$$

This reaction is used for identification of primary amines (both aliphatic and aromatic).

5. Reaction with HNO_2

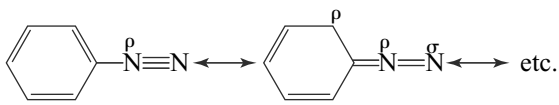
(a) *Primary aromatic amines*

Aniline (other aromatic primary amines also) reacts with nitrous acid at low temperature (0–5°C) to give benzene diazonium chloride. This reaction is known as diazotization.



Benzene diazonium chloride

Unlike aliphatic diazonium compounds, aromatic diazonium compounds are stable. They achieve stability by resonance.



Diazonium salts of aliphatic primary amines are not stable due to lack of resonance stabilization. They dissociate spontaneously to liberate N_2.

$$RN_2^{\rho}Cl^{\sigma} \xrightarrow{H_2O} R—OH + N_2\uparrow + H_2O$$

Diazonium salts are an important intermediate in synthetic chemistry. Its reactions will be discussed at the end of this chapter.

(b) *Secondary aromatic amines + HNO_2*

Secondary aromatic amines react with HNO_2 to form N- nitroso compounds similar to aliphatic amines. The N-nitroso compounds are yellow or green oils insoluble in water.

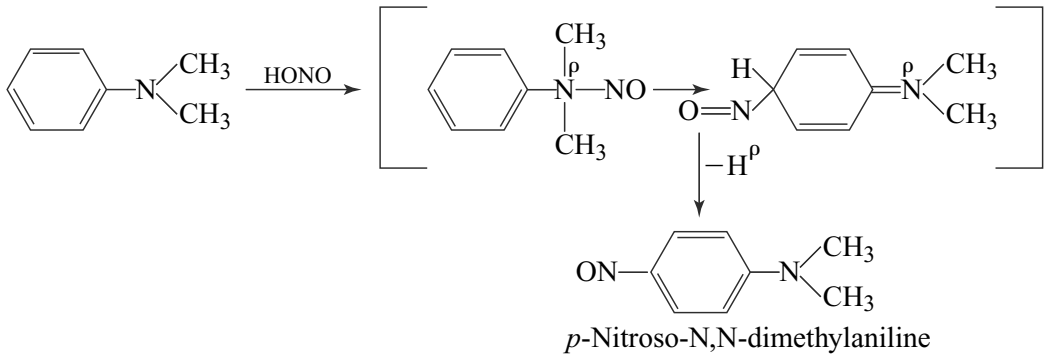
$$H—O—H=O + H^{\rho} \rightleftharpoons H_2O^{\rho}—N=O \longrightarrow H_2O + N^{\rho}O$$

$$C_6H_5—\underset{\cdot\cdot}{\overset{H}{N}}—CH_3 + N^{\rho}O \longrightarrow C_6H_5—\overset{H}{\underset{CH_3}{N}}—NO \xrightarrow{-H^{\rho}} C_6H_5—\underset{CH_3}{N}—N=O$$

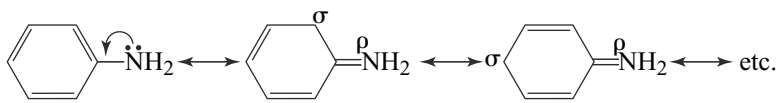
(Yellow oil)

(c) *Tertiary aromatic amines + HNO_2*

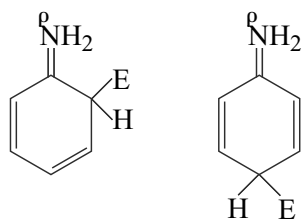
Tertiary aromatic amines undergo C-nitrozation, preferably in the para-position with HNO_2. It is believed that an N-nitroso compound is formed first, which isomerizes to the *p*-nitroso derivative (aliphatic tertiary amines react differently).



Reaction of aromatic nucleus The lone pair at N of NH_2 establishes resonance with the benzene ring.

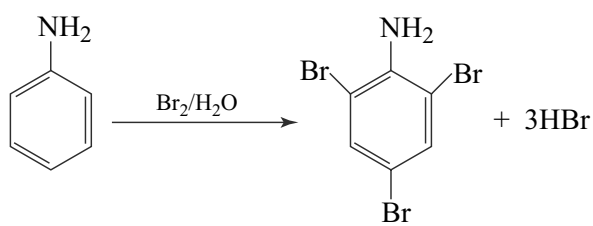


It makes benzene nucleus electron rich and more active towards electrophiles. Thus, NH_2 group activates benzene ring and is *o*-, *p*-directing. The Wheland intermediate in the cases of *o*- and *p*-substitution are further stabilized by the structures.

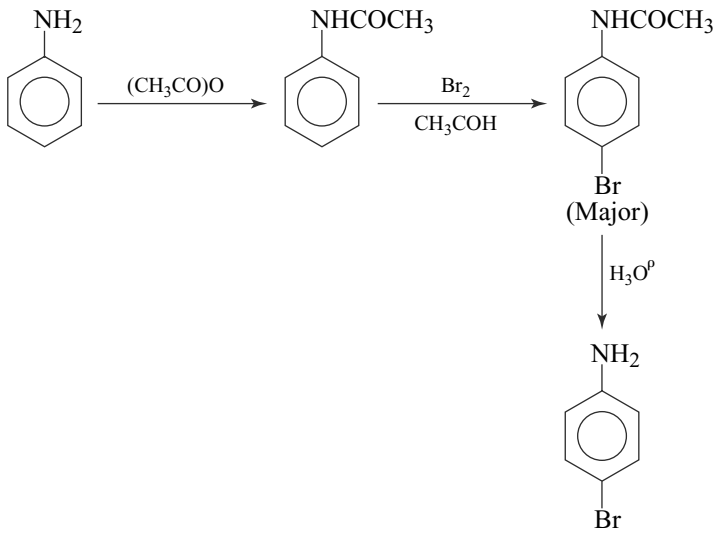


Activation of ring is pronounced and many times polysubstitution takes place.

1. *Reaction with Br_2*
   Aniline reacts with Br_2 water to give a precipitate of 2,4,6-tribromoaniline.

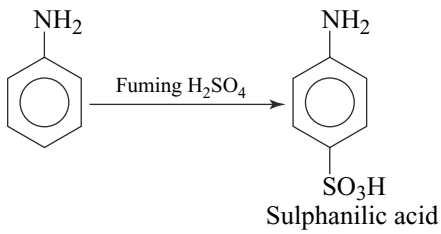


Monobromo derivative is prepared by converting NH_2 into –NHCOR, which is weak-activating group than NH_2.



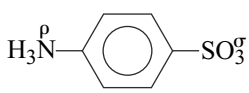
2. *Sulphonation*

Aniline on heating with fuming H_2SO_4 forms sulphanilic acid.



Sulphanilic acid

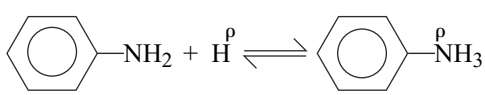
Sulphanilic acid contains both acidic (SO_3H) and basic (NH_2) groups. The proton, therefore, migrates to more basic NH_2 group. The compound, thus, has a dipolar structure.

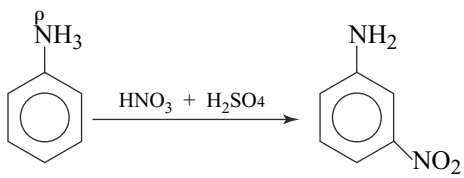


(Dipolar)

3. *Nitration*

Direct nitration gives *m*-nitro compound. It is because, in acidic medium NH_2 group converts into $\overset{\oplus}{N}H_3$, which is *m*-directing.



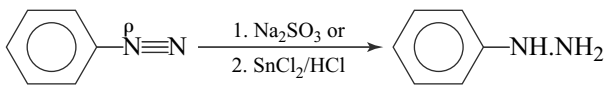


Reactions of diazonium salts Diazonium salts are useful intermediate in synthetic organic chemistry. Main reactions of diazonium compounds are the following.

1. Without loss of nitrogen and
2. With loss of nitration.

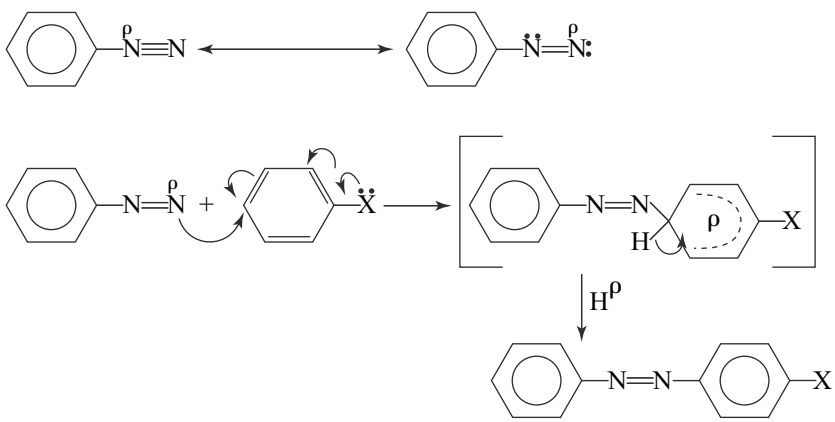
Reactions of diazonium compounds without loss of nitrogen

1. *Reduction to hydrazine*
   Diazonium salts are reduced to phenylhydrazine by $SnCl_2$/HCl or Na_2SO_3.



Phenylhydrazine

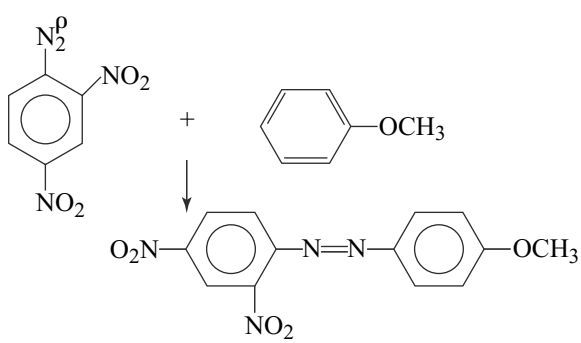
2. *Diazo coupling*
   Electrophilic aromatic substitution in which diazonium salt acts as an electrophile is known as diazo coupling. Diazonium cation is a weak electronphile. Therefore, it attacks highly active substrates, such as phenols and amines. The reaction is believed to proceed as given below.



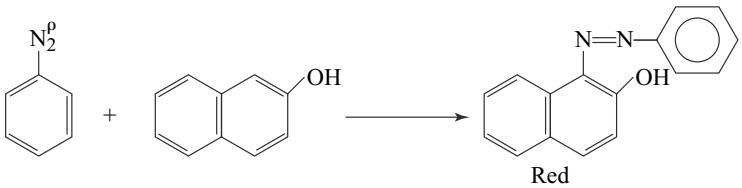
Azo-compound

In the above reaction, X = $-O^-$, $-N(CH_3)_2$ and –OH. The azo-compounds that are produced are highly coloured and useful as dyes and colouring matters. This reaction is the basis of azo-dye industry.

Anisole (C_6H_5–OCH_3) does not enter into coupling reaction with simple benzene diazonium cation ($C_6H_5N_2\ N_2^{\oplus}$). However, it couples with active diazonium cation. For example,

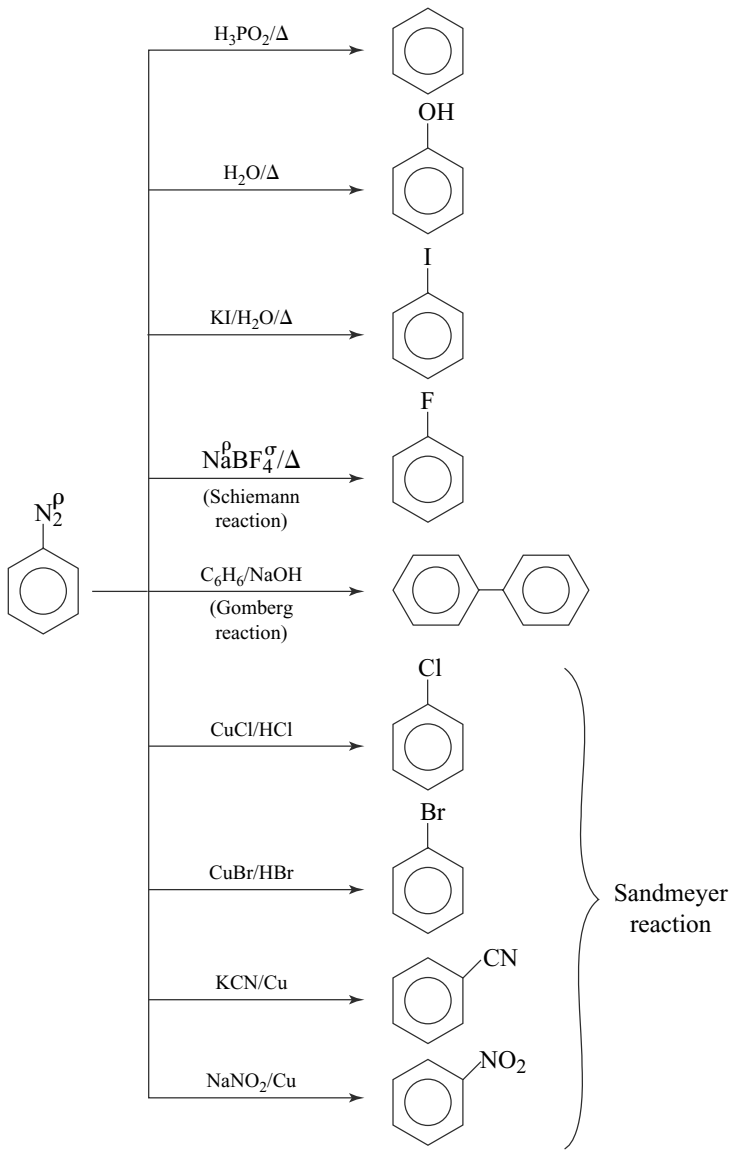


The diazo coupling involving benzene diazonium chloride and β-naphthol gives bright red product.



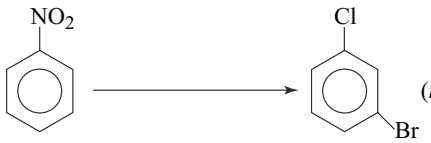
This reaction is used to characterize $-NH_2$ group in qualitative organic analysis.

Reactions of diazonium compounds with loss of nitrogen: The replacement of diazonium group by different groups produces variety of benzene derivatives. Important reactions are given below.

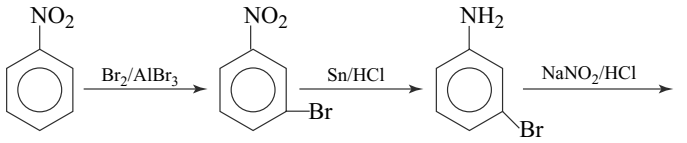


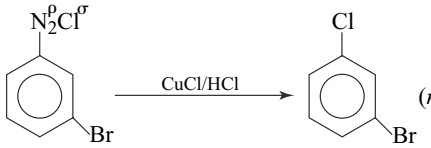
Some syntheses involving diazonium salts

1.



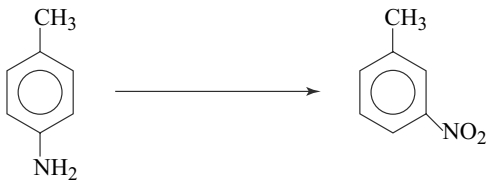
(*m*-Bromochlorobenzene)



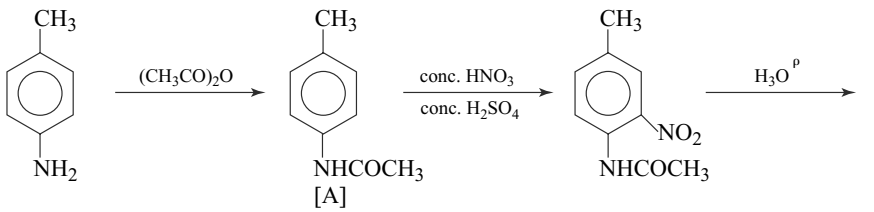


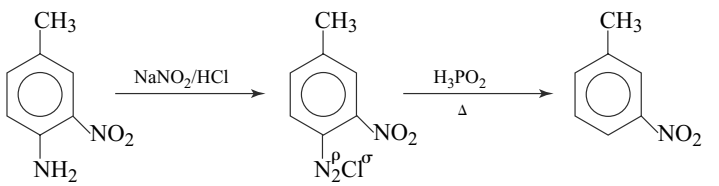
(*m*-Bromochlorobenzene)

2.



p-Toluidine *m*-Nitrotoluene





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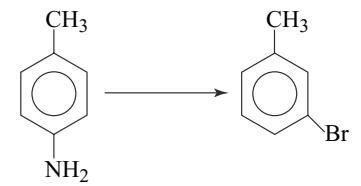
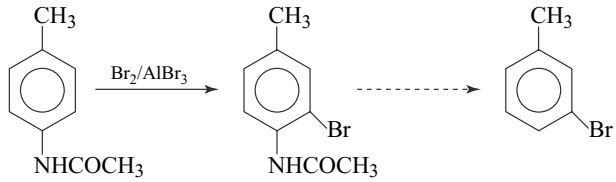


p-Toluidine *m*-Bromotoluene

If [A] in the above reaction [B] is brominated and the same reactions are followed, the product will be *m*-bromotoluene.



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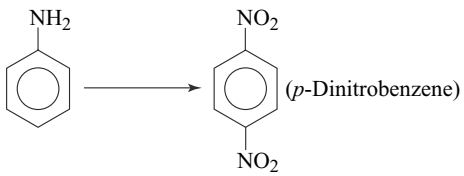

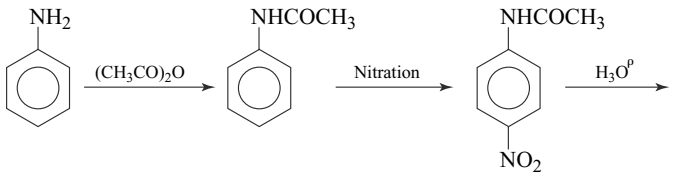

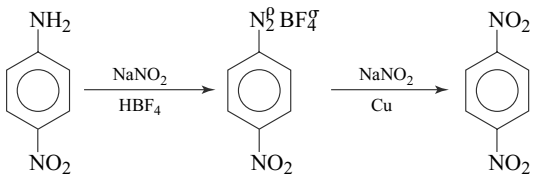

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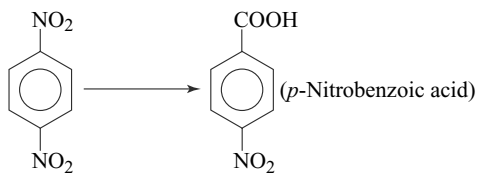

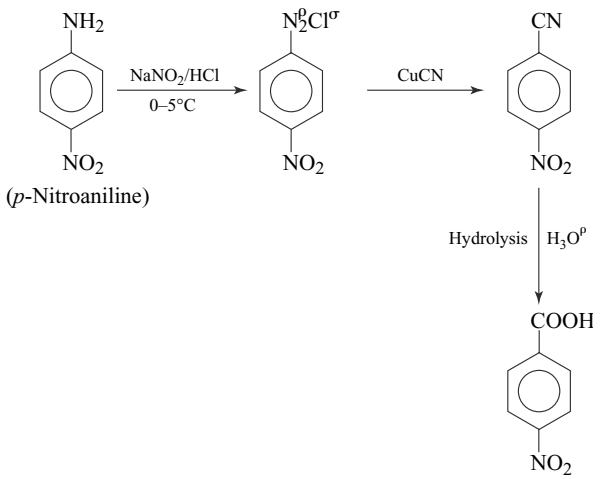

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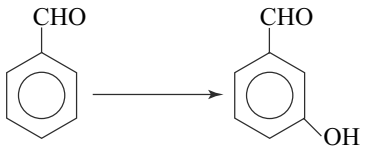
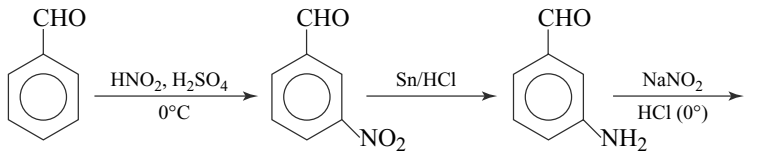
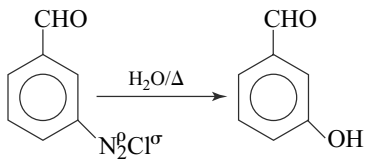


It is carried out carefully to avoid oxidation of the aldehyde group.





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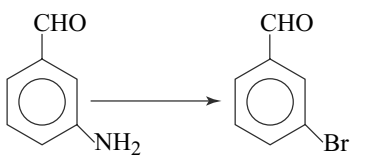

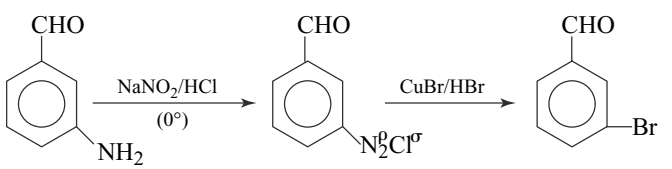

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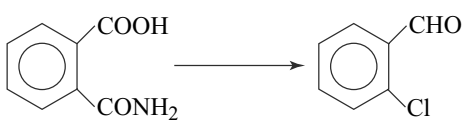
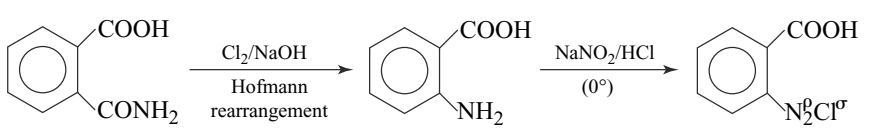
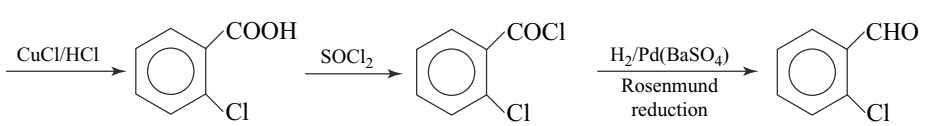
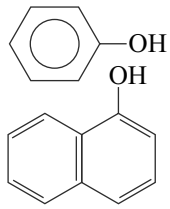






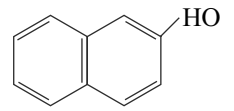
PHENOLS

Phenols are compounds in which the hydroxyl group (–OH) is directly attached to the aromatic nucleus (Ar–OH). Phenols differ from the aliphatic alcohols (R–OH) due to the aromatic ring. Phenols may be monohydric or polyhydric. Some common examples are given below.



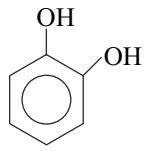
Phenol (hydroxybenzene)

1-Naphthol
(α-Naphthol)

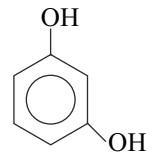


2-Naphthol
(β-Naphthol)

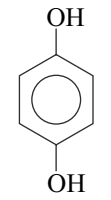
Di- and trihydric species occur in isomeric forms.



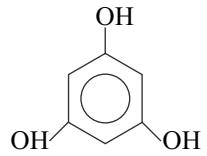
Catechol
(*o*-Dihydroxybenzene)



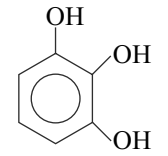
Resorcinol
(*m*-Dihydroxybenzene)



Hydroquinol
(*p*-Dihydroxybenzene)



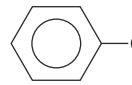
Phloroglucinol
(1,3,5-Trihydroxybenzene)



Pyrogallol
(1,2,3-Trihydroxybenzene)

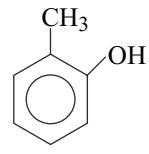
Another class of aromatic hydroxy compounds are those in which the hydroxyl group (–OH) is not attached to the aromatic nucleus but to an alkyl side chain.

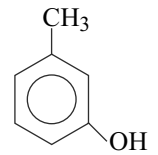
For example,

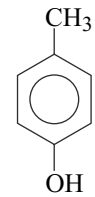


Benzyl alcohol
(Phenyl methanol)

These compounds are very much similar to aliphatic alcohols.
Hydroxy derivatives of toluene are called cresols. For example,



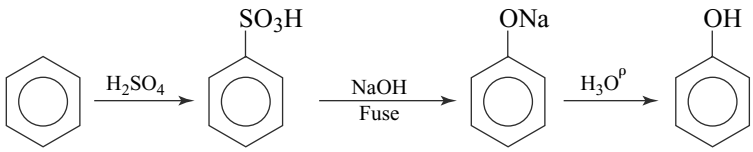




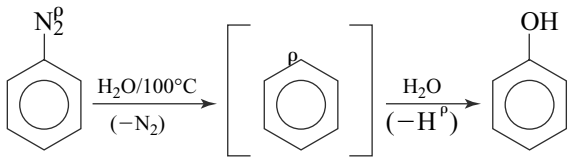
o-Cresol *m*-Cresol *p*-Cresol
(*o*-, *m*- and *p*-Methyl phenols)

Synthesis of Phenol

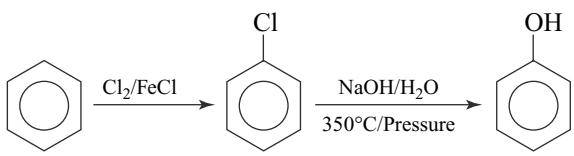
1. *From benzene sulphonic acid*
   Benzene sulphonic acid is fused with solid NaOH or KOH; the fused mass is dissolved in water and the solution is acidified. It gives phenol.



2. *From diazonium salt*
   Diazonium salt on boiling with water gives phenol.

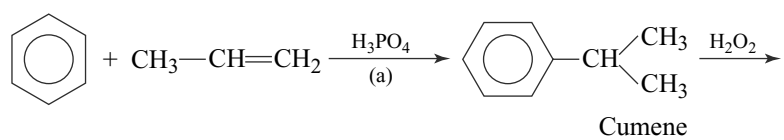


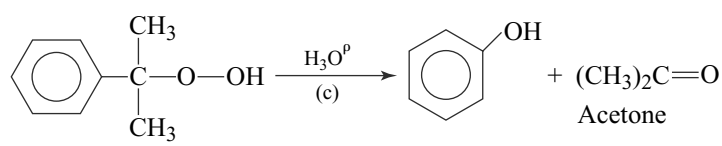
3. *From chlorobenzene*
   Chlorobenzene is used to introduce the hydroxyl group by nucleophilic substitution using strong alkali (NaOH). This is known as Dow's process.



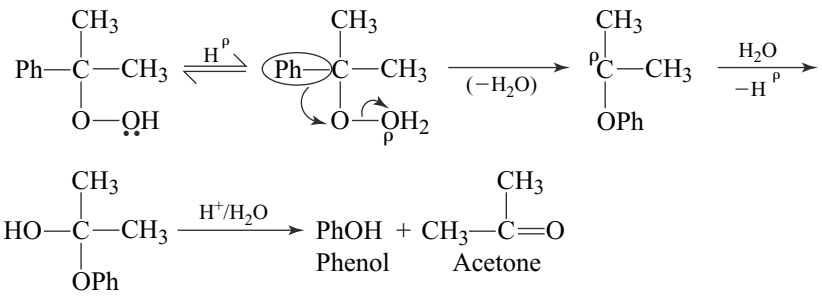
4. *From cumene*
   It is the most economic commercial synthesis of phenol. The steps involved in this synthesis are as under.
   (a) Conversion of benzene to cumene using propene and H_3PO_4 (F–C type alkylation).
   (b) Aerial oxidation of cumene to cumene hydroperoxide.
   (c) Acid-catalyzed rearrangement of hydroperoxide to phenol (Beckmann-type rearrangement).

This method also produces an industrially important compound called 'acetone' as the by-product.





The decomposition of hydroperoxide to phenol and acetone is believed to proceed in the following way.



Properties

1. Pure phenol is colourless crystalline solid but samples of it are slightly pink or brown due to air oxidation.
2. It has specific odour and is snake repellent.
3. It is poisonous and caustic (that is burns the skin).
4. Phenols are more acidic, more polar and able to form stronger H-bonds than the corresponding saturated alcohols. It is seen in the properties of phenol and cyclohexanol in the table below.

Property	Phenol	Cyclohexanol
MP (°C)	43	26
BP (°C]	181	161
Solubility g/100 g H_2O, 20°C	9.3	3.5
K_a	1.0×10^{-10}	$\sim 10^{-18}$

Phenols are more acidic than alcohols. Acidity of phenol and its derivatives is explained in the Chapter 4, *Organic acids and bases*.

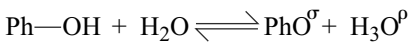
Chemical Reactions

Phenol has different sites of reaction. They may be located as follows:

1. Reaction of O–H bond.
2. 'C' versus O-alkylation of phenol.
3. Reactions of C–O bond.
4. Reactions of the aromatic ring.

Reaction of O–H bond

Phenols are acidic.



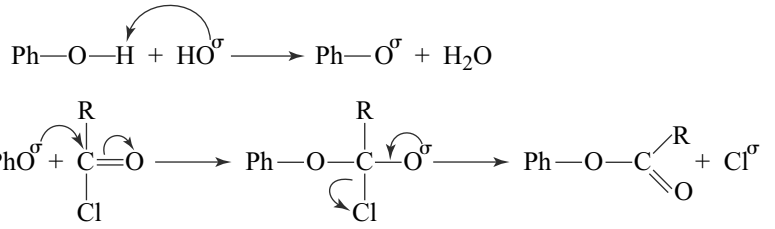
It turns blue litmus red and dissolves in alkalis to form salts, known as phenoxides.

However, PhOH acid is weak enough to react with $NaHCO_3$. A carboxylic acid liberates CO_2 with $NaHCO_3$. Thus, phenol and a carboxylic acid can be distinguished using $NaHCO_3$.

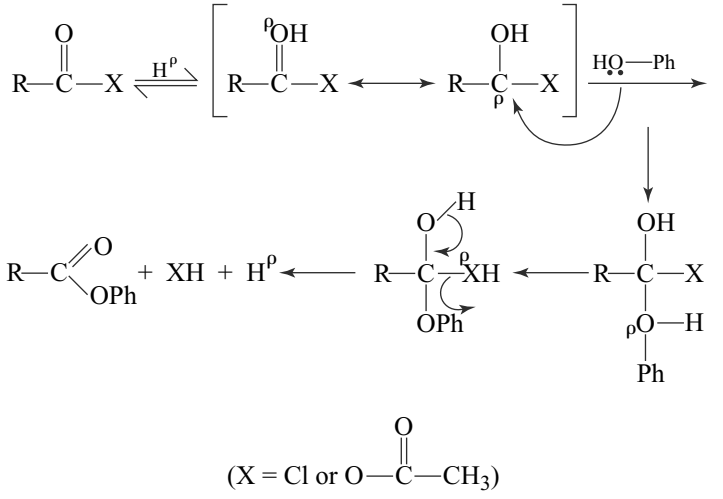
Formation of ester

Phenol reacts with acid chloride or acid anhydride to form an ester. This reaction involves breaking of O–H bond in phenol and formation of new C–O bond. It is catalysed by base or acid.

1. **Base-catalyzed reaction**



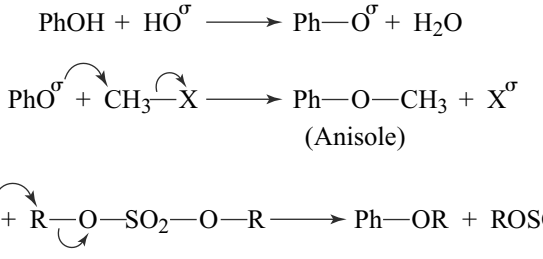
2. **Acid-catalysed reaction**



Phenolic esters upon heating with $AlCl_3$ undergo Fries rearrangement. It is explained under name reactions (Chapter 6).

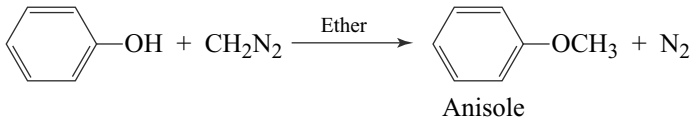
Formation of ether

Phenol converts into alkyl ether on reaction with alkyl halide or with dialkyl sulphate in weak alkaline solution.



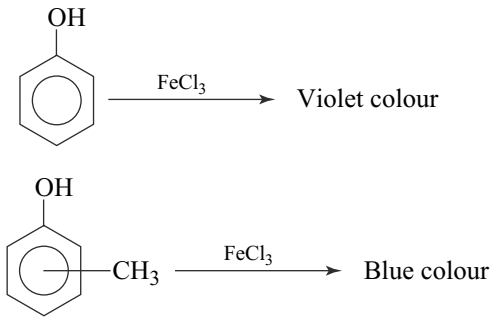
The reaction is of S_N2 type.

Phenol is acidic enough to form methoxy derivative with diazomethane.



Colour with $FeCl_3$

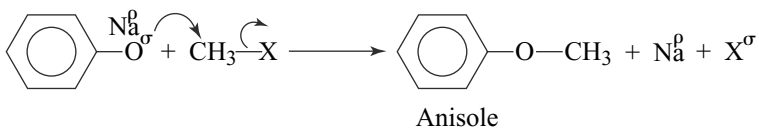
Almost all phenols give colours with $FeCl_3$ in dilute water or alcohol solution.



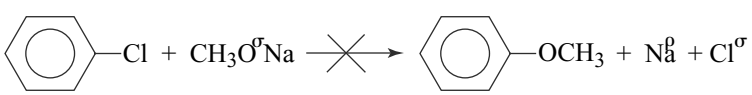
The coloured products are ferric phenoxides, $(PhO)_3Fe$. It absorbs visible light to give excited state. Electrons are delocalized over both the iron atom and the aromatic system. This reaction is used to characterize phenolic compounds using $FeCl_3$.

C versus O-alkylation of phenol

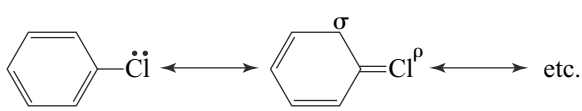
A phenoxide salt may undergo C and O-alkylation. Normally, O-alkylation is found after giving phenyl ether. This reaction proceeds by S_N2-mechanism. This reaction is known as *Williamson's synthesis*.



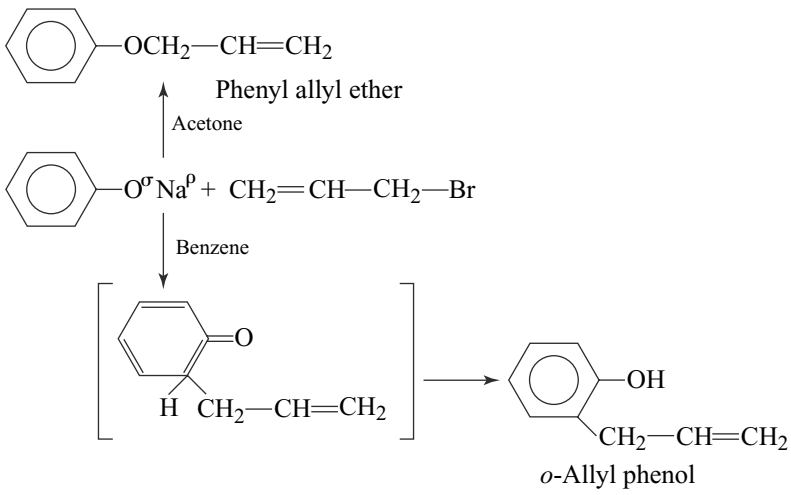
But the reaction of CH_3ONa with Ph–Cl does not undergo Williamson's synthesis.



It is because C–Cl bond in Ph–Cl has multiple bond nature and Cl is not replaced by CH_3O^- .



The reaction of phenoxide ion ($-O^-$) with allyl halide, however, is different and product depends upon solvent. In more polar solvents, *o*-allylation (acetone) while in non-polar solvents C–allylation (benzene) takes place leading to *o*-allyl phenol.

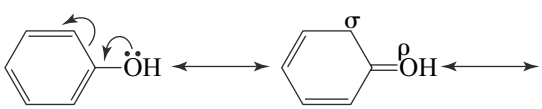


In non-polar solvents, the lack of dissociation of the $-O^-Na^+$ part of the phenoxide salt increases the steric hindrance at O– atom and makes attack on the ring more favourable.

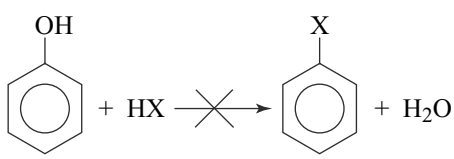
Also, allyl phenyl ether undergoes a rearrangement on heating to *o*-allyl phenol. It is known as *Claisen rearrangement* (see name reactions for details)

Reactions of the C–O bonds

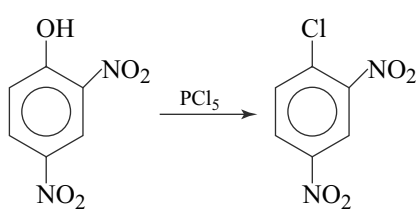
It is very difficult to break the C–O bonds in phenols or phenol derivatives (the other aromatic C–O bond also). The reason is C–O multiple bond nature due to conjugation with π-electrons of the ring.



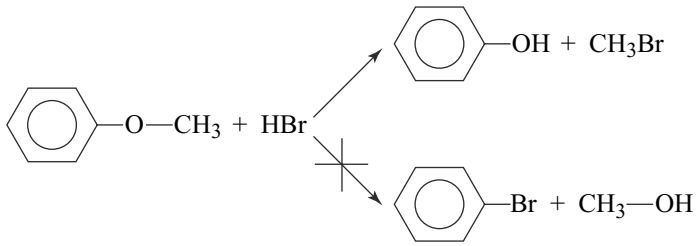
Thus,



But phenols having *o*- or *p*-nitro group are active towards nucleophile. Thus, 2,4-dinitrophenol is easily converted to 2,4-dinitrochlorobenzene with PCl_5.



Also cleavage of phenyl alkyl either with HBr or HI produces phenol and R–X is not an aryl halide or an alcohol.

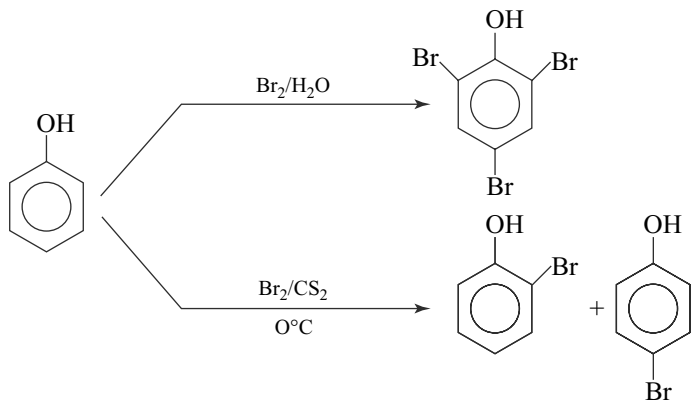


And diphenyl ether, Ph–O–Ph, does not react with HI even at 200°C (the Ph–O bond has multiple bond nature).

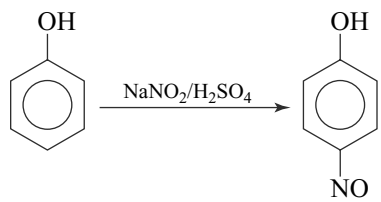
Reaction of the aromatic ring

The –OH and $-O^{\sigma}$ groups of phenol and phenoxide ion strongly activates benzene ring and are *o*- and *p*-directing (see orientation and reactivity).
Electrophilic substitutions, therefore, take place at *o*- and *p*-positions.

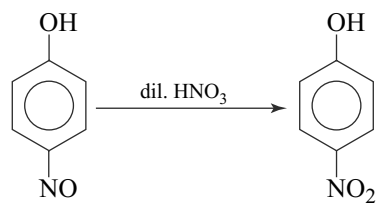
1. Phenol reacts rapidly with Br_2 in aqueous solution to give 2,4,6-tribromophenol. However, monobromoderivative is obtained when Br_2 is used in CCl_4 or CS_2 or $CHCl_3$ at 0°C.



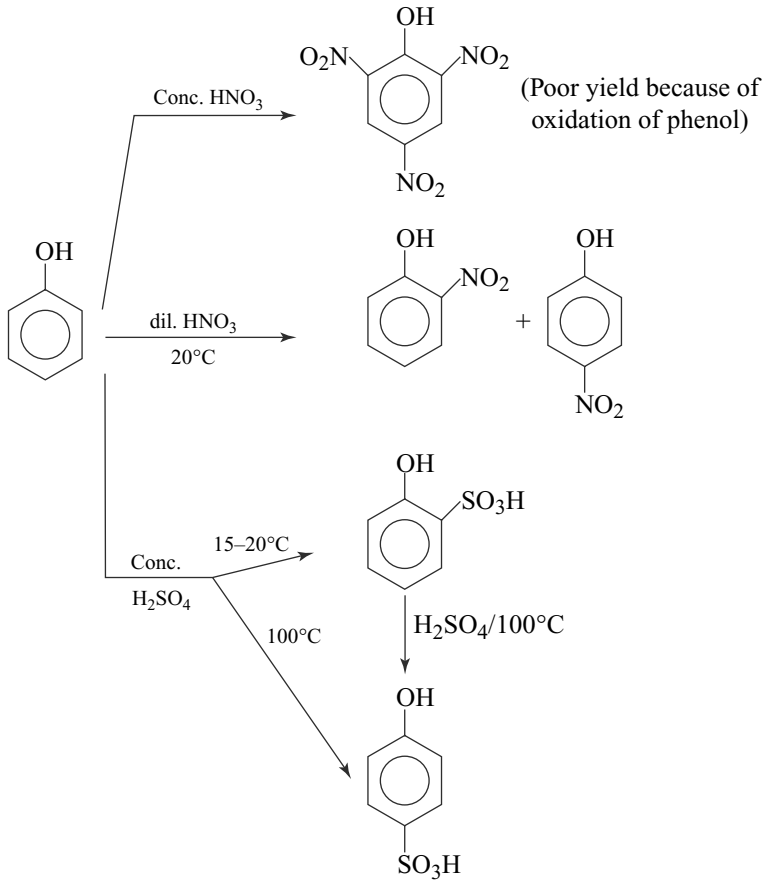
2. Phenol reacts with nitrous acid to give *p*- nitrosophenol.



Nitrosophenol is easily oxidized with dil. HNO_3 to nitrophenol. It is a good method of preparing *p*-nitrophenol.



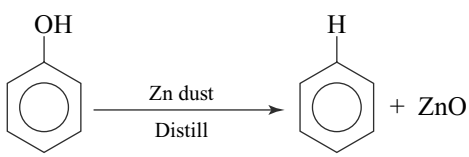
3. Some general electrophilic substitutions are given as under.



A number of electrophilic aromatic substitution reactions of phenol involve phenoxide ion. They are: (a) Kolbe reaction and (b) Reimer–Tiemann reaction (see name reactions).

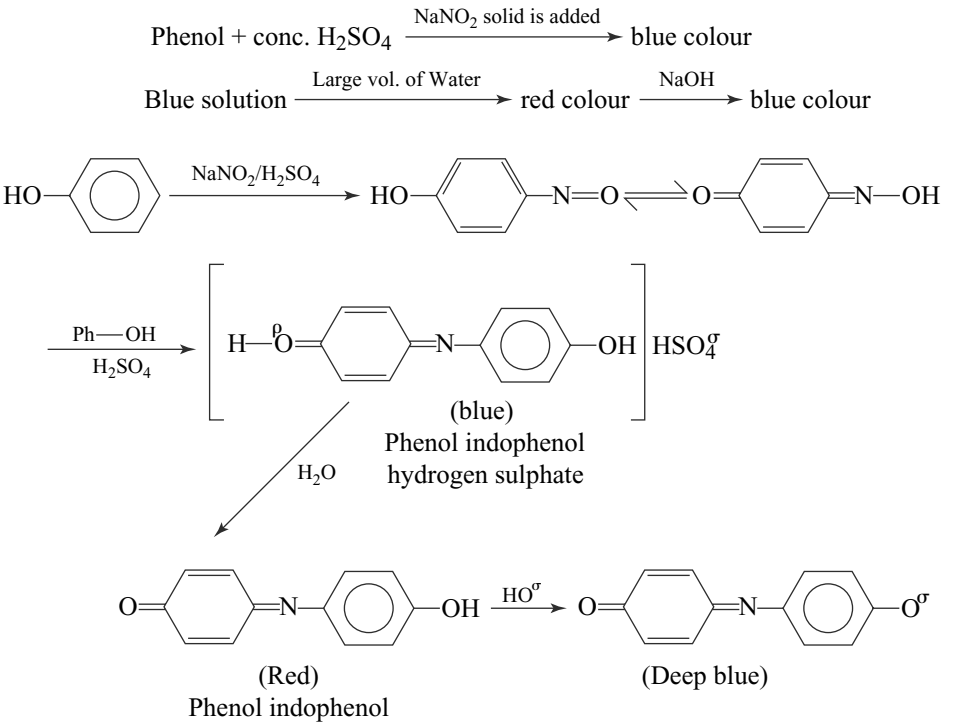
Replacement of –OH group by H

When phenol is distilled with Zn dust, benzene is formed.



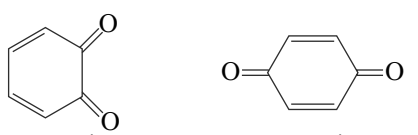
Tests of Phenol

1. Phenol dissolves in NaOH solution.
2. It gives violet colour with $FeCl_3$ solution due to the formation of ferric phenoxide.
3. It does not liberate CO_2 with $NaHCO_3$ (a distinction from carboxylic acids).
4. Liebermann reaction



QUINONES

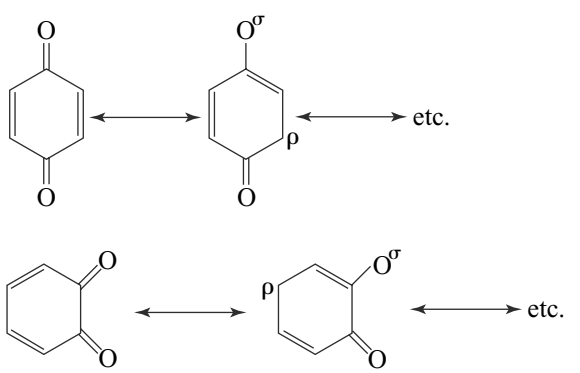
Quinones are conjugated cyclic diketones. For example,



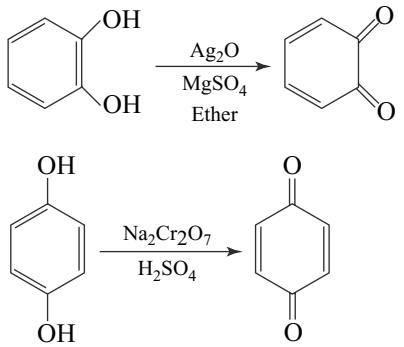
o-Benzoquinone *p*-Benzoquinone

In these compounds, the keto group and the double bonds are conjugated. Thus, strictly speaking, quinones are not aromatic compounds.

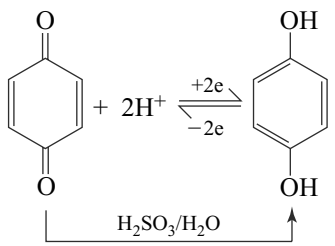
A variety of quinones have been prepared. The common examples are 1,2- (or *o*-) and 1,4 (or *p*-)-benzoquinones. They are stable due to resonance.



The *m*-quinone cannot have resonance structure like *o*- and *p*- quinones and so is not stable.
Quinones are prepared by oxidation of dihydroxybenzenes.

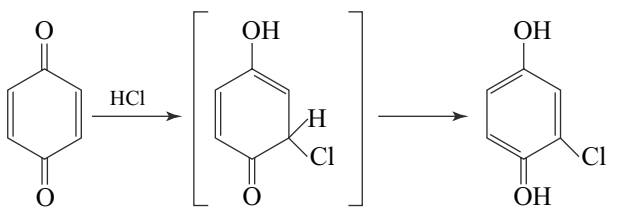


The *m*-dihydroxybenzenes undergo oxidation giving complex products but no *m*-quinone as it is not stable.
Quinones are readily reduced to the corresponding dihydroxy compounds.



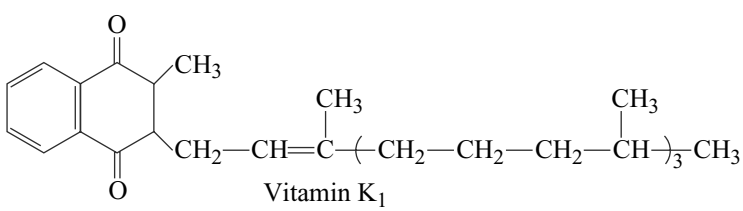
Addition Reactions of Quinones

Quinones are α,β-unsaturated ketones. Therefore, they undergo 1,4-addition reactions. For example, addition of HCl to *p*-benzoquinone.



Naturally Occurring Quinones

Many naturally occurring species have quinone type structure. The most important being Vitamin K_1 that has blood-clotting effect. It is found in green plants and is a substituted 1,4-naphtaquinone product.

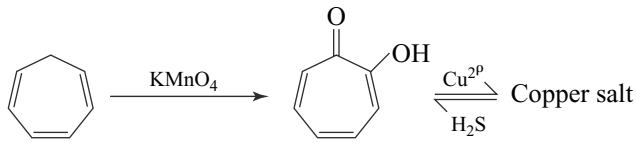


Vitamin K_1

Tropolones and Related Compounds

Tropolones are non-benzenoid aromatic compounds. This nucleus is found in several different kinds of natural products.

Tropolone can be prepared by oxidation of 1,3,5-cycloheptatriene (tropilidene) with alkaline $KMnO_4$.

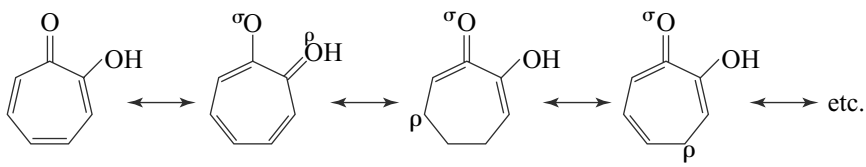


Tropilidene Tropolone

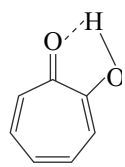
Tropolone has some aromatic character as it

1. Resists hydrogenation.
2. Undergoes nitration, sulphonation, etc.

It is stable due to resonance structures.

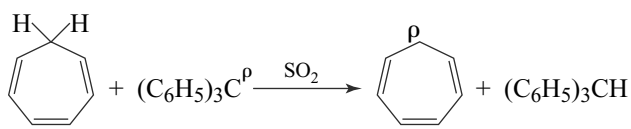


Intramolecular H-bonding also contributes towards its stability.



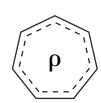
Tropolone

A fully aromatic species having seven-membered rings is tropylium cation. It has $(4n + 2)\pi$ electrons, that is it follows Huckel's rule.



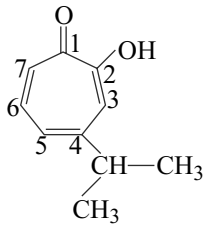
Tropilidene Tropylium cation

Tropylium cation is resonance stabilized.



Hybrid structure for tropylium ion

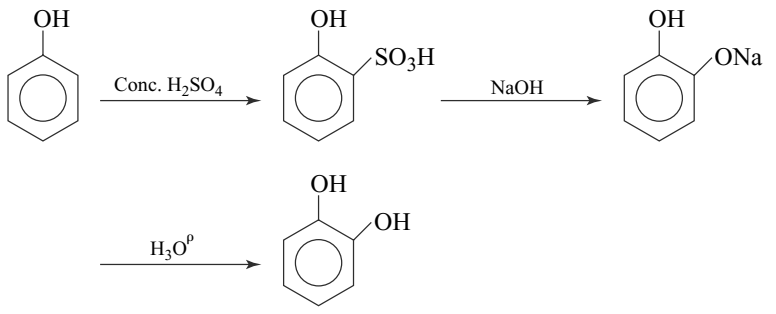
An example of naturally occurring compound, which contains tropolone, is β-thujaplicin (or hinokitiol). It has been isolated from the oil of the western red cedar. The wood of these trees rots very slowly because β-thujaplicin and its some isomers have fungicidal activity.



β-Thujaplicin
(4-Isopropyltropolone)

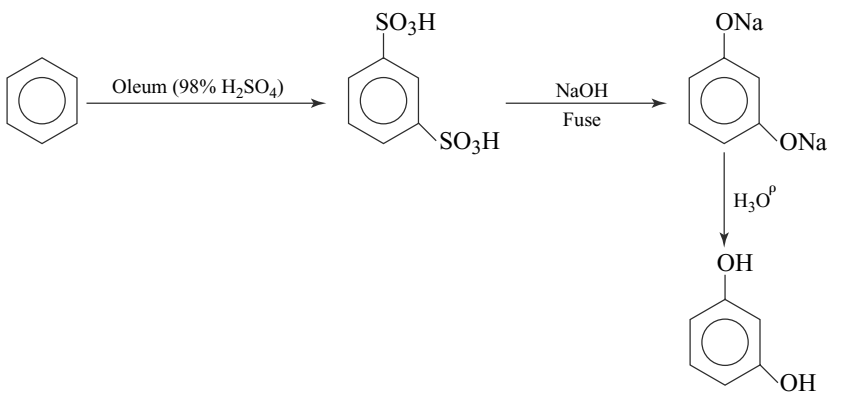
Synthesis of some hydroxy benzenes

1. Phenol to catechol (*o*-dihydroxybenzene)

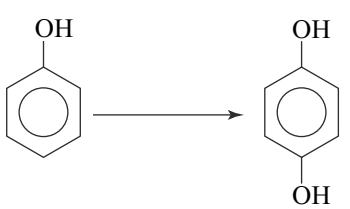


Catechol

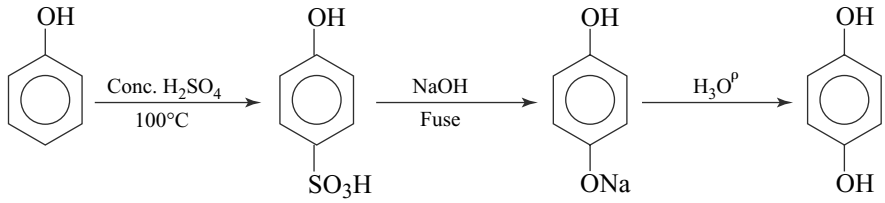
2. Benzene to resorcinol (*m*-dihydroxybenzene)



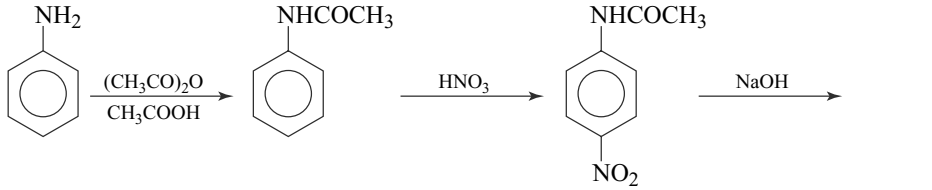
3.

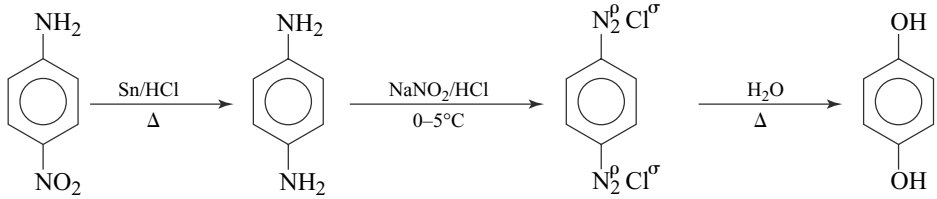


Phenol *p*-Dihydroxybenzene (quinol)
(Hydroquinone)

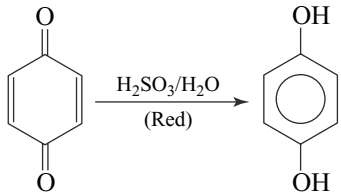


4. Aniline to quinol

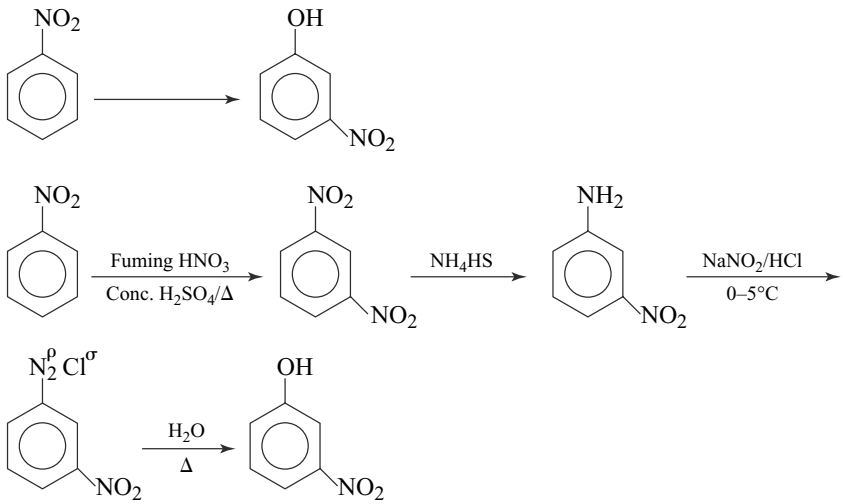




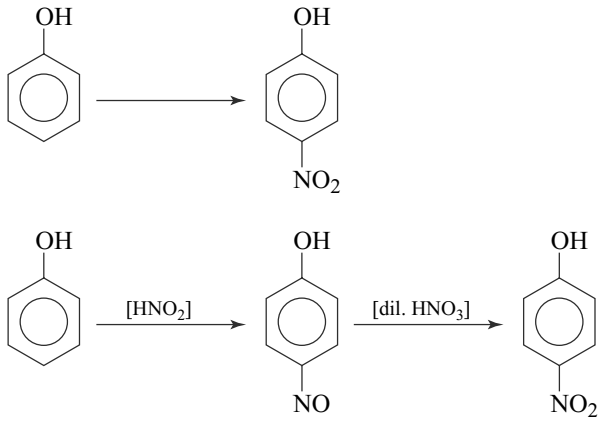
5. *p*-benzoquinone to hydroquinone



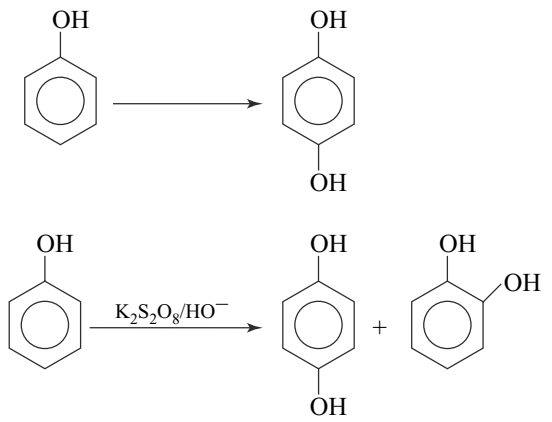
6. Nitrobenzene to *m*-nitrophenol



7. Phenol to *p*-nitrophenol

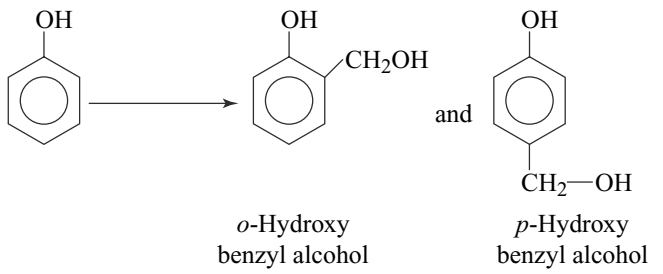


8. Elbs persulfate oxidation



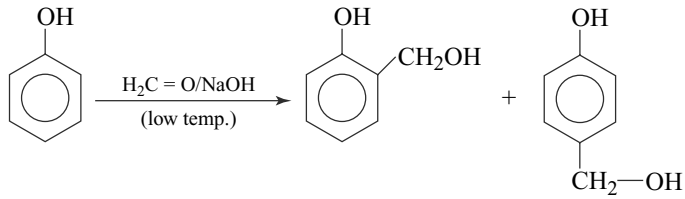
(Very small amount)

9. Phenol to *o*- and *p*-hydroxybenzyl alcohol



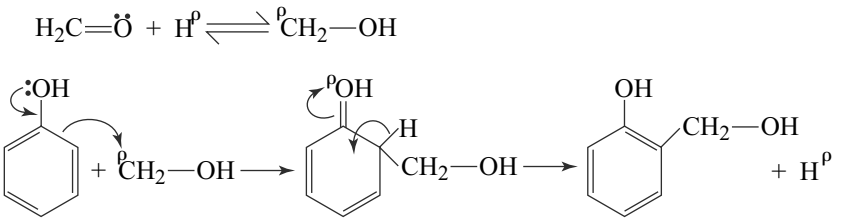
o-Hydroxy benzyl alcohol

p-Hydroxy benzyl alcohol

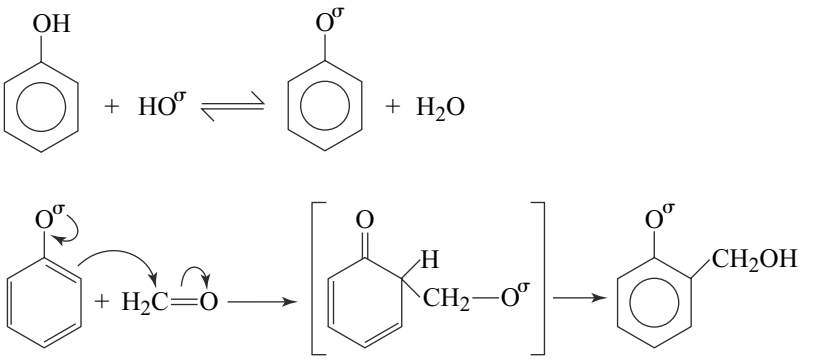


This reaction is known as *Leaderer–Manasse reaction*. It may be catalyzed by acid or base.

Acid-catalyzed reaction

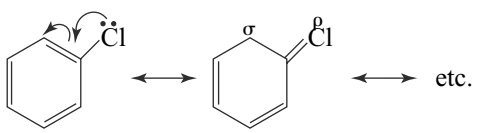


Base-catalyzed reaction



AROMATIC ALDEHYDES, KETONES AND ACIDS

The reactivity of halogen, amino (–$\ddot{N}H_2$) and hydroxyl (–$\ddot{O}H$) groups is greatly modified when they are linked to aromatic carbon. The reason being conjugation of electron pair at the substituent atom with ring the π-electrons.

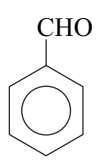


Other groups which are linked to an aromatic ring through C–C bond are also influenced by the ring, but to a lesser degree. Such groups include –CHO, $-COCH_3$, –COOH and –CN.

Aromatic Aldehydes

Most common is benzaldehyde (phenylmethanal) in which aldehyde group (–CHO) is directly attached to the benzene ring.

It is known as oil of bitter almonds as it is present in amygdalin (a glucoside) that occurs in bitter almonds.



Preparation

1. By the hydrolysis of benzyl chloride with dil. acid.

$$C_6H_5—CHCl_2 + H_2O \longrightarrow C_6H_5—CHO + 2HCl$$

2. *By Rosenmund reduction*
Reduction of benzoyl chloride by H_2 over Pd catalyst, poisoned by S quinoline to restrict reduction of aldehyde to alcohol.

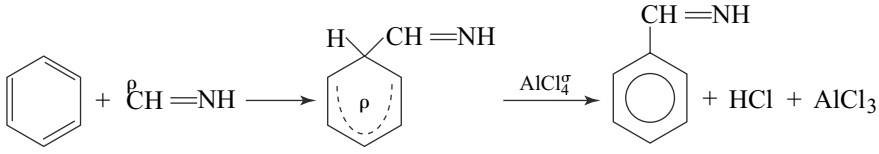
$$Ph—\overset{\overset{O}{\|}}{C}—Cl \xrightarrow[Pd\ (S\text{-quinoline})]{H_2} Ph—\overset{\overset{O}{\|}}{C}—H + HCl$$

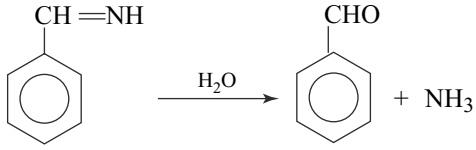
3. By oxidation of toluene with chromyl chloride (CrO_2Cl_2). It is known as *Etard's reaction*.

$$C_6H_5—CH_3 + 2CrO_2Cl_2 \xrightarrow{CCl_4} C_6H_5CH(OCrCl_2OH)_2 \xrightarrow{H_2O} C_6H_5—CHO$$

4. *By Gattermann synthesis*
Benzene is treated with HCN + HCl in the presence of $AlCl_3$. The product, aldimine, is decomposed with water to benzaldehyde.

$$HCN + HCl + AlCl_3 \rightleftharpoons \overset{\rho}{C}H{=}NH + AlCl_4$$

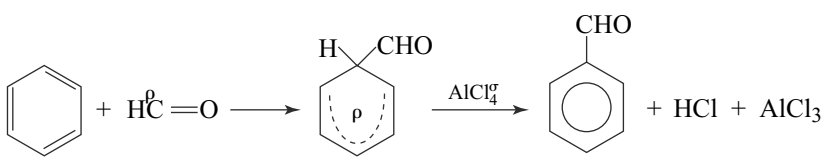




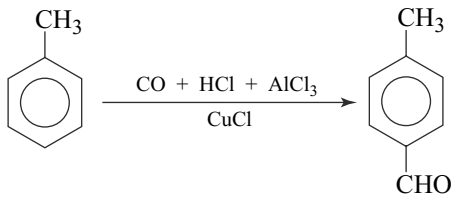
This reaction is applicable to phenols and phenolic ethers but not to nitrobenzene.

5. *Gattermann–Koch synthesis*
When benzene is treated with a mixture of CO + HCl in the presence of $AlCl_3$ and a trace of CuCl, benzaldehyde is formed.

$$CO + HCl + AlCl_3 \xrightarrow{CuCl} \overset{\rho}{H}C{=}O + AlCl_4^{\sigma}$$



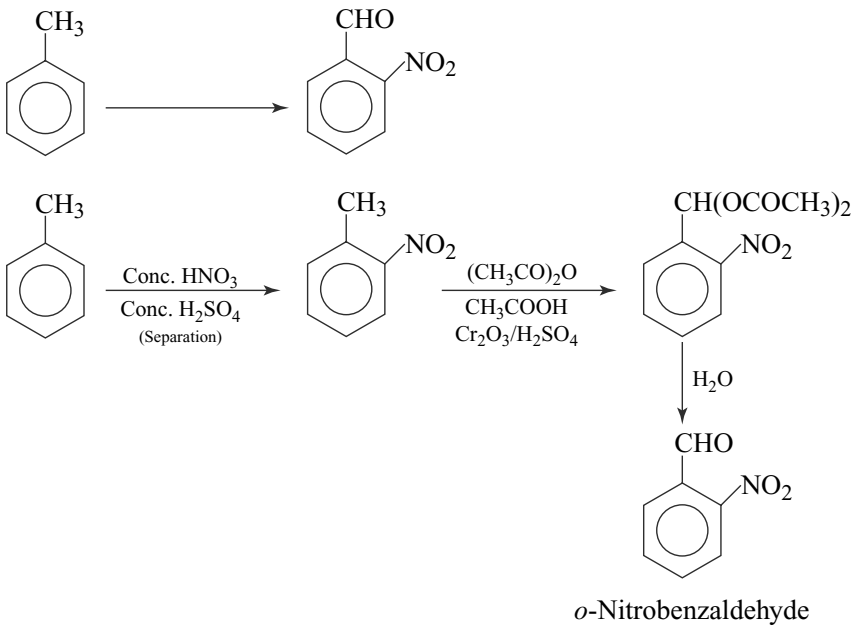
In toluene, aldehyde group is introduced into the para-position.



Gattermann–Koch synthesis is not applicable to phenols, their ethers and nitrobenzene.

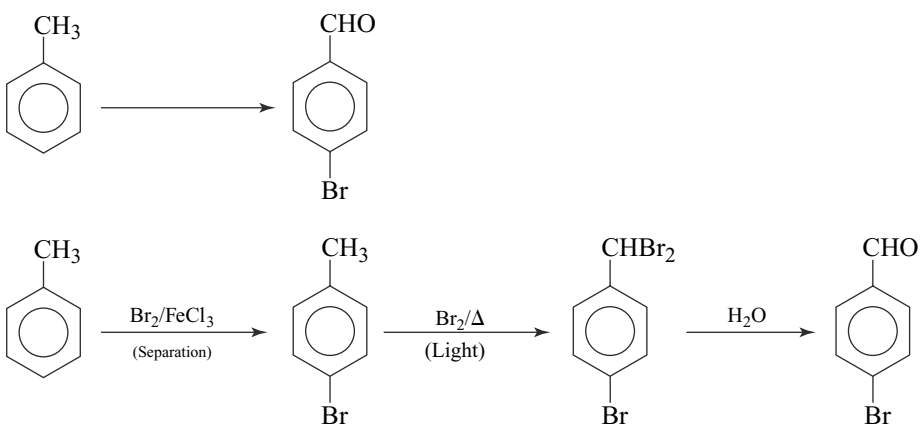
Benzaldehyde Derivatives

1.

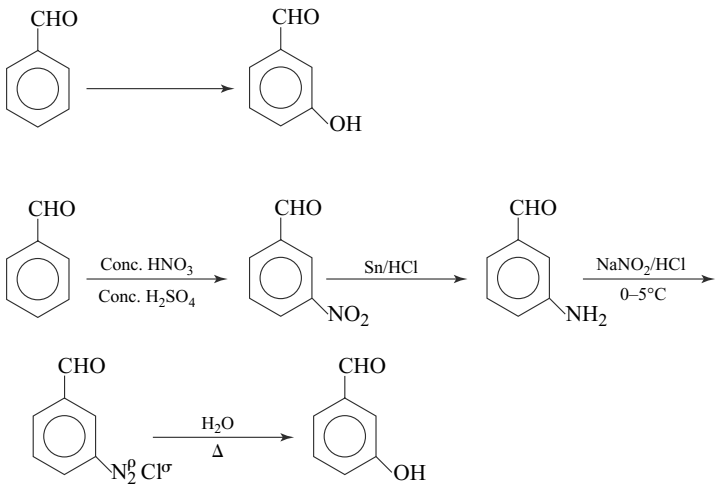


o-Nitrobenzaldehyde

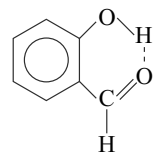
2.



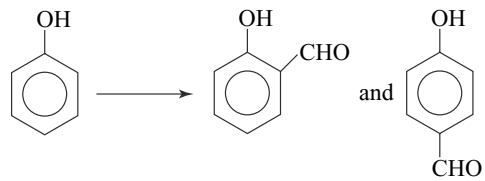
3.



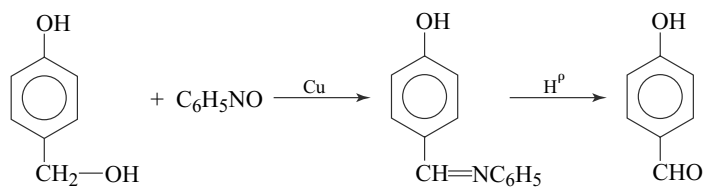
The –OH group of salicylaldehyde is not so reactive like *m*- and *p*- isomers. It may be due to intramolecular H-bonding which also explains its high volatility.



4. *o*- and *p*-hydroxybenzaldehydes from phenol.



o- and *p*-hydroxybenzyl alcohols are oxidized to the corresponding hydroxy aldehydes. This oxidation is carried out by nitrosobenzene in the presence of Cu catalyst.

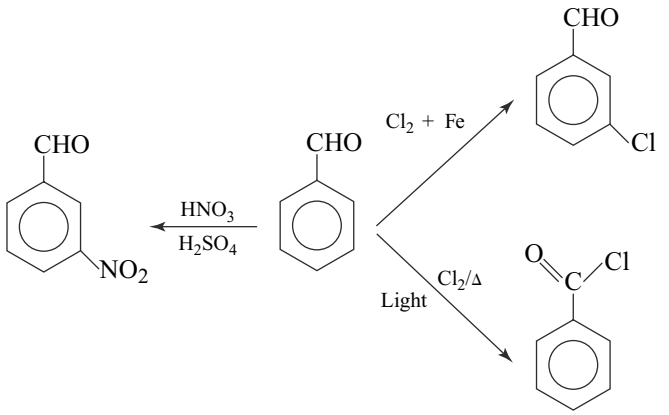


o- and *p*-hydroxybenzyl alcohols are obtained by Leaderer–Manasse reaction from phenol (see Chapter 7, Phenol).

Properties and reactions

Benzaldehyde is a colourless liquid having a strong almond like smell. It is used in perfumes and in the manufacture of flavourings and dyes.

1. Benzaldehyde gives usual substitution reaction of the aromatic ring. The –CHO group deactivates benzene ring and is *m*-directing.

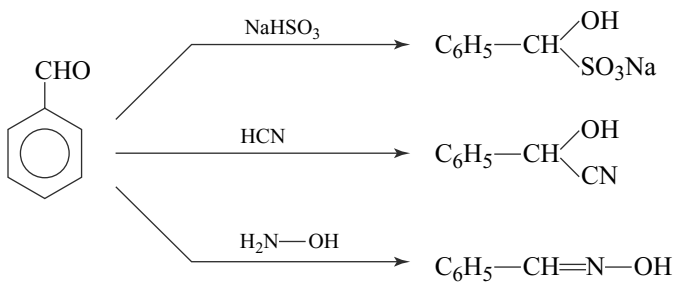


Benzoyl chloride

2. Benzaldehyde resembles aliphatic aldehydes but due to the presence of the benzene ring it differs from them in a number of ways.

Similarity with aliphatic aldehydes

1. It gives Schiff's reaction.
2. It reduces ammoniacal $AgNO_3$, that is readily oxidized. It is oxidized to benzoic acid when exposed to air.
3. It forms bisulphite addition compound with $NaHSO_3$, cyanohydrine with HCN, oxime with NH_2OH, etc.



Differences from aliphatic aldehydes

1. Benzaldehyde does not reduce Fehling's solution.
2. It fails to form simple addition compound with NH_3.
3. It does not polymerize, but undergoes Cannizzaro reaction with NaOH.

Condensation reactions of Ph–CHO

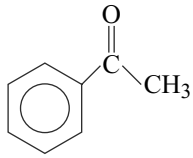
1. Benzoin condensation (see *Name reactions*).
2. Claisen condensation (see *Name reactions*).
   Benzaldehyde condenses with aldehydes (or Ketones) having α-H atom in the presence of dil. alkali. It is known as Claisen condensation.

$$C_6H_5 - CHO + CH_3 - CHO \xrightarrow{NaOH} \underset{\text{Cinnamaldehyde}}{C_6H_5 - CH = CH - CHO} + H_2O$$

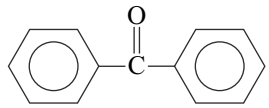
3. Perkin reaction (see Name reactions).

AROMATIC KETONES

Aromatic ketones may be either alkyl aryl or diaryl ketone. For example,



Acetophenone
(Methyl phenyl ketone)



Benzophenone
(Diphenyl ketone)

Preparation

Acetophenone

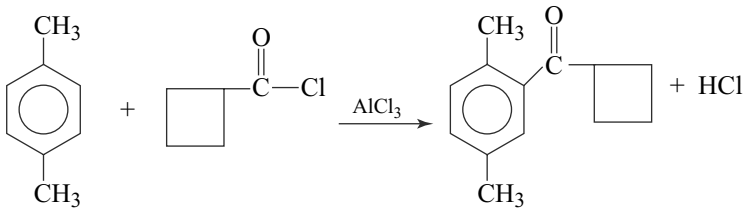
1. It may be prepared by distilling a mixture of calcium acetate and calcium benzoate.

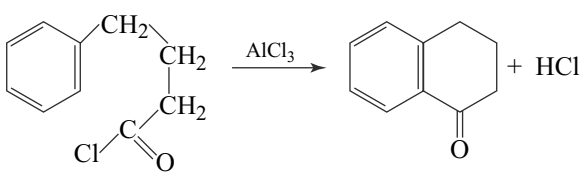
   $(CH_3COO)_2Ca + (C_6H_5COO)_2Ca \longrightarrow 2C_6H_5COCH_3 + 2CaCO_3$

   Iron salt of these acids gives better yield.
2. By Friedel–Crafts acylation reaction
   It is a good laboratory method. A wide variety of ketones can be synthesized (see name reaction).

$$C_6H_6 + CH_3{\cdot}COCl \xrightarrow{AlCl_3} C_6H_5COCH_3 + HCl$$

Some more examples are given below. $C_6H_6 + ClCH_2{\cdot}COCl \xrightarrow{AlCl_3} C_6H_5COCH_2Cl + HCl$

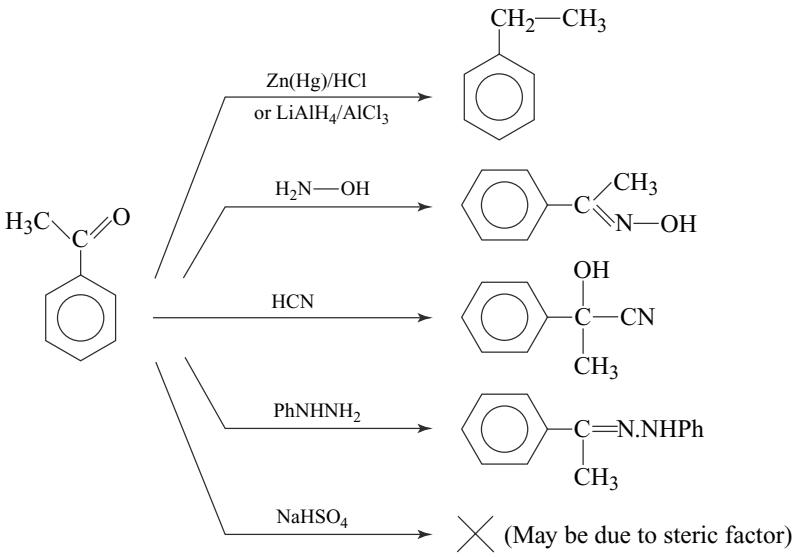
1. 

2. 

Tetralone

Properties and Reactions

1. Acetophenone is used in perfumery and as a hypnotic (hypnone).
2. It gives general reaction of >C=O group.



3. Oxidation

(a) Cold $KMnO_4$ forms phenylglyoxalic acid, which on further oxidation gives benzoic acid.

$$C_6H_5COCH_3 \xrightarrow{KMnO_4} C_6H_5COCOOH \xrightarrow{[O]} C_6H_5COOH$$

(b) Selenium dioxide (SeO_2) oxidizes acetophenone to phenylglyoxal.

$$C_6H_5COCH_3 + SeO_2 \longrightarrow C_6H_5{-}\overset{\overset{O}{\|}}{C}{-}CHO + H_2O + Se$$

(c) Baeyer–Villigar oxidation

Acetophenone undergoes Baeyer–Villiger oxidation with peracid, the main product is phenylacetate.

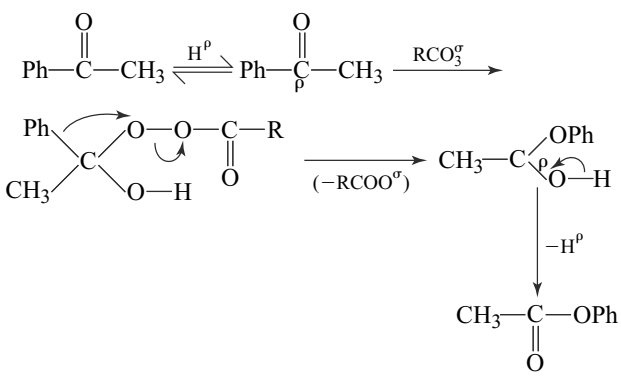
$$Ph{-}\overset{\overset{O}{\|}}{C}{-}CH_3 \xrightarrow[(Peracid)]{RCO_3H} CH_3{-}\overset{\overset{O}{\|}}{C}{-}OPh$$

Careful study of the reaction indicates the following.

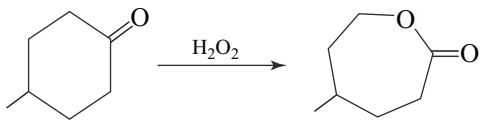
(i) It is an intramolecular rearrangement.

(ii) Key step is heterolytic cleavage of O–O bond (formed from a peracid and >C=O group).

(iii) The group, which supports a positive charge, migrates most easily.



The rearrangement is migration to an electron deficient oxygen atom. The migratory aptitude found is tert R > Sec R > Pri R.
Cyclic ketones also undergo this reaction and the product is a lactone (cyclic ester).



4. Willgerodt reaction
In this reaction, alkyl aryl ketone is converted into amide having the same number of C atoms by heating with aq. Yellow ammonium polysulphide, $(NH_4)_2\,S_x$

$$PhCOCH_3 \xrightarrow[\Delta]{\substack{(NH_4)_2S_X \\ H_2O}} PhCH_2CONH_2 + PhCH_2COONH_4$$
(Small amount)

The amido group is always formed at the end of the chain irrespective of its length. Thus,

$$PhCOCH_2—CH_2—CH_3 \xrightarrow[\Delta]{\substack{(NH_4)_2S_X \\ H_2O}} PhCH_2{\cdot}CH_2CH_2CONH_2$$
Butyrophenone — γ-Phenylbutyramide

BENZOPHENONE (DIPHENYL KETONE)

1. It may be prepared by heating calcium benzoate.

$$(C_6H_5COO)_2Ca \xrightarrow{\Delta} C_6H_5—\overset{\overset{O}{\|}}{C}—C_6H_5 + CaCO_3$$

2. By Friedel–Crafts reaction

$$C_6H_6 + C_6H_5COCl \xrightarrow{AlCl_3} C_6H_5—\overset{\overset{O}{\|}}{C}—C_6H_5 + HCl$$

Carbonyl chloride may also be used in place of benzoyl chloride.

$$2C_6H_6 + COCl_2 \xrightarrow{AlCl_3} C_6H_5—\overset{\overset{O}{\|}}{C}—C_6H_5 + HCl$$

Properties and Reactions

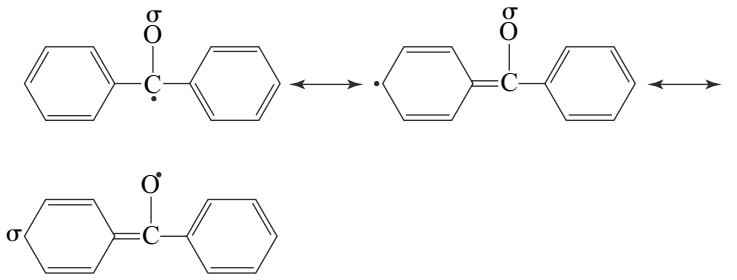
Benzophenone is colourless crystalline solid, mp, 49°C.
It has pleasant smell and is used in perfumes.

1. It gives general reaction of aromatic ketones.

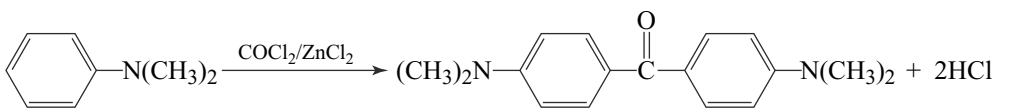
2. Benzophenone in ether dissolves sodium and gives a blue solution that contains a radical anion known as ketyl. Hydrogen (H_2) is not formed in this reaction.

$$(C_6H_5)_2C{=}O + Na \xrightarrow{Ether} (C_6H_5)_2\dot{C}{=}O^{\ominus}Na^{\oplus}$$

Aromatic ketyls are resonance stabilized.

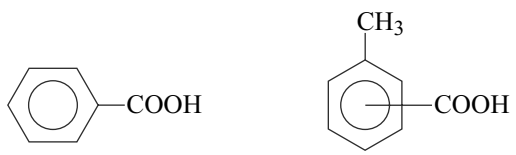


3. Michler's ketone
It may be taken as a derivative of benzophenone and may be prepared as follows.



AROMATIC CARBOXYLIC ACIDS

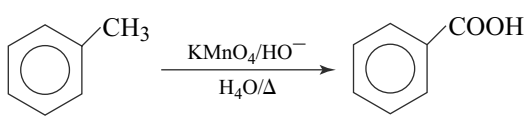
In aromatic carboxylic acids, the carboxyl group (–COOH) is linked directly to the aromatic ring.



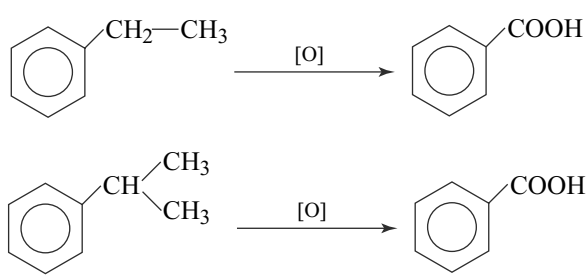
Benzoic acid *o*- or *m*- or *p*-Toluic acid

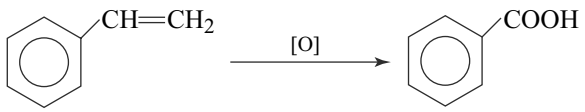
Preparations

1. Oxidation of alkylbenzenes by $KMnO_4$ or $K_2Cr_2O_7$ or HNO_3.



Entire side chain is oxidized to a carboxyl group, whatever be its size and nature.

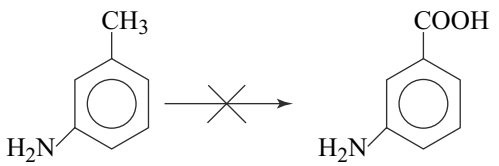




This reaction, thus, indicates the point of attachment of the side chain to the benzene ring.

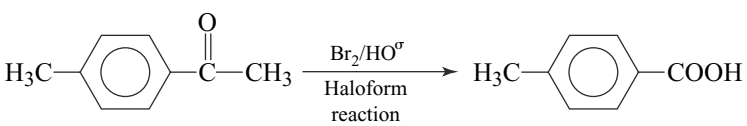
Some important points

1. Halogen and nitro group resist the effect of oxidation.
2. Presence of –OH or NH_2 in the ring may cause the ring to degrade before oxidation of the side chain.



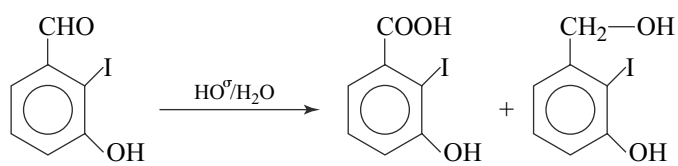
3. To protect a side chain, selective methods of oxidation are needed.

(a) Haloform reaction



The reagent acts upon methyl ketonic group ($-\overset{\overset{O}{\|}}{C}-CH_3$) only.

(b) Cannizzaro's reaction

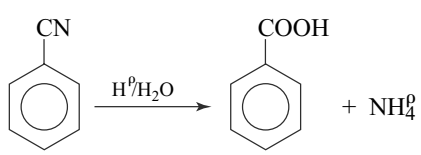


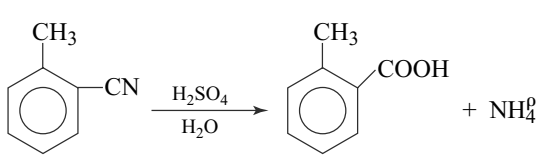
2-Iodo-3-hydroxy benzaldehyde

In this reaction, aldehyde disproportionates to acid and alcohol.

4. **Hydrolysis of nitrile**

Hydrolysis of nitrile by acid or base gives the corresponding acid.

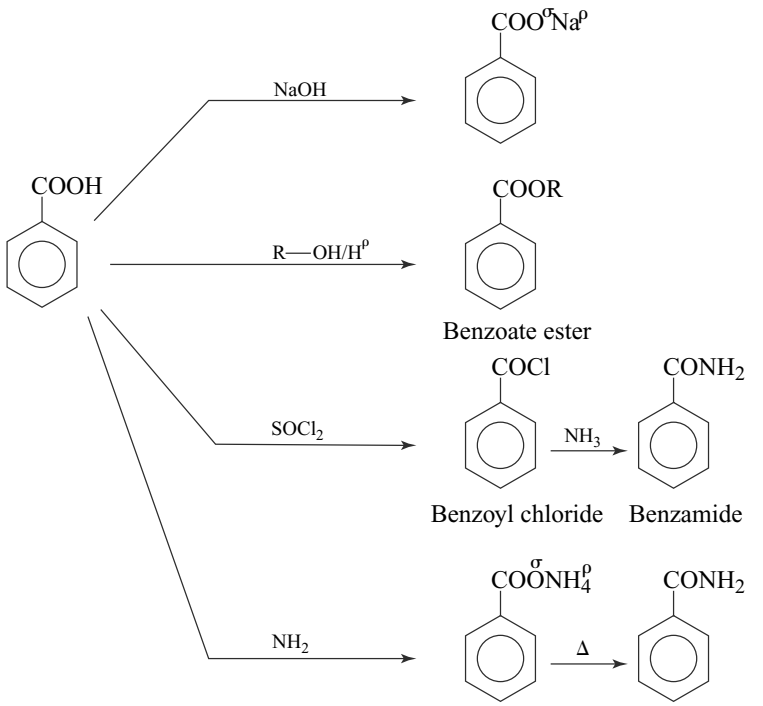




Properties and Reaction

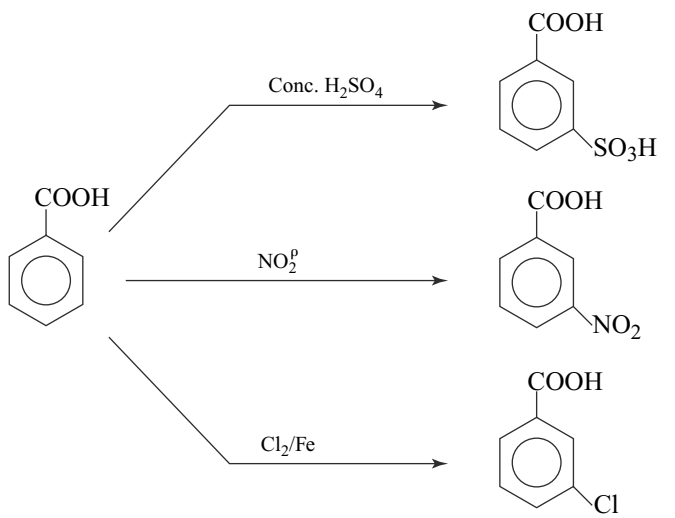
Benzoic acid is white crystalline solid, MP 122°C.
It is sparingly soluble in cold water, but more soluble in hot water.
Benzoic acid gives reactions of (a) –COOH group and (b) benzene ring.

Reaction of –COOH group



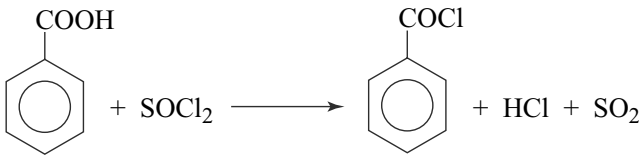
Reactions of benzene ring

The –COOH group is *m*-directing. Therefore, aromatic electrophilic substitution mainly gives *m*-derivatives.



Benzoyl chloride (BP 197°C)

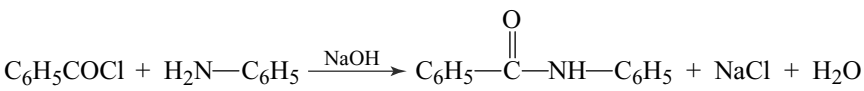
It is the first acid chloride to be discovered. It may be obtained by the reaction of benzoic acid with PCl_5 or better with $SOCl_2$.



This reaction is synthetically very useful as the side products are gaseous (HCl and SO_2) and no problem of separation remains.

Schotten–Baumann reaction

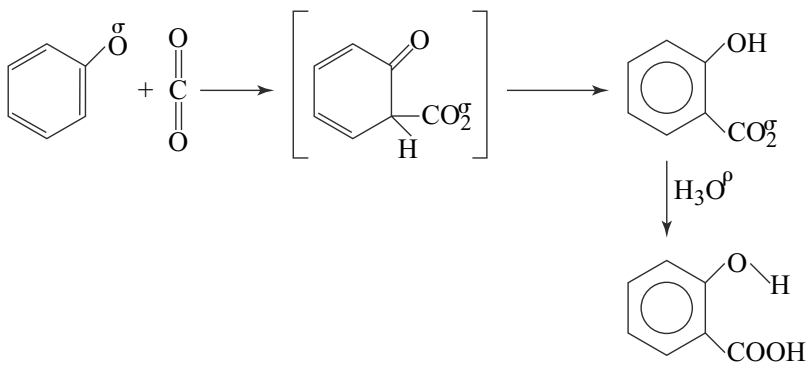
Compounds containing active H atom can be benzoylated using benzoylchloride and aq. NaOH. It is known as Schotten–Baumann reaction.



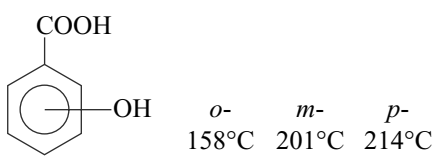
N-Benzoyl phenylamine

Some Important Derivatives of Benzoic Acid

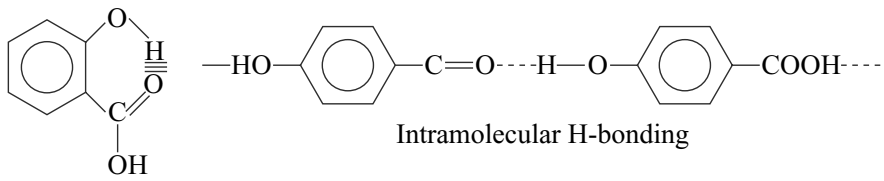
1. Salicylic acid (*o*-hydroxy benzoic acid)
It can be made by Kolbe acid synthesis (see *Name Reactions*).



Among the three isomeric hydroxy acids, salicylic acid has the lowest MP.



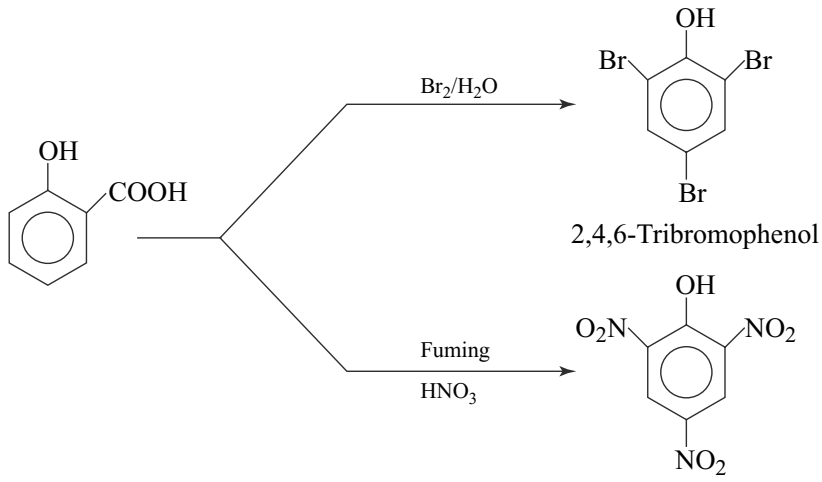
It is because of the fact that the –OH and –COOH groups in salicylic acid are locked in intramolecular H-bonding. The *m*- and *p*-isomers form interamolecular H-bond.



Intramolecular H-bonding

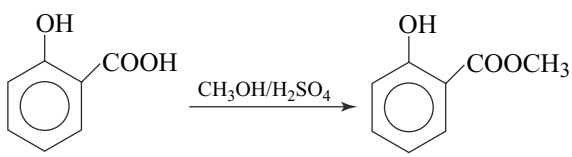
Intramolecular H-bonding

Salicylic acid behaves as a phenol also and gives violet colour with $FeCl_3$.
The carboxyl group of salicylic acid is replaced during nitration and reaction with bromine water.



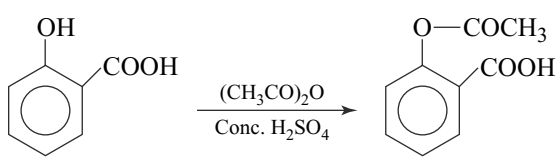
Important Derivatives of Salicylic Acid

1. Methyl salicylate (Oil of wintergreen BP 224°C) It is used in perfumery and as a flavouring substance in tooth pastes and tooth powders and for curing rheumatic pain.



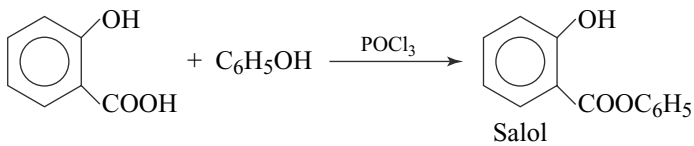
Methyl salicylate

2. Acetylsalicylic Acid (Aspirin, MP 135°C)
It has medicinal use as an analgesic and antipyretic. It also thins blood (girls are advised not to take disprin as an analgesic).



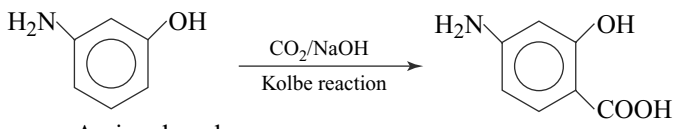
Aspirin

3. Phenyl salicylic acid (Salol, MP 43°C)
It is used in medicine as an internal antiseptic.



Salol

4. *p*-Aminosalicylic acid (PAS)
It is used with antibiotic (streptomycin) for the treatment of TB.

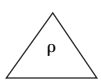


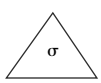
m-Aminophenol PAS

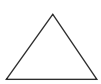
PROBLEMS

Objective-Type Questions

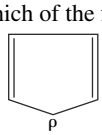
1. Which of the following will be aromatic?

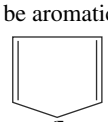
(a) 

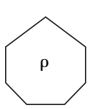
(b) 

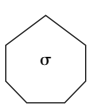
(c) 
(d)

2. Which of the following will be aromatic?

(a) 

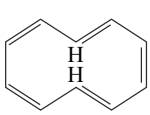
(b) 

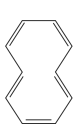
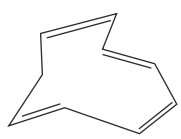
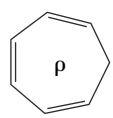
(c) 

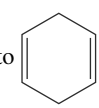
(d) 

3. Aniline under acidic medium, when chlorinated, produces
(a) *o*-chloro aniline
(b) *m*-chloro aniline
(c) *p*-chloro aniline
(d) mixture of orto- and para-chloro aniline

4. Which of the following is aromatic?

(a) 

(b) 
(c) 
(d) 

5. The conversion of benzene into  using liquid ammonia and Li in ethanol is known as
(a) Friedel–Crafts reaction (b) Etard reaction
(c) Birch reduction (d) none of these

6. The reaction of toluene with Cl_2 in the presence of light and heat followed by treatment with aq. NaOH gives
(a) *p*-cresol (b) *o*-cresol
(c) 2,4-dihydroxytoluene (d) benzoic acid

7. Phenol reacts with Br_2 in CS_2 at low temperature to give
(a) *m*-promophenol (b) *o*- and *p*-bromophenol
(c) *p*-bromophenol (d) 2,4,6-tribromophenol

8. When phenol is treated with excess of Br_2, the water produced is
(a) 2,4,6-tribromophenol
(b) *m*-bromophenol
(c) 2,4-dibromophenol
(d) *o*- and *p*-bromophenol

9. Mark correct order of hydrolysis of the following acid halides.

1. C_6H_5COCl 2. p-$O_2NC_6H_4COCl$
3. p-$CH_3OC_6H_4COCl$

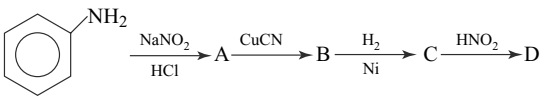
(a) 1 > 3 > 2 (b) 1 > 2 > 3
(c) 2 > 1 > 3 (d) 3 > 2 > 1

10. What is the reaction intermediate in the following reaction?

$$C_6H_6 \xrightarrow[\text{(ii) } NaNH_2 \text{ in } NH_3 \text{ at } -32°C]{\text{(i) } Br_2/Fe} C_6H_5NH_2$$

(a) Nitrene (b) Benzyne
(c) Carbonium ion (d) Free radical

11. Aniline in a set of reactions yielded a product D, which is



(a) C_6H_5NHOH (b) $C_6H_5NH\,CH_2CH_3$
(c) $C_6H_5CH_2NH_2$ (d) $C_6H_5CH_2OH$

12. Electrolytic reduction of nitrobenzene in weak acidic medium gives
(a) N-phenylhydroxylamine (b) nitrosobenzene
(c) aniline (d) p-hydroxylaniline

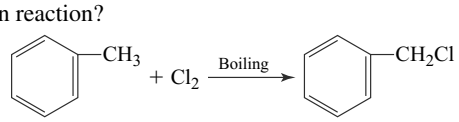
13. In a set of the given reactions, acetic acid yielded a product C.

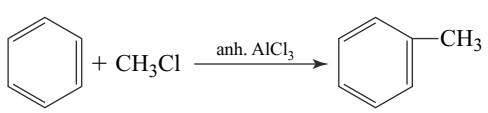
$$CH_3COOH + PCl_5 \longrightarrow A \xrightarrow[\text{anh. } AlCl_3]{C_6H_6} B \xrightarrow[\text{Ether}]{C_2H_5MgBr} C$$

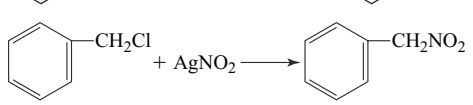
Product C would be
(a) $CH_3CH(OH)C_2H_5$ (b) $CH_3COC_6H_5$
(c) $CH_3CH(OH)C_6H_5$ (d) $CH_3-C(C_2H_5)(OH)-C_6H_5$

14. The correct order of reactivity towards the electrophilic substitution of the compounds aniline (I), benzene (II) and nitrobenzene (III) is
(a) III > II > I (b) II > III > I
(c) I < II < III (d) I > II > III

15. Which one of the following is a free-radical substitution reaction?

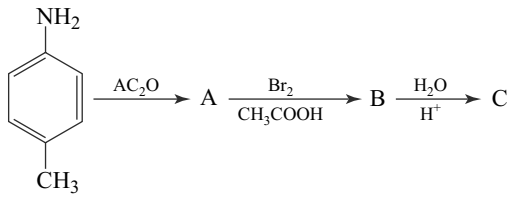
(a) 

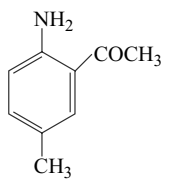
(b) 

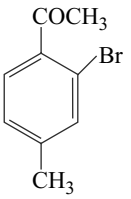
(c) 

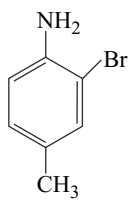
(d) $CH_3CHO + HCN \longrightarrow CH_3CH(OH)CN$

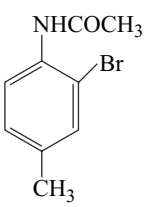
16. The final product C obtained in the reaction given below is



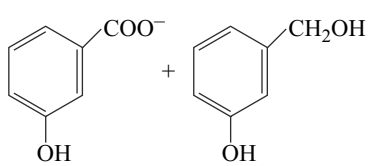
(a) 

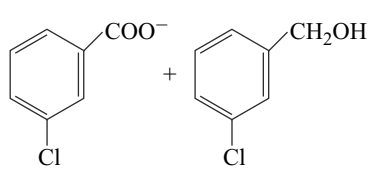
(b) 

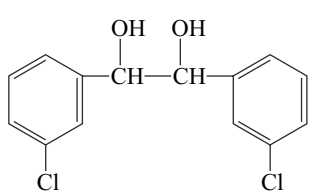
(c) 

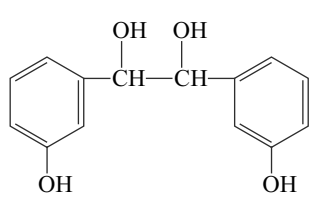
(d) 

17. When m-chlorobenzaldehyde is treated with 50 per cent KOH solution, the product(s) obtained is/are

(a) 

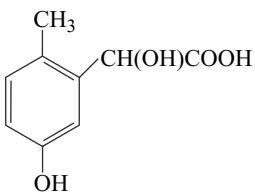
(b) 

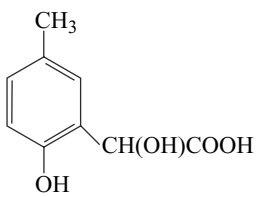
(c) 

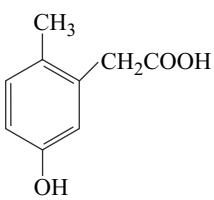
(d) 

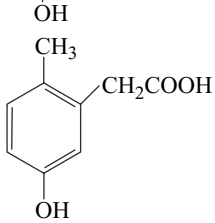
18. Benzamide on reaction with $POCl_3$ gives
(a) aniline (b) chlorobenzene
(c) benzyl amine (d) benzonitrile

19. *p*-Cresol reacts with chloroform in alkaline medium to give the compound A, which adds hydrogen cyanide, to form the compound B. The latter on acidic hydrolysis gives chiral carboxylic acid. The structure of the carboxylic acid is

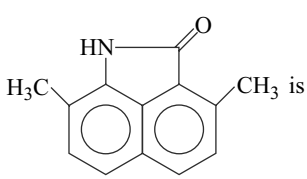
(a) 

(b) 

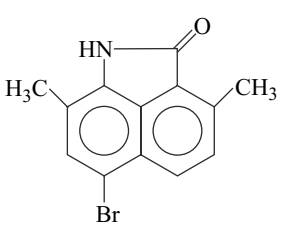
(c) 

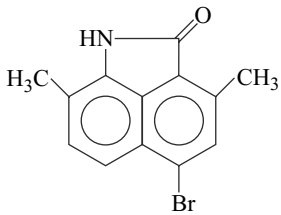
(d) 

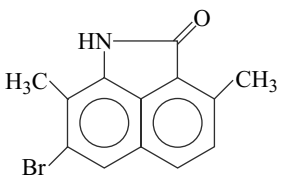
20. The major product is obtained when Br_2/Fe is treated with

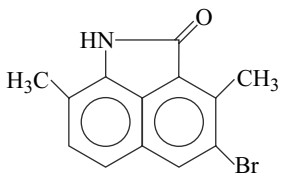


is

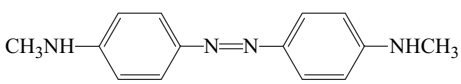
(a) 

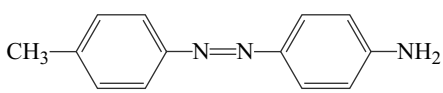
(b) 

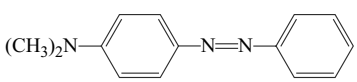
(c) 

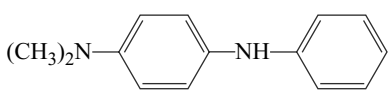
(d) 

21. Aniline when diazotized in cold and then treated with dimethyl aniline gives a coloured product. Its structure would be

(a) 

(b) 

(c) 

(d) 

22. The reaction of toluene with chlorine in presence of ferric chloride gives predominantly
(a) benzoyl chloride (b) *m*-chlorotoluene
(c) benzyl chloride (d) *o*- and *p*-chlorotoluene

23. Chlorination of toluene in the presence of light and heat followed by treatment with aqueous NaOH gives
(a) *o*-cresol (b) *p*-cresol
(c) 2,4-dihydroxytoluene (d) benzoic acid

24. The treatment of benzene with benzoyl chloride in the presence of $AlCl_3$ gives
(a) benzaldehyde (b) benzophenone
(c) diphenyl (d) cyclohexane

25. Chlorination of toluene with excess of chlorine under the condition of light and heat produces
(a) *o*-chlorotoluene (b) *p*-chlorotoluene
(c) benzyl chloride (d) benzotrichloride

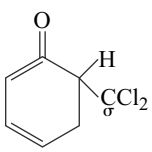
26. Picric acid is
(a) 2-nitrophenol (b) 4-nitrophenol
(c) 2,6-dinitrophenol (d) 2,4,6-trinitrophenol

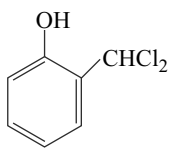
27. Chlorobenzene can be prepared by reacting aniline with
(a) hydrochloric acid
(b) cuprous chloride
(c) chlorine in the presence of anhydrous aluminium chloride.
(d) nitrous acid followed by heating with cuprous chloride.

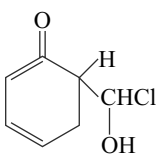
28. Activation of benzene ring by $-NH_2$ in aniline can be reduced by treating with
(a) dilute HCl (b) ethyl alcohol
(c) acetic acid (d) acetyl chloride

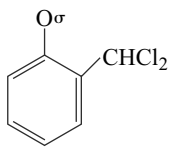
29. The reduction of $PhNO_2$ with $Zn/NH_4Cl(aq)$ gives
(a) PhNHOH (b) $PhNH_2$
(c) PhNHNHPh (d) PhON

30. When phenol is reacted with $CHCl_3$ and NaOH followed by acidification, salicylaldehyde is obtained. Which of the following species are involved in the above-mentioned reaction as intermediates?

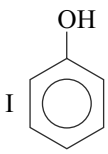
(a) 

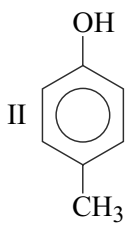
(b) 

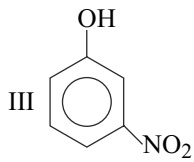
(c) 

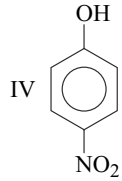
(d) 

31. In the following compounds, the order of activity is

(a) 

(b) 

(c) 

(d) 

(a) III > IV > I > II (b) I > IV > III > II
(c) II > I > III > IV (d) IV > III > I > II

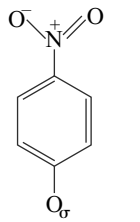
32. In the reaction, *p*-chlorotoluene with KNH_2 in liquid NH_3, the major product is
(a) *o*-toluidine (b) *m*-toluidine
(c) *p*-toluidine (d) *p*-chloroaniline

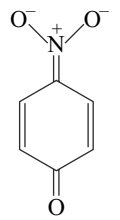
33. *p*-Chloroaniline and anilinium hydrochloride can be distinguished by
(a) Sandmeyer reaction (b) $NaHCO_3$
(c) $AgNO_3$ (d) Carbylamine test

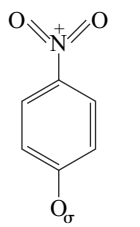
34. Benzyl chloride ($C_6H_5CH_2Cl$) can be prepared from toluene by chlorination with
(a) SO_2Cl_2 (b) $SOCl_2$ (c) Cl_2 (d) NaOCl

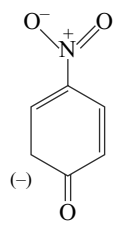
35. Benzenediazonium chloride on reaction with phenol in weak basic medium gives
(a) diphenyl either (b) *p*-hydroxyazobenzene
(c) chlorobenzene (d) benzene

36. The most unlikely representation of resonance structure of *p*-nitrophenoxide ion is

(a) 

(b) 

(c) 

(d) 

37. Toluene, when treated with Br_2/Fe, gives *p*-bromotoluene as the major product because the CH_3 group
(a) is *o*- and *p*-directing
(b) is *meta* directing
(c) activates the ring by hyperconjugation
(d) deactivates the ring

38. Benzoyl chloride is prepared from benzoic acid by

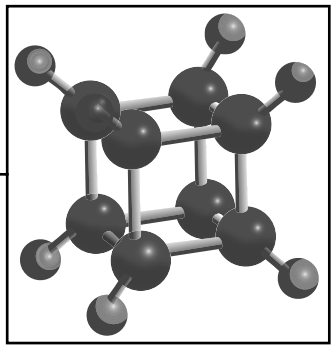
(a) Cl_2, hν (b) SO_2Cl_2

(c) $SOCl_2$ (d) Cl_2, H_2O

Answers

1. (a)	2. (b)	3. (b)	4. (d)	5. (c)
6. (d)	7. (b)	8. (a)	9. (c)	10. (b)
11. (d)	12. (a)	13. (d)	14. (d)	15. (a)
16. (c)	17. (b)	18. (d)	19. (b)	20. (a)
21. (c)	22. (d)	23. (d)	24. (b)	25. (d)
26. (d)	27. (d)	28. (d)	29. (a)	30. (a,b,d)
31. (b)	32. (b)	33. (c)	34. (c)	35. (b)
36. (c)	37. (a,c)	38. (c)		

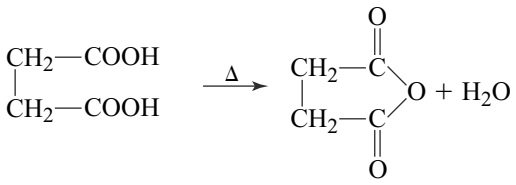
CHAPTER 8



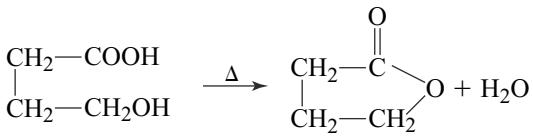
FORMATION OF RING

Ring formation is an important reaction in organic chemistry. So, this is a separate chapter about formation of rings in carbon compounds.

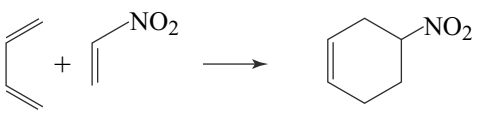
Ring formation may take place when functional groups in the same molecule react intramolecularly. For cyclization to take place, the functional groups should favourably be situated with respect to one another. Two separate species may also react to form a ring. For example,



Succinic anhydride

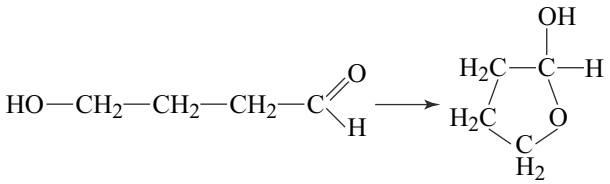


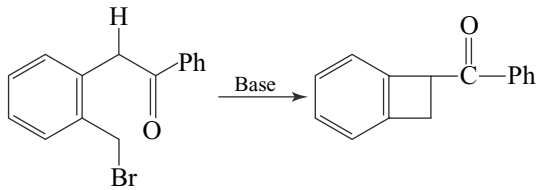
γ-Hydroxybutric acid γ-Butyrolactone



4-Nitrocyclohexene

Spontaneous cyclization occurs with γ- and δ-hydroxyaldehydes and ketones to form hemiacetals.

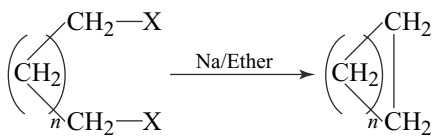




Variety of reactions can lead to ring formation. Some common of them are given below.

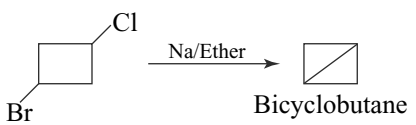
INTERNAL WURTZ REACTION

The α,ω-dihaloalkanes cyclize by Wurtz reaction.



The *n* can be as less as 1 or it may be greater than 6, i.e., small and big rings can be created.

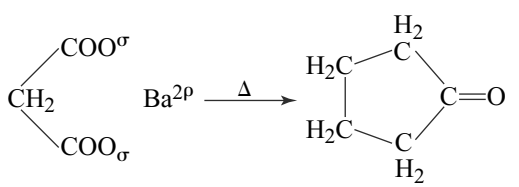
One highly strained molecule, bicyclobutane, has been prepared in this way.



These reactions are called intramolecular Wurtz reaction.

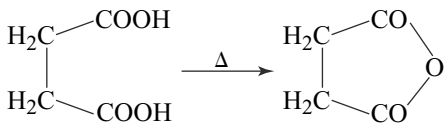
RING COMPOUNDS FROM DICARBOXYLIC ACIDS

Barium, calcium or thorium salts on heating yield cyclic ketones.

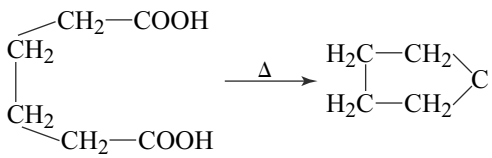


Product in this pyrolytic reaction depends on the number of C atoms (Blanc's rule).

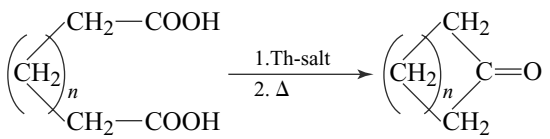
1. 1,4- and 1,5-diacid salts $\xrightarrow{\Delta}$ Cyclic anhydride



2. 1,6- and 1,7-dicarboxylic acid $\xrightarrow{\Delta}$ Cyclic ketone



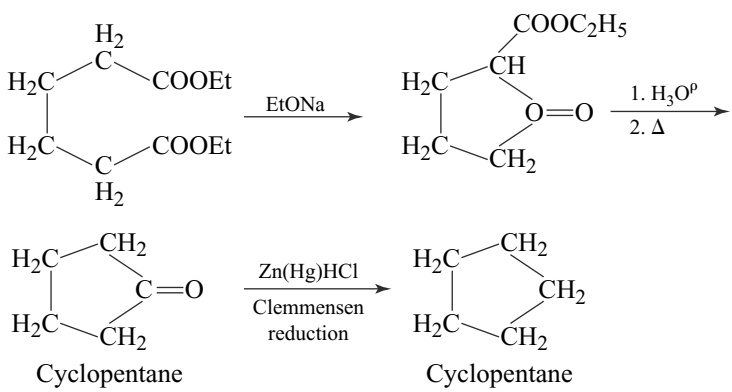
However, thorium salt can form macrocyclic ring (here, the value of *n* is 34).



(n + 4) C atoms (n + 3) C atoms

DIECKMANN CYCLIZATION

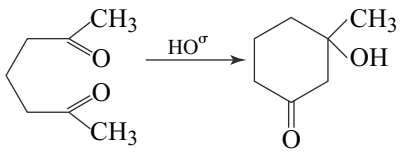
It is the intramolecular Claisen condensation (see name reaction).



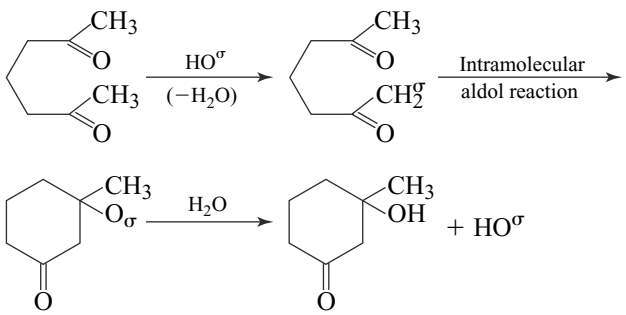
Cyclopentane Cyclopentane

INTERNAL ALDOL CONDENSATION AND CYCLIZATION

If functional groups are properly placed, internal aldol condensation may lead to cyclization. For example,



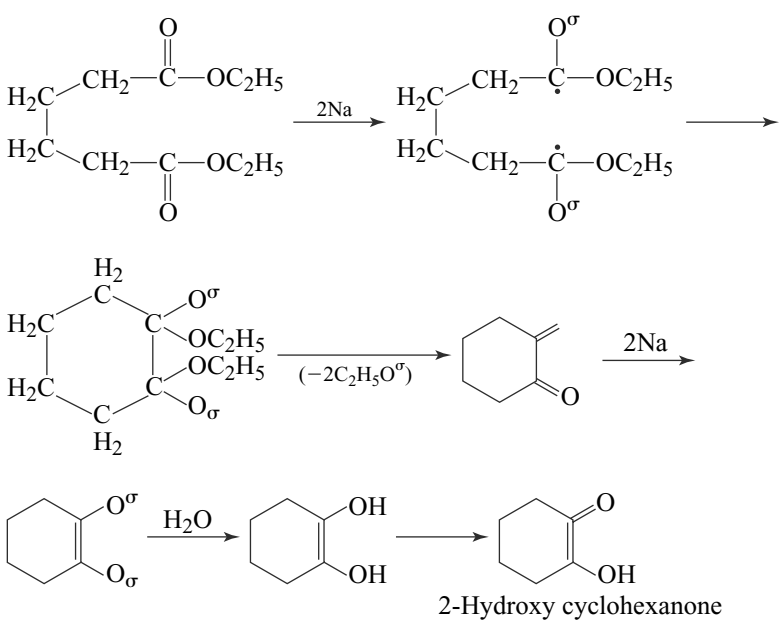
This conversion may proceed as



(The hydrogen atom in $-CH_3$ is more acidic.)

ACYLOIN CONDENSATION

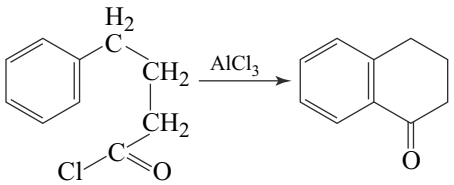
A dicarboxylic ester cyclizes in the presence of sodium dispersed in a hydrocarbon solvent xylene. This reaction has preparative value in the synthesis of large ring hydroxy ketones using diester of the type $EtO_2C(CH_2)_nCO_2Et$ where $n = 8$ to 18. This reaction gives good yield and is believed to proceed as



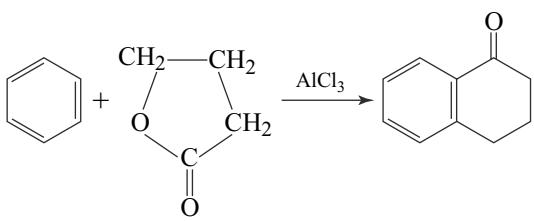
2-Hydroxy cyclohexanone

RING FORMATION THROUGH FRIEDEL–CRAFTS ACYLATION

Intramolecular acylation leads to ring formation. It is an important synthetic process for the formation of cyclic ketones.

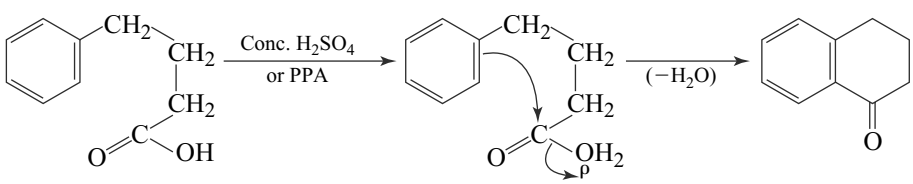


α-Tetralone may also be prepared by reacting benzene and γ-butyrolactone in the presence of $AlCl_3$. It is also a reaction of the same type as given above.



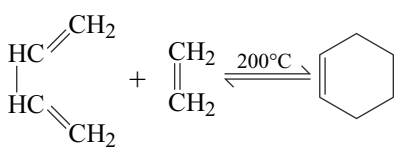
ACID-CATALYSED CYCLIZATION

Concentrated H_2SO_4, HF or polyphosphoric acid (PPA) catalyse the process of cyclization.



DIELS–ALDER REACTION AND RING FORMATION

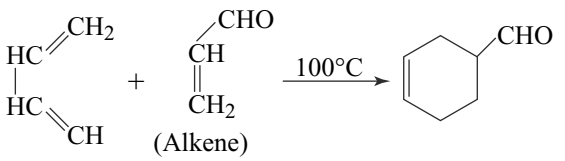
The 1,4- addition of an alkene to a conjugated diene yields a six-membered ring compound. It is known as Diels–Alder reaction.



The alkene is called the dienophile in this reaction. The reaction is faster when the dienophile has electron-attracting substituents. For example, –CN, $–NO_2$, –COOH, –CHO and –COOR. On the other hand,

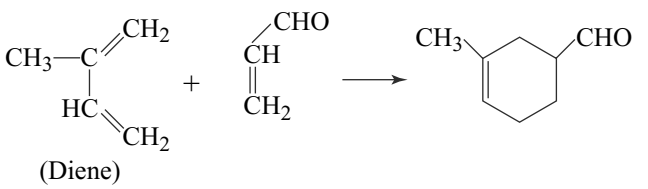
electron-donating groups in the diene promote reaction. Thus, methyl 1,3-butadiene reacts faster than 1,3-butadiene. Some examples relating to the above facts are given below:

1. Electron-attracting group in the dienophile.



This reaction is faster than the reaction with ethylene.

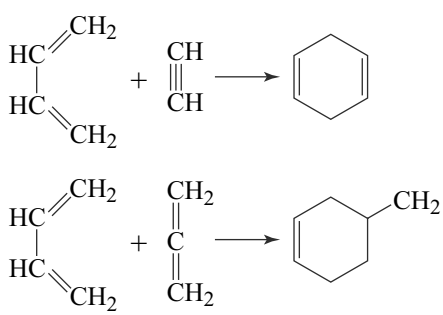
2. Electron-donating group in the diene.



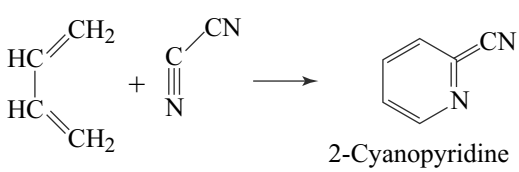
This reaction is faster than the reaction between 1,3-butadiene and acraldehyde

IMPORTANT POINTS

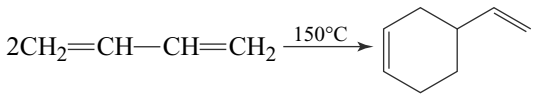
1. Triple bond and allenes may also act as dienophile.



2. The carbon heteroatomic π bonds (C≡N) may also act as dienophile.



3. Two molecules of 1,3-butadiene may follow Diels–Alder reaction.

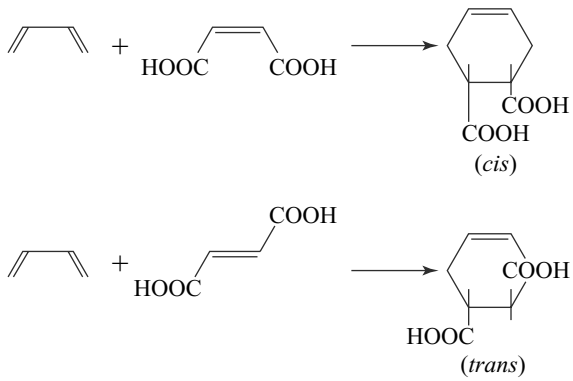


MECHANISMS

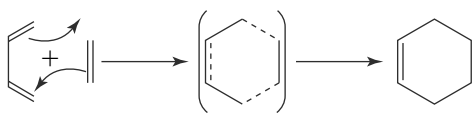
Diels–Alder reaction is an example of pericyclic reaction (i.e., a reaction proceeding through cyclic transition state). It is highly stereospecific.

1. The diene reacts in S–*cis* conformation (the S–*cis* means that the double bonds lie in a plane on the same side of the single bond joining them).

2. The configuration of the diene and the dienophile are retained in the product.

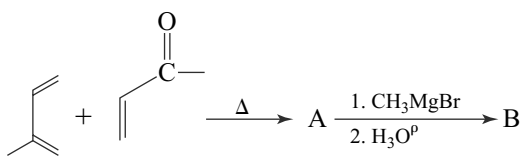


The reaction follow orbital symmetry rule. The most accepted mechanism is a concerted process. It proceeds through a six-centred transition state.

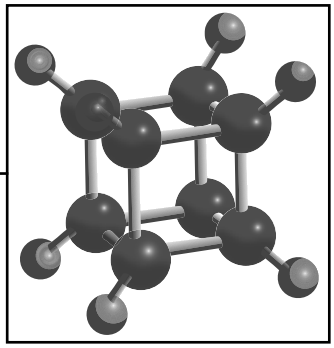


PROBLEM

Name the compounds A and B in the reaction given below.



CHAPTER 9



Alkanes

Alkanes are hydrocarbons that have only carbon and hydrogen. They have the general formula $C_nH_{2n}+2$ and form a homologous series. There is the possibility of the formation of continuous and branched-chain isomers (on the basis of carbon being tetravalent and hydrogen monovalent).

Branching is only possible with alkanes having four (C_4) or more carbon atoms. For example,

1. There are two structural isomers of C_4H_{10}, one the continuous chain and other the branched chain.

$$CH_3—CH—CH_2—CH_3$$

n-Butane
(or simply butane)

$$\begin{array}{c} CH_3 \\ | \\ CH_3—CH—CH_3 \end{array}$$

2-Methyl propane
(isobutane)

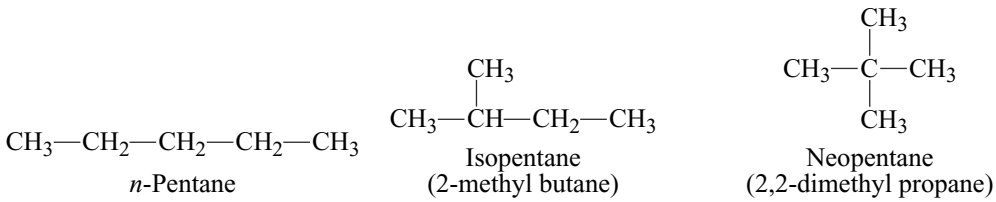
2. The tetrahedral structure makes all three methyl groups equivalent in isobutane.

$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ & & C & & \\ & \diagup & & \diagdown & \\ H_3C & & & & CH_3 \\ & & \diagdown & \diagup & \\ & & & CH_3 & \end{array}$$

ISOMERS OF PENTANE AND HEXANE

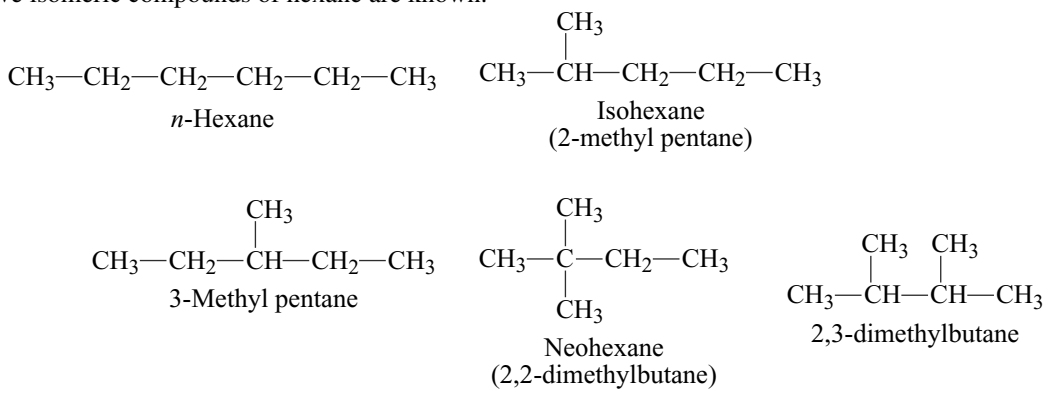
Pentane (C_5H_{12})

There are three pentanes:



Hexane (C_6H_{14})

Five isomeric compounds of hexane are known.



It is seen that the number of branched-chain isomers increases with the length of the chain. It is given in the table below.

Table 9.1 Alkanes, C_nH_{2n+2}

n	Name	Branched-chain isomers
1	Methane	0
2	Ethane	0
3	Propane	0
4	Butane	1
5	Pentane	2
6	Hexane	4
7	Heptane	8
8	Octane	17
9	Nonane	34
10	Decane	74
20	Eicosane	366318

Alkanes also have conformational isomers (see Chapter 2, Isomerism).

PREPARATION

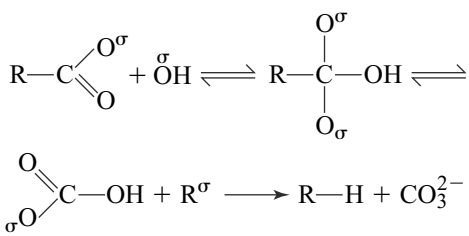
Alkanes can be prepared by any one of the following methods:

Decarboxylation of the Salts of Carboxylic Acid

When sodium salt of a carboxylic acid is heated with soda lime (NaOH.CaO), an alkane is formed. This reaction is known as decarboxylation as CO_2 is lost. The alkane contains one carbon atom less than the carbon atoms in carboxylic acid.

$$R{-}COO^{-}Na^{+} \xrightarrow[\Delta]{NaOH(CaO)} R{-}H + Na_2CO_3$$

This reaction may proceed as



Wurtz Reaction

Alkyl halides when treated with Na (or Cu or Ag) in dry ether give higher alkanes. This is known as Wurtz reaction.

$$2CH_3Cl \xrightarrow{Na/Ether} CH_3{-}CH_3 + 2NaCl$$

When different alkyl halides are used, mixture of alkanes is formed.

$$R{-}X + R'{-}X \xrightarrow{Na/Ether} R{-}R + R{-}R' + R'{-}R'$$

This method works well for the preparation of alkanes having even number of carbon atoms, such as ethane, butane and hexane.

The reaction may follow two mechanistic paths: (i) ionic or (ii) free radical.

Ionic mechanism

It operates when the reaction is carried out in the solution.

$$R{-}X + 2Na \longrightarrow R^{\sigma}Na^{\rho} + NaX$$

$$R^{\sigma} + R{-}X \longrightarrow R{-}R + X^{\sigma}$$

The reaction, thus, involves a carbanion (R^{σ}) and S_N2-type substitution. The carbanion may also act as a strong base and promote elimination giving an alkene.

$$R{-}CH_2{-}CH_2{-}Cl + 2Na \xrightarrow{\text{Ether}} R{-}CH_2{-}\overset{\sigma}{C}H_2\overset{\rho}{N}a + NaCl$$

$$R{-}CH_2{-}\overset{\sigma}{C}H_2 \quad H \quad R{-}\underset{Cl}{CH}{-}CH_2 \longrightarrow \underset{\text{(Alkane)}}{R{-}CH_2{-}CH_3} + \underset{\text{(Alkene)}}{R{-}CH{=}CH_2}$$

This is reaction is called disproportionation, which is a side reaction to the normal Wurtz reaction.

Free- radical mechanism

It operates when the reaction is carried out in the vapour state (it favours free-radical formation).

$$R{-}CH_2{-}X + N\dot{a} \longrightarrow R\dot{C}H_2 + NaX$$

$$R\dot{C}H_2 + R{-}\dot{C}H_2 \longrightarrow R{-}CH_2{-}CH_2{-}R$$

Radicals may also undergo disproportionation generating alkane and alkene.

$$CH_3{-}\dot{C}H_2 + CH_3{-}\dot{C}H_2 \longrightarrow \underset{\text{(Alkane)}}{CH_3{-}CH_3} + \underset{\text{(Alkene)}}{CH_2{=}CH_2}$$

Kolbe's Electrolytic Method

Electrolysis of a saturated aqueous solution of Na or K salt of a saturated carboxylic acid gives higher alkane.

$$\underset{\text{(Sol)}}{RCOONa} \xrightarrow{\text{Electrolysis}} \underbrace{R{-}R + CO_2}_{\text{(Anode)}} + \underbrace{H_2 + NaOH}_{\text{(Cathode)}}$$

Accepted path of the reaction is a free-radical mechanism.

$$R{-}COONa \xrightarrow{\text{Water}} RCOO^{\sigma} + Na^{\rho}$$

Anode reaction

$$R{-}C(=O){-}O_{\sigma} \longrightarrow R{-}C(=O){-}O\cdot + e$$

$$R{-}C(=O){-}O\cdot \longrightarrow R\cdot + CO_2$$

$$R\cdot + R\cdot \longrightarrow R{-}R$$

Cathode reaction

$$Na^{\rho} + e \longrightarrow Na$$

$$Na + H_2O \longrightarrow NaOH + H_2$$

Synthetic utility of this method is limited as a result of many side reactions of the free radical.

Reduction of Alkenes and Alkynes

Alkenes (or alkynes) are reduced by H_2 in the presence of metal catalysts, like Ni, Pd or Pt, to alkanes. The yield of the reaction is almost quantitative.

$$R—CH{=}CH_2 + H_2 \xrightarrow{Ni/\Delta} R—CH_2—CH_3$$

$$R—C{\equiv}CH + H_2 \xrightarrow{Ni/\Delta} R—CH{=}CH_2 \xrightarrow[\Delta]{H_2/Ni} R—CH_2—CH_3$$

This reaction is also called hydrogenation and is exothermic in nature.

Action of Grignard Reagent with Active Hydrogen Compounds

Grignard reagents react with active hydrogen compounds (H_2O, R–OH, acids, etc.) to give alkane.

$$RMgX + H_2O \longrightarrow R—H + Mg(OH)X$$

$$R—CH_2MgX + CH_3OH \longrightarrow R—CH_3 + Mg(CH_3O)X$$

Even phenyl magnesium halides give benzene.

$$C_6H_5MgBr + H_2O \longrightarrow C_6H_6 + Mg(OH)Br$$

These reactions are easy as Grignard reagents contain carbanionic species (C is more electronegative than Mg).

$$\overset{\delta-\ \delta+}{R\ MgX} \qquad \overset{\delta-\ \delta+}{Ar\ MgX}$$

Reduction of Alkyl Halides, Aldehydes and Ketones

Reduction of alkyl halides, aldehydes and ketones can also produce alkane. Alkyl halides can be reduced to alkane in a number of ways. For example,

1. By metal + acid (Zn + HCl)
2. By Zn + NaOH
3. Zn–Cu couple + $CH_3.CH_2.OH$

In these reactions, metal transfers its electrons to R–X generating carbanion that takes up proton from the acid or even from the solvent to give alkane.

$$Zn \longrightarrow Zn^{2+} + 2e$$
$$R{-}X + e \longrightarrow R + X^{\sigma}$$
$$R + e \longrightarrow R^{\sigma}$$
$$R^{\sigma} + H^{\rho} \longrightarrow R{-}H$$

(For reduction of aldehydes and ketones, see chapter on aldehydes and ketones.)

PROPERTIES AND REACTIONS

The *n*-alkanes from

(i) methane to butane (C_4H_{10}) are colourless gas,

(ii) C_5 to C_{17} are colourless **liquids** and

(iii) C_{18} onwards are colourless **solids**.

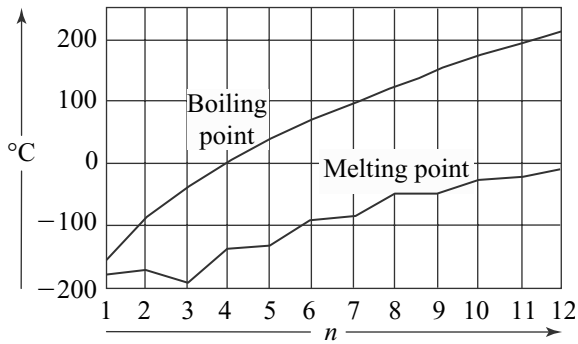
Alkanes are almost nonpolar molecules. The forces holding nonpolar molecules together are weak Van der Waal's force, which is a force having short range. This force has been found to increase with the surface area. Therefore, larger the surface area stronger is the intermolecular force.

The boiling points of *n*-alkanes increase with the chain length and rises from 20° to 30° for each CH_2 added to the chain. (This increase in the boiling point is also found for other homologous series.) It is because of the addition of CH_2 that increases the chain length, i.e., surface area, and, consequently, increases the intermolecular forces. But the increase in the melting points is not regular. It is because of the forces in a crystal that depends not only upon how well the molecules fit into a crystal lattice but also upon their sizes. The variations in the melting points and boiling points of n-alkanes are given in the table below:

Table 9.2 Physical properties of *n*-alkanes, $CH_3(CH_2)_{n-2}CH_3$

n	Name	Boiling point (°C) (760 mm)	Melting point (°C)
1	Methane	–161.5	–183
2	Ethane	–88.6	–172
3	Propane	–42.1	–188
4	Butane	–0.5	–135
5	Pentane	36.1	–130
6	Hexane	68.7	–95
7	Heptane	98.4	–91
8	Octane	125.7	–57
9	Nonane	150.8	–54
10	Decane	174.1	–30
11	Undecane	195.9	–26
12	Dodecane	216.3	–10
15	Pentadecane	270.6	10
20	Eicosane	342.7	37
30	Triacontane	446.4	66

MELTING POINTS AND BOILING POINTS OF STRAIGHT-CHAIN ALKANES, $CH_3(CH_2)_{n-2}CH_3$



Branched-chain alkanes do not show smooth gradation of melting points and boiling points but the n-alkane always has the highest melting point and boiling point. On the other hand, boiling point decreases (volatility increases) when branching increases.

The effect of branching on boiling point is seen within all homologous series. With increased branching, the molecule becomes compact. It leads to decrease in the surface area, decreasing the intermolecular forces (Table 9.3).

Table 9.3 Physical properties of hexane isomers

Isomers	Structure	Boiling point (°C)	Melting point (°C)
Hexane	$CH_3(CH_2)_4CH_3$	68.7	–94
3-Methylpentane	$CH_3CH_2\underset{\displaystyle CH_3}{\underset{\vert}{C}}HCH_2CH_3$	63.3	–118
2-Methylpentane (isohexane)	$CH_3\underset{\displaystyle CH_3}{\underset{\vert}{C}}HCH_2CH_2CH_3$	60.3	–154
2,3-Dimethylbutane	$CH_3\underset{\displaystyle CH_3}{\underset{\vert}{C}}H—\underset{\displaystyle CH_3}{\underset{\vert}{C}}HCH_3$	58.0	–129
2,2-Dimethylbutane (neohexane)	$CH_3\underset{\displaystyle CH_3}{\underset{\vert}{\overset{\displaystyle CH_3}{\overset{\vert}{C}}}}CH_2CH_3$	49.7	–98

Reaction

Alkanes are also called paraffins (parum ⟶ less and affins ⟶ affinity), i.e. they are less reactive.

Combustion

Alkanes when heated in O_2 or air are completely oxidized to CO_2 and H_2O.

$$CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(l)}$$

These reactions are highly exothermic. This property of alkanes makes it a good fuel. Butane is the common alkane used in burners of the cooking gas.

Halogenation

Alkanes readily react with Cl_2 or Br_2 in the presence of sunlight or on heating. The products are alkyl halides. This reaction is an example of free-radical substitution reaction.

The H atoms of alkane are replaced one by one, $CH_4 \longrightarrow CH_3Cl \longrightarrow CH_2Cl_2 \longrightarrow CHCl_3 \longrightarrow CCl_4$. The reaction is a free-radical chain reaction.

Chain initiation

$$Cl_2 \xrightarrow{h\nu} Cl^{\bullet} + Cl^{\bullet}$$

Chain propagation

$$CH_4 + Cl^{\bullet} \longrightarrow {}^{\bullet}CH_3 + HCl$$
$${}^{\bullet}CH_3 + Cl_2 \longrightarrow CH_3Cl + Cl$$

Chain termination

$${}^{\bullet}CH_3 + {}^{\bullet}CH_3 \longrightarrow CH_3{-}CH_3$$
$${}^{\bullet}Cl + {}^{\bullet}Cl \longrightarrow Cl_2$$
$${}^{\bullet}CH_3 + {}^{\bullet}Cl \longrightarrow CH_3Cl$$

Halogenation can proceed with all alkanes. The general reaction may be represented as

$$-\overset{|}{\underset{|}{C}}-H + X_2 \longrightarrow -\overset{|}{\underset{|}{C}}-X + HX$$

The ΔH values for different halogens are given in the Table 9.4 below (calculated).

Table 9.4 ΔH values for halogenation in kcal/mole

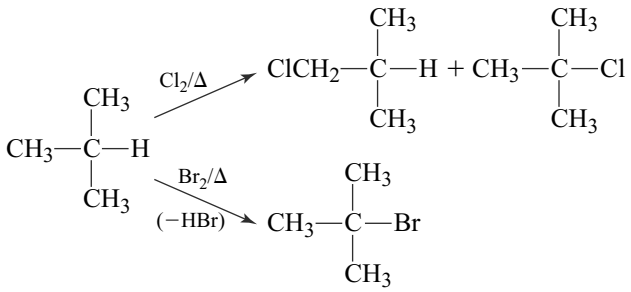
X	X–X	C–X	H–X	ΔH
F	36.6	116	134.5	–115
Cl	58.0	81	103.2	–27
Br	46.1	68	87.5	–10
I	36.1	51	71.4	12

C–H bond energy is 99.0 kcal/mole (average value).

The above table shows that ΔH is negative and very large for fluorine, negative and moderate for chlorine and bromine and positive for iodine. Thus, the reaction with fluorine and iodine is not satisfactory. It is because of the highly exothermic reaction with F_2 that may cause degradation of the organic compound (many organic compounds inflame in F_2) and reaction with iodine can take place only in the presence of an oxidizing agent HNO_3, HIO_3, etc. (it decomposes HI and restricts reverse reaction).

$$CH_4 + I_2 \rightleftharpoons CH_3I + HI$$
$$5HI + HIO_3 \longrightarrow 3I_2 + 3H_2O$$

The reaction with Cl_2 is general but with bromine is highly selective, and bromine attacks only tertiary hydrogen. For example,



Reactivity

Halogen F > Cl > Br > I
Alkane tert C–H > sec C–H > pri C–H

This result indicates that dissociation energy of C–H bonds decrease in the given order.

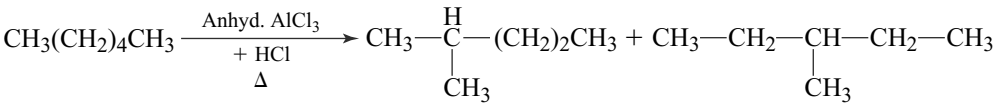
primary (C–H) > secondary (C–H) > tertiary (C–H)

This order compares with the stability of the free radicals that is

tertiary—C• >secondary—C• >primary—C•

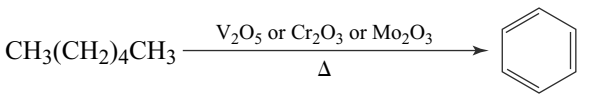
Isomerization

Alkanes when heated with anhydrous $AlCl_3$ + HCl isomerize to branched-chain isomers.



Aromatization

Alkane having six or more carbon atoms when heated (~500°C) at high pressure (10–20 atm) with catalyst (Cr_2O_3 or V_2O_5 or Mo_2O_3) converts into aromatic hydrocarbon. It is called aromatization.

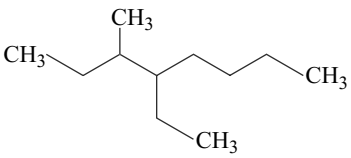


PROBLEMS

Objective-Type Questions

1. The highest boiling point is expected for
   (a) *iso*-octane
   (b) *n*-octane
   (c) 2,2,3,3-tetramethyl butane
   (d) *n*-butane

2. The name of the compound given below is



   (a) 4-ethyl-3-methyl octane
   (b) 3-methyl-4-ethyl octane
   (c) 2,3-dimethyl heptane
   (d) 5-ethyl-6-methyl octane

3. The IUPAC name of the hydrocarbon given below is

   (a) tetraethyl methane (b) neononane
   (c) 3,3-diethyl pentane (d) 2-ethyl pentane

4. The C–H bond distance is the longest in
   (a) C_2H_4 (b) C_2H_2
   (c) CH_3–CH_2Br (d) C_2H_6

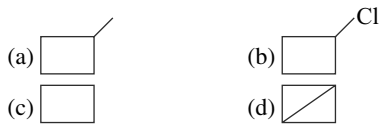
5. When ethyl magnesium bromide is treated with D_2O, the product is
   (a) C_2H_5–C_2H_5 (b) C_2H_6
   (c) C_2H_5D (d) C_2H_5–OH

6. Isopropyl bromide on Wurtz reaction gives
   (a) propane (b) hexane
   (c) neohexane (d) 2,3-dimethyl butane

7. Heating a mixture of sodium benzoate and soda lime gives
   (a) methane (b) benzene
   (c) calcium benzoate (d) methyl benzene

8. 1,1,2,2-Tetrabromoethane on heating with Zn gives
   (a) ethane (b) ethene
   (c) ethyne (d) ethyl bromide

9. Which of the following will be formed when 1-bromo-3-chlorobutane is treated with two equivalents of Na, in the presence of ether?



10. Which of the following has the minimum boiling point?
    (a) *n*-Butane (b) 1-Butyne
    (c) 1-Butene (d) *iso*-Butene

11. The reactivity of C–H bond with Cl_2 varies as
    (a) tert C–H > sec C–H > pri C–H
    (b) pri C–H > sec C–H > tert C–H
    (c) sec C–H > tert C–H > pri C–H
    (d) pri C–H > tert C–H > sec C–H

12. $CH_3—CH_2—\underset{\displaystyle CH_3}{\overset{|}{C}}HCH_3 \xrightarrow{Br_2}$ monobromo compound. The expected number of monobromo compound is
    (a) one (b) two
    (c) three (d) four

13. 2-methylpropane $\xrightarrow{Cl_2}$ monochloro compounds. The number of monochloro derivatives is
    (a) three (b) four
    (c) two (d) one

14. Which of the following alkanes will give only one monobromo (or chloro) derivative?
    (a) iso-Butane (b) neo-Pentane
    (c) neo-Hexane (d) iso-Pentane

15. X $\xrightarrow[\Delta,\ \text{high P}]{V_2O_5}$ C_6H_6. The compound X is
    (a) 1-hexane (b) hexane
    (c) 1,3-hexadiene (d) 1,4-hexadiene

16. Which of the following compounds does not dissolve in conc. H_2SO_4 even on warming?
    (a) Benzene (b) Ethylene
    (c) Aniline (d) Hexane

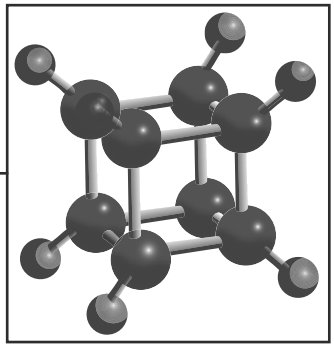
17. The homolytic dissociation energy of C–H bond decreases in the order
    (a) pri (C–H) > sec (C–H) > tert (C–H)
    (b) tert (C–H) > sec (C–H) > pri (C–H)
    (c) sec (C–H) > pri (C–H) > tert (C–H)
    (d) tert (C–H) > pri (C–H) > sec (C–H)

18. 3-Methyl heptane $\xrightarrow{\text{conc. } H_2SO_4}$ Product. The product is
(a) purely dextro
(b) purely laevo
(c) racemic mixture
(d) unequal amounts of *d* and *l* isomer

Answers

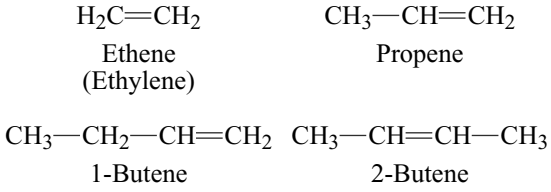
1. (b)	2. (b)	3. (c)	4. (d)	5. (c)
6. (d)	7. (b)	8. (c)	9. (d)	10. (a)
11. (a)	12. (a)	13. (c)	14. (b)	15. (b)
16. (d)	17. (b)	18. (c)		

CHAPTER 10



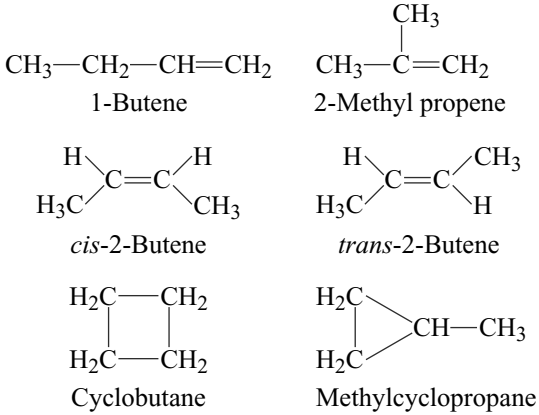
Alkenes

Alkenes are open-chain hydrocarbons those have one carbon–carbon double bond. Their general formula is C_nH_{2n} and they are also called olefins. For example,



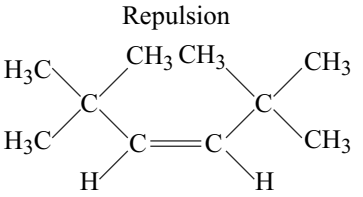
ISOMERISM IN ALKENES

Alkenes show structural as well as stereoisomerism. For example, the compound C_4H_8 can form six isomers.



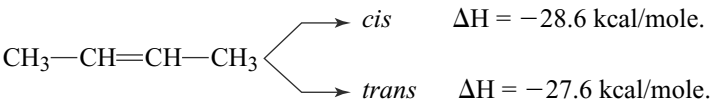
The last two compounds are cycloalkanes, not alkenes. The compound 2-butene can only exist in two different configurational arrangements, the *cis*- and *trans*-isomers.

The *trans*-isomers are more stable than the corresponding *cis*-isomers. It is because of the greater steric repulsion in *cis*-alkenes.



(2,2,5,5-Tetramethyl-*cis*-3-hexene)

Heat of hydrogenation data can be used to decide the stability of *cis*- and *trans*-isomers. The smaller is the heat of hydrogenation more stable is the alkene and vice versa.



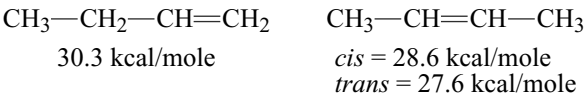
Thus, *trans*-2-butene is more stable than *cis*-2-butene by 1 kcal/mole.

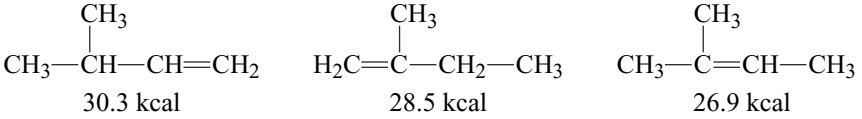
STABILITY OF ALKENES

The relative stabilities of alkenes vary. It is found to depend upon

1. the position of the double bond in the chain and
2. the configuration of the alkene (i.e., *cis*- and *trans*-isomers).

The heat of hydrogenation (or combustion) data is used to determine the stability, which is shown in the following examples.





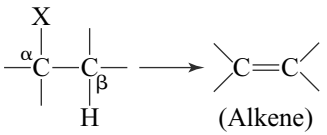
Each set in the above examples will give the same alkane on hydrogenation. The differences in the heat of hydrogenation must, therefore, be due to differences in the stability. In general, it is found that *the greater is the number of alkyl groups attached to doubly bonded carbon atoms (C=C), the more stable is the alkene.* The order of stability varies as

$$R_2C{=}CR_2 > R_2C{=}CHR > R_2C{=}CH_2,\ RCH{=}CHR > RCH{=}CH_2 > CH_2{=}CH_2$$

The greater stability of alkyl-substituted alkenes is explained using the concept of hyperconjugation (See Chapter 3, *Electron Shift*).

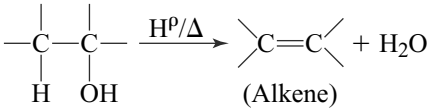
PREPARATION

Alkenes are prepared by the elimination reactions. In most of the reactions, an H atom is lost as a proton from β-carbon and a nucleophile is lost from α-carbon (i.e. the groups are removed from the adjacent carbons).

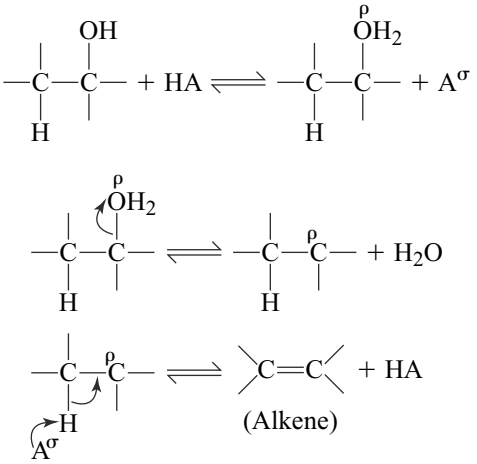


Such elimination reactions are known as 1,2-elimination or β-elimination (See Chapter 5, *Reaction Mechanism*).

1. *Dehydration of Alcohols*
Dehydration of alcohols is an acid-catalysed elimination to form an alkene in which a water molecule is removed.



The accepted mechanism of dehydration is



The various important aspects of dehydration are given as follows:

1. The ease of dehydration depends upon the class of the alcohol.

2. Saytzeff's elimination is followed (i.e., more substituted alkene is preferred).

3. Alkene may correspond to the rearranged alkyl group if it gives more stable carbocation. The examples given below correlate all the points mentioned above.

(i)

$$\underset{\text{1° Alcohol}}{CH_3—CH_2—OH} \xrightarrow[170°]{95\%\ H_2SO_4} \underset{\text{Ethene}}{CH_2=CH_2}$$

(ii)

$$\underset{\text{1-Butanol (Pri alcohol)}}{CH_3—CH_2—CH_2—CH_2—OH} \xrightarrow[140°]{74\%\ H_2SO_4} \underset{\text{2-Butene (major)}}{CH_3—CH=CH—CH_3}$$

(iii)

$$\underset{\text{2-Butanol (sec. alcohol)}}{CH_3—CH_2—\overset{\overset{OH}{|}}{CH}—CH_3} \xrightarrow[100°]{60\%\ H_2SO_4} \underset{\text{2-Butene (major)}}{CH_3—CH=CH—CH_3}$$

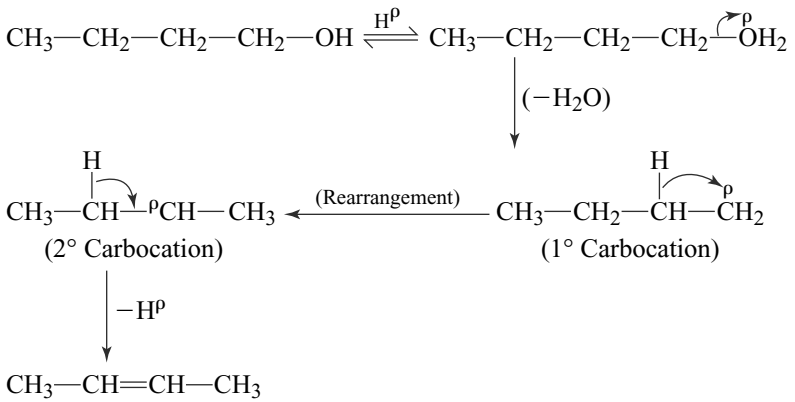
(iv)

$$\underset{\text{(Tert. alcohol)}}{CH_3—\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}—CH_3} \xrightarrow[\sim 85°]{20\%\ H_2SO_4} \underset{\text{2-Methyl propene}}{CH_3—\overset{\overset{CH_3}{|}}{C}=CH_2}$$

The concentration of the acid and the temperature of the reactions are decreasing from (i) to (iv). It shows that the reaction is getting easy from (i) to (iv). Thus, ease of dehydration for various classes of alcohols is

tert alcohol (3°) > sec alcohol (2°) > pri alcohol (1°)

The reaction marked as (ii) above is the result of a rearrangement (it involves breaking of C–H bond and migration of H with the bond pair of electrons. This generates more stable 2° carbocation from 1° carbocation).



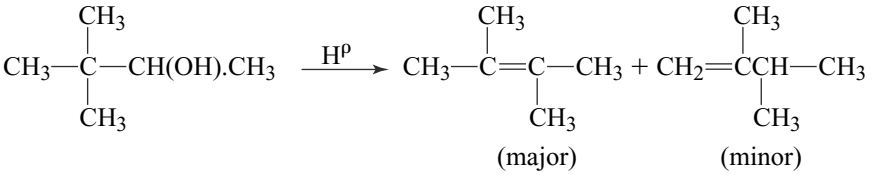
Problem

$$\underset{\text{2-Methyl-2-butene (major)}}{CH_3.CH_2=\overset{\overset{CH_3}{|}}{C}—CH_3} + \underset{\text{2-Methyl-1-butene (minor)}}{CH_3—CH_2—\overset{\overset{CH_3}{|}}{C}=CH_2}$$

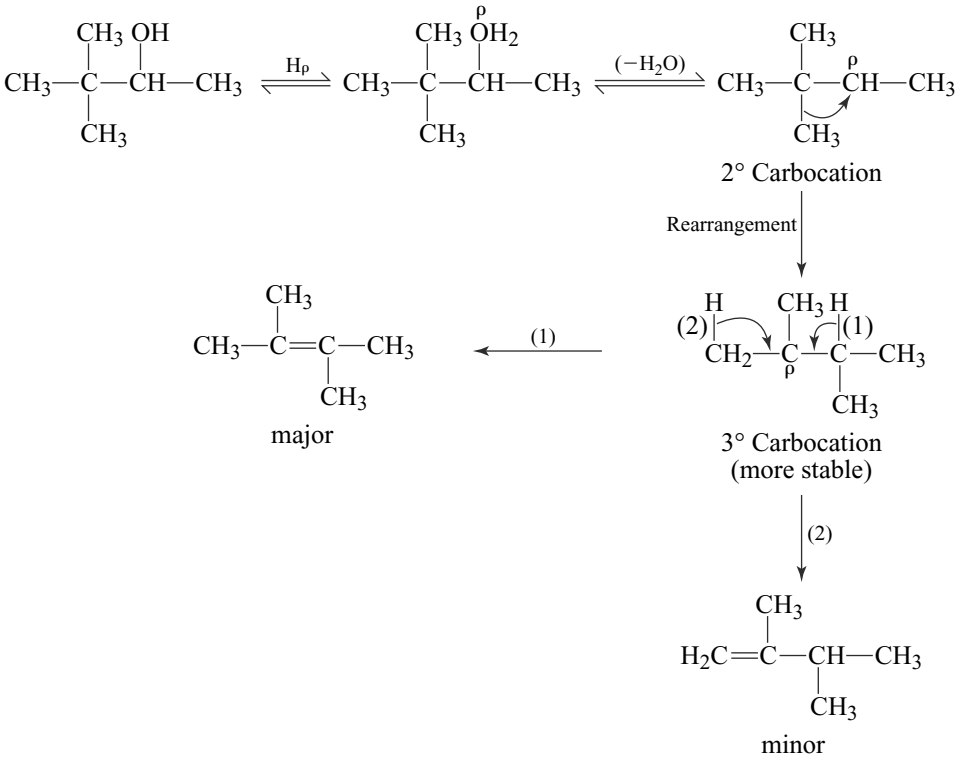
$$\underset{}{CH_3—CH_2—\overset{\overset{CH_3}{|}}{CH}—CH_2—OH} \xrightarrow{H^=}$$

Account the formation of the major product and propose plausible mechanism.

Rearrangements may also involve cleavage of C–C bond in the dehydration of alcohols. For example,

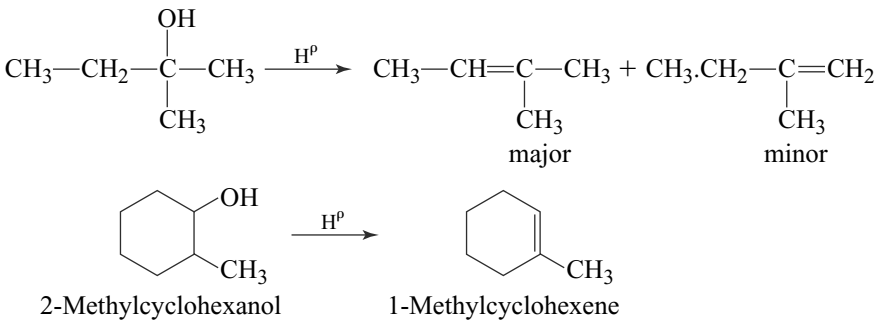


Rearrangement in the above reaction may proceed as



In each of the above examples, elimination completes when the initially formed carbocation rearranges to form more stable carbocation.

Elimination also follows Saytzeff's rule, i.e., the major product is the more substituted alkene. For example,



Alcohols may also be dehydrated to alkenes by passing their vapour over hot Al_2O_3.

$$CH_3—CH_2—OH \xrightarrow[375°]{Al_2O_3} CH_2=CH_2 + H_2O$$

2. *Dehydrohalogenation*

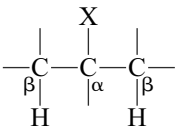
Elimination of a hydrogen halide (HX) from an alkyl halide is called dehydrohalogenation. The reaction takes place on heating the alkyl halide with a strong base.

$$CH_3—CH_2—CH_2—Br \xrightarrow[\Delta]{KOH,\ Alcohol} CH_3—CH=CH_2 + KBr + H_2O$$

Alcoholic KOH generates strong base alkoxide, i.e., RO^{σ}.

This reaction is 1,2- or β-elimination. Mechanistically, it may follow either E_1 or E_2 route (see Chapter 5, *Reaction Mechanism*).

The carbon attached to the halogen is marked α-carbon. Any carbon attached to the α-carbon is a β-carbon and its H is the β-hydrogen.



The various important aspects of dehydrohalogenation are that

1. it requires strong base and relatively high temperature,

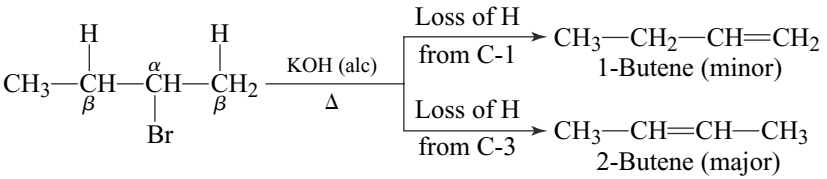
2. Saytzeff's rule is followed and

3. rearrangement may also take place during elimination (if structure permits to produce more stable carbocation).

The following examples illustrate the above points.

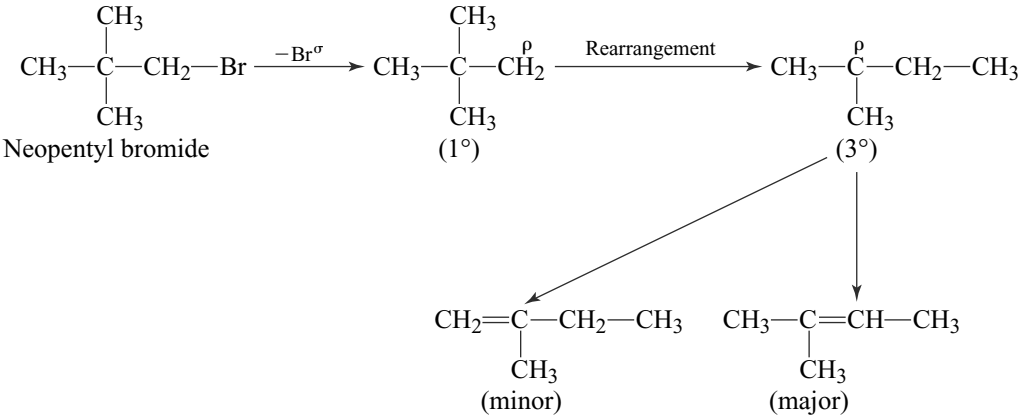
$$CH_3—\underset{Br}{\underset{|}{CH}}—CH_3 \xrightarrow[\Delta]{C_2H_5O^{\sigma}\ or\ (KOH + EtOH)} CH_3—CH=CH_2$$

Potassium ethoxide is a strong base and so is used for elimination. Many halides have β-hydrogens at both the adjacent carbons but the major product is always the more alkyl-substituted alkene (Saytzeff's rule).



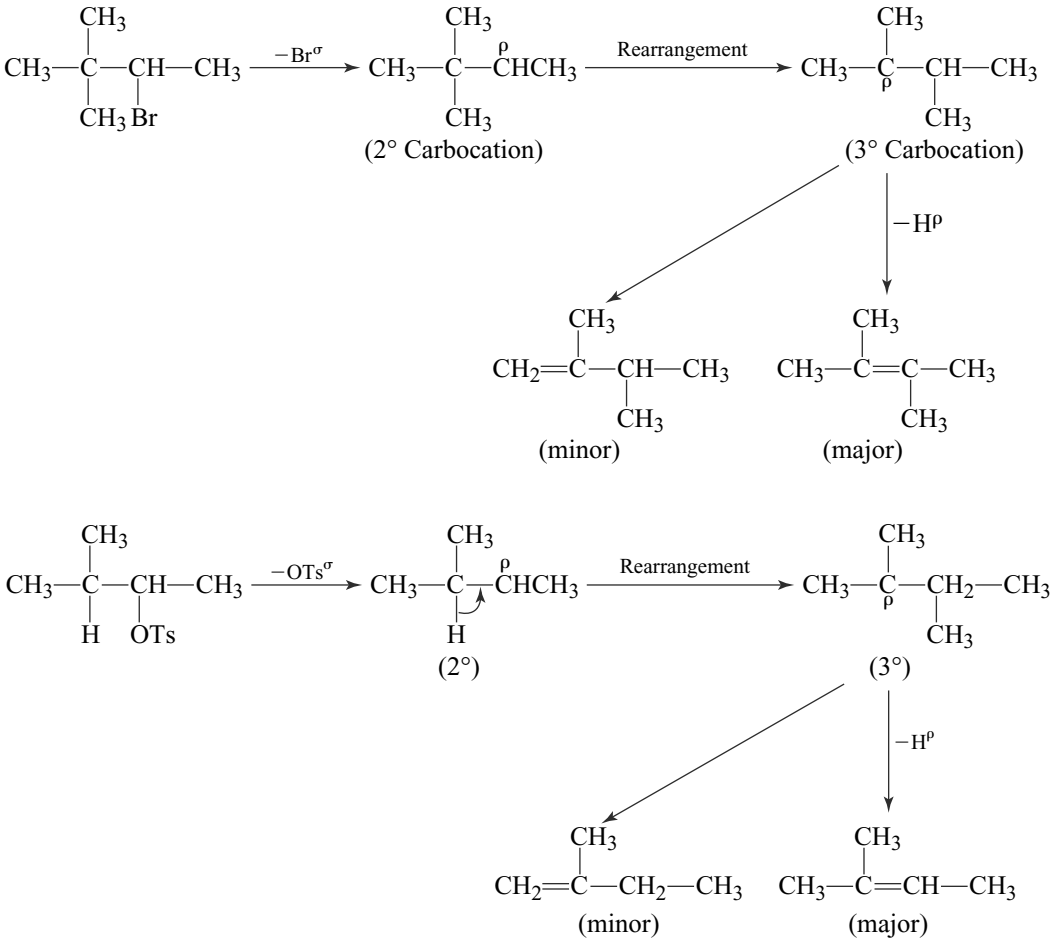
Rearrangement is also common during elimination if the initially formed carbocation can rearrange (by a 1,2-shift) to a more stable carbocation (i.e., 1° ⟶ 3° or 2° ⟶ 3° or 1° ⟶ 2°).

1° ⟶ 3° rearrangement



In the above reactions, the β-carbon has no H atom but the elimination takes place because of the rearrangement in carbon skeleton.

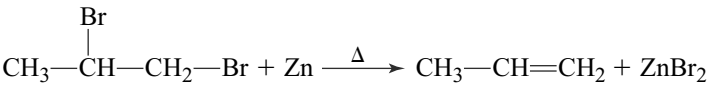
2° ⟶ 3° rearrangement



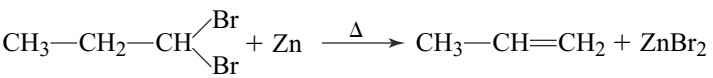
Problem

Give structures of the possible products from dehydrohalogenation of
- **(a)** 2-bromo-2-methyl pentane
- **(b)** 3-bromo-2-methyl pentane
- **(c)** 2-bromo-4-methyl pentane
- **(d)** 3-bromo-2,3-dimethyl pentane

3. *Dehalogenation of vic-dihalides*
(Vic-dihalide means dihalide having halogens at adjacent, i.e., 1,2-, C atoms). On heating with Zn and methanol, the 1,2-dihalides produce alkenes.



Gemdihalides also give alkene on heating with Zn and methanol.



4. *Pyrolysis of quaternary ammonium hydroxide (Hofmann Elimination)*
(See Chapter, *Reaction Mechanism*)

PROPERTIES AND REACTIONS

Alkenes upto four carbon atoms are gases, five to seventeen are liquids and eighteen onwards are solids. Physical properties of alkenes are similar to alkanes. It is because of the weak van der Waals forces that are present between the molecules. They are insoluble in water.

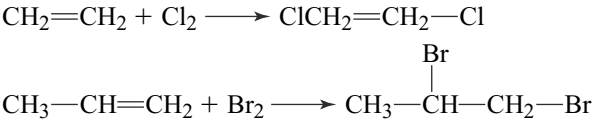
In contrast to alkanes, alkenes are highly reactive. The reactivity is due to the presence of double bonds. (See Chapter, *Reaction Mechanism*.) Important reactions given by alkenes are (a) addition reactions, (b) oxidation reactions and (c) polymerization reaction.

Addition Reactions

A reaction in which reactants combine to form a single product is called addition reaction. Thus, in this type of reaction a reagent is added to the substrate.

The C–C double bond includes one σ and one π bond. The σ electrons are held strongly but the π electrons are held loosely and are easily polarizable. This makes reaction with an electrophile easy. As two σ bonds are formed at the cost of a single π bond, the reaction is energetically favourable. Thus, electrophilic addition is characteristic reaction of alkenes. (See Chapter 5 for mechanism to the addition of C=C.) Addition reactions are summarized below.

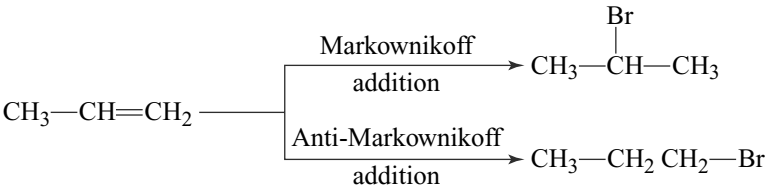
1. *Addition of halogen*
When chlorine and bromine is added to an alkene, bromine water quickly gets decolourized by the alkenes (a test for C=C).



2. *Addition of HX (X = Cl, Br or I)*
The HX molecule adds to an alkene to form alkyl halide.

$$H_2C{=}CH_2 + HBr \longrightarrow \underset{\text{Ethyl bromide}}{CH_3{-}CH_2{-}Br}$$

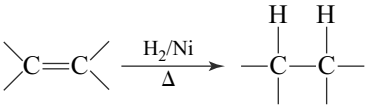
The addition of HX to an unsymmetrical alkene (CH_3–CH=CH_2) may follow Markownikoff's rule or anti-Markownikoff's rule (See Chapter 5 for Markownikoff's rule).

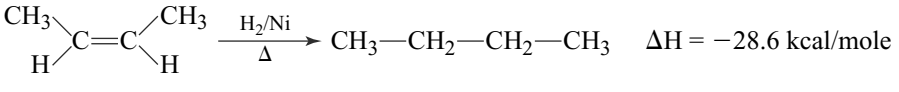


3. *Addition of H_2 (hydrogenation)*
Addition of H_2 to an alkene gives alkane. This reaction is catalysed by metals like Ni, Pd and Pt or by organometallic compound like Wilkinson's catalyst [$Rh(PPh_3)_3Cl$].

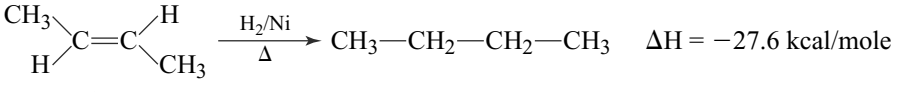
Metal catalyst

This is an example of heterogeneous catalysis where the *cis*-addition takes place. The reaction is exothermic and is known as hydrogenation. The amount of heat evolved when 1 mole of an alkene is hydrogenated is known as the heat of hydrogenation. It is a measure of the stability of an alkene.





cis-2-Butene *n*-Butane

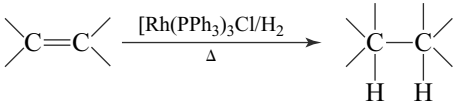


trans-2-Butene *n*-Butane

Thus, *trans*-2-butene is more stable than *cis*-2-butene by 1 kcal/mole. The number of mole of H_2 absorbed by an unsaturated compound indicates the number of double bonds.

Organomatallic catalyst

It is an example of homogenous catalysis. Wilkinson's catalyst is very effective for selective hydrogenation at room temperature and pressure. The C=C at the end of the chain is hydrogenated but double bonds at other points in the chain are not affected. The addition is overall syn-addition.



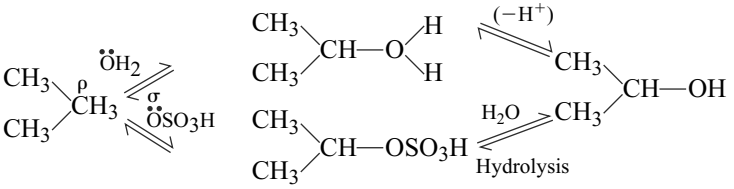
1. *Addition of H_2O (hydration)*
Addition of components of water (H and OH) to C═C (or C≡C or C═O) is called hydration reaction. Variety of methods can be used. They are (a) acid-catalysed hydration, (b) hydration through hydroboration and (c) hydration through oxymercuration–demercuration (or reduction).

Acid-catalysed hydration of C═C

This reaction is by H^+. A proton is added to the C═C in Markownikoff way to form a carbocation. It is then attached by the nucleophile H_2O or chlorobenzene (CB) of an acid catalyst. The final product is an alcohol. The reaction follows the path as given below.

$$H_2SO_4 \equiv H^{\rho} + H_2SO_4^{\sigma}$$

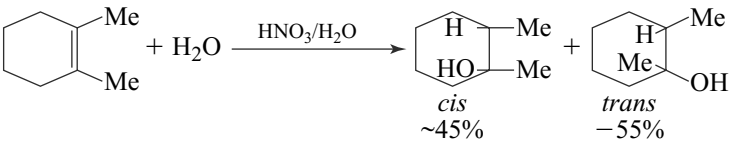
$$CH_3—CH=CH_2 \overset{H^{\rho}}{\equiv} CH_3—\overset{\rho}{C}H—CH_3$$



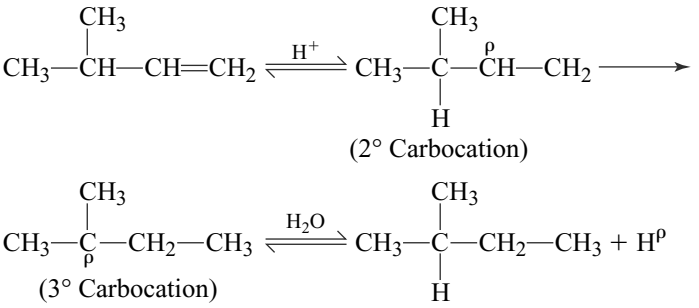
Feature of the reaction

1. Addition of proton, i.e., formation of carbocation seems a rate-controlling step.

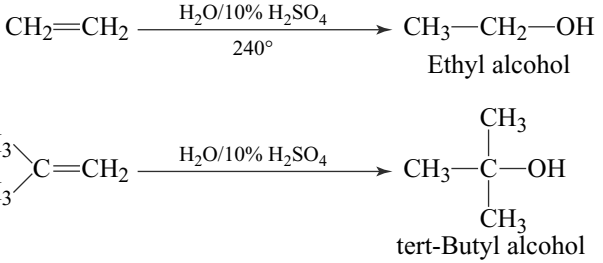
2. The overall reaction is Markownikoff addition (i.e., a regioselective reaction) .



3. Rearrangement in carbocation may also take place.

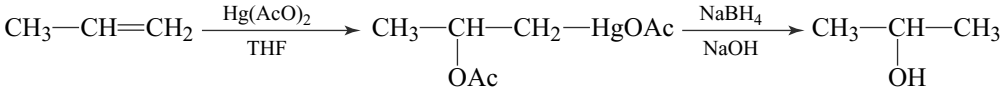


Hydration is commercially an important reaction. Ethyl and tert-butyl alcohols are prepared on a large scale by this method using H_2SO_4 or H_3PO_4.



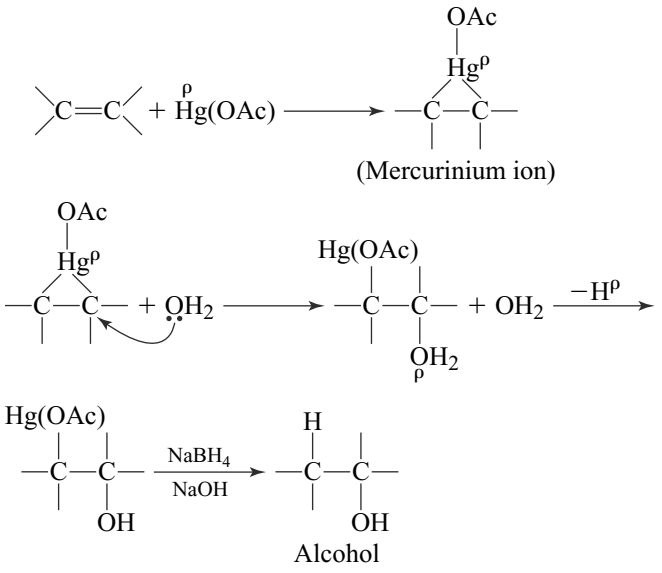
Oxymercuration–demercuration

An alkene quickly adds to mercuric acetate in tetrahydrofuran. $NaBH_4$ reduces the addition product in NaOH and gives alcohol as the final product. The addition follows Markownikoff's rule.



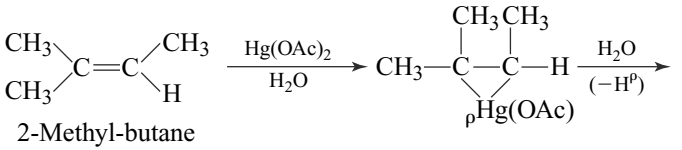
Mechanism

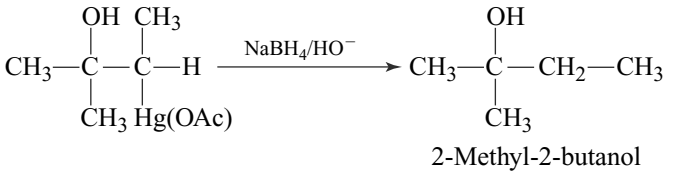
Oxymercuration is believed to proceed by the electrophile $^{\rho}Hg(OAc)$, which is formed as Ac—O—Hg—OAc≡$AcOHg^{\rho}$ + AcO^{σ}. The reaction then proceeds as given below.

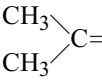


Features of this reaction

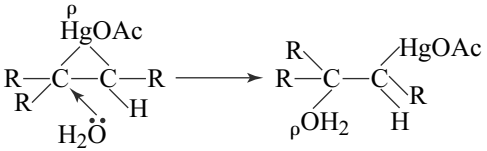
1. The reaction of unsymmetrical alkene follows Markownikoff addition.



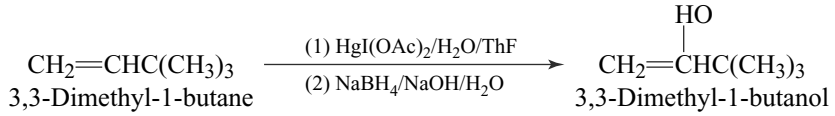


In symmetrical alkenes, the carbon that is substituted more (here, ) is more electrophilic. Therefore, it is attached by H_2O (Markownikoff way).

2. Anti-attack by the nucleophile (H_2O) takes place on cyclic mercurinium ion. It is because of the bulky mercuric acetate group that hinders frontside attack, i.e., the first step is stereospecific.



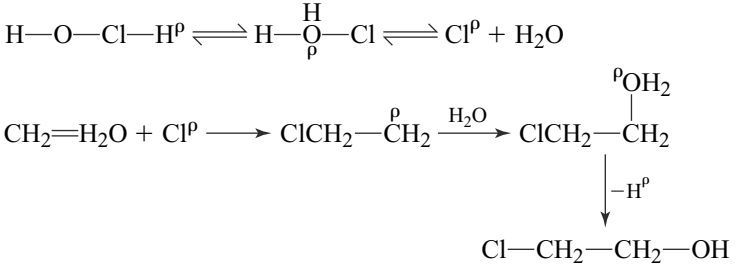
3. No free carbocation is formed, so no rearrangement is found in this overall hydration.



4. The second step, i.e., reduction, is not stereospecific.

Addition of HOCl

Hypochlorous acid adds to C═C in the presence of a strong acid to form chlorohydrine. The mechanism probably is as follows:



With unsymmetrical alkene, Cl adds on to the C atom joined with more of H atoms (i.e. the addition follows Markownikoff's rule).

$$CH_3—CH{=}CH_2 \xrightarrow{HOCl} CH_3—\underset{\displaystyle OH}{\overset{|}{CH}}—CH_2—Cl$$

This reaction may be carried out with chlorine or bromine water. In this case, dihalocompound is also formed. This suggests the following mechanism.

$$CH_2{=}CH_2 + Cl—Cl \longrightarrow Cl^{\sigma} + \overset{\rho}{C}H_2—CH_2—Cl \xrightarrow{H_2O} \underset{\displaystyle OH}{\overset{|}{CH_2}}—CH_2Cl + H^{\rho}$$

Addition of boron hydride (hydroboration)

The reagent diborane (B_2H_6) may be taken as a dimmer of the electron-deficient species, BH_3. It is BH_3 that adds to the double bond to give trialkyl boron compound.

$$6CH_2{=}CH_2 + (BH_3)_2 \longrightarrow 2(CH_3—CH_2)_3B$$

This reaction is known as hydroboration. It proceeds in three stages.

$$H_2C{=}CH_2 + BH_3 \longrightarrow \left[\begin{array}{l} H—BH_2 \\ \overset{\rho}{C}H_2—CH_2 \end{array}\right] \longrightarrow \begin{array}{ll} H & BH_2 \\ | & | \\ CH_2—CH_2 & \end{array}$$

In the above way, two more alkene molecules are added.

$$2CH_2{=}CH_2 + CH_3—CH_2—BH_2 \longrightarrow (CH_3—CH_2)_3B$$

With an unsymmetrical alkene, hydroboration proceeds in such a way that boron adds to the less-substituted end of the double bond (i.e. anti-Markownikoff addition). For example,

$$3CH_3—CH{=}CH_2 + BH_3 \longrightarrow (CH_3—CH_2—CH_2)_3B$$

The reactions are carried out in diethyl ether, $(C_2H_5)_2O$, diglyme, $(CH_3OCH_2–CH_2)_2OCH_3$, or tetrahydrofuran, $(CH_2)_4O$.

Hydroboration has high synthetic utility. The alkylboranes undergo oxidation with alkaline H_2O_2 to the corresponding primary alcohol. The product corresponds to anti-Markownikoff addition of water to the C=C.

$$(CH_3—CH_2—CH_2)_3B + 3H_2O_2 \xrightarrow[20–30°]{HO^{\sigma}} \underset{\substack{n\text{-Propyl alcohol} \\ (1°)}}{3CH_3—CH_2—CH_2—OH} + B(OH)_3$$

The alkyl boranes may also be cleaved with aqueous CH_3COOH (or better anhydrous $CH_3—CH_2—COOH$) to give alkanes.

$$(CH_3—CH_2—CH_2)_3B + 3H_2O \xrightarrow[25–30°]{H^{\oplus}} 3CH_3—CH_2—CH_3 + B(OH)_3$$

Oxidation

Alkenes can be oxidized by many reagents to give variety of products. Many of the oxidation products can further be degraded to get structural information.

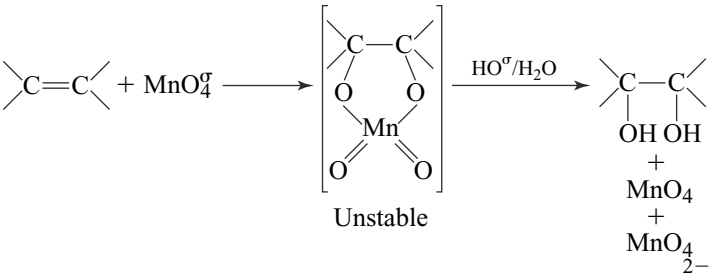
Hydroxylation (oxidation by $KMnO_4$ and OsO_4)

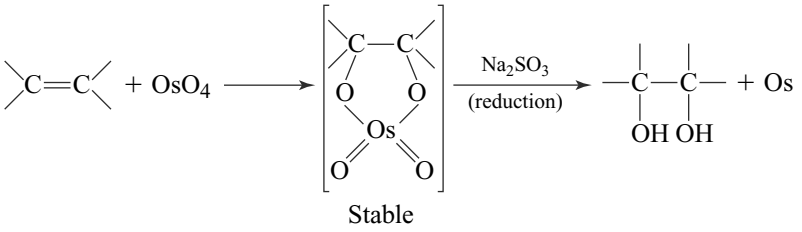
Dilute alkaline $KMnO_4$ (1% solution is known as Bayer's reagent) reacts with alkenes to give 1,2-diols (the glycols) but acidic $KMnO_4$ forms acids or ketones with it.

$$CH_2=CH_2 \xrightarrow[\text{(Bayer's reagent)}]{\text{1\% alk. } KMnO_4} \underset{\text{Ethylene glycol}}{HO—CH_2—CH_2—OH}$$

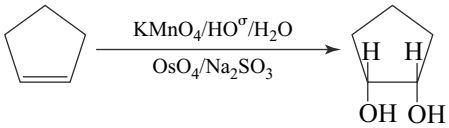
$$CH_3—CH=CH—CH_3 \xrightarrow{KMnO_4/H^{\oplus}} \underset{\text{Acetic acid}}{2CH_3—C(=O)—OH}$$

Formation of 1,2-diols is known as hydroxylation. Both $KMnO_4$ and OsO_4 can cause hydroxylation. The reactions proceed as follows:



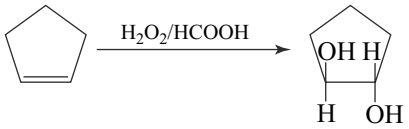


Both these reactions produce *cis*-glycols (diols) that is supported by the reaction.



Cyclopentene *cis*-1,2-Cyclopentanediol

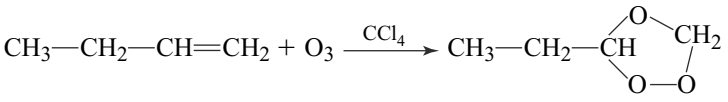
Another reagent for hydroxylation is H_2O_2 in formic acid. In this case, *trans*-addition product is formed.



trans-1,2-Cyclopentanediol

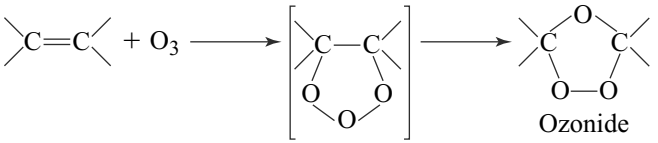
Oxidation by ozone

Alkenes react with ozone (also at low temperature) to form cyclic peroxide derivatives known as ozonide.



Ozonide

It is a multistep reaction.

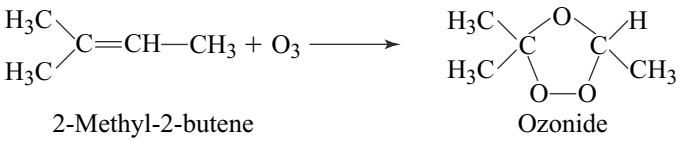


Ozonide

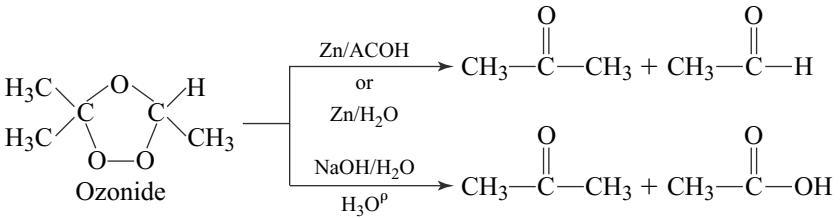
Ozonides are very reactive and unstable species. They can be cleaved by either of the methods given below.

(a) Zn/CH_3COOH (or water) to aldehydes or ketones.

(b) $H_2O_2/NaOH$ to acids or ketones.

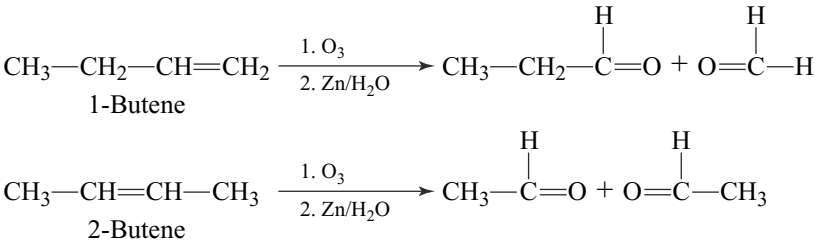


2-Methyl-2-butene Ozonide



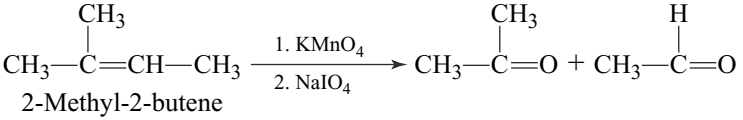
Ozonide

That is, in the cleaved products, a >C═O group is generated to each of the C═C in the alkene. Thus, the overall reaction (called ozonolysis) provides a means for locating the position of the double bonds in alkenes. It is illustrated taking 1- and 2-butenes as examples.

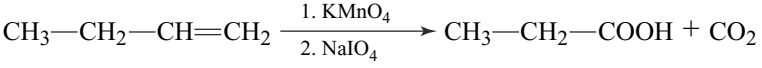


If O atoms from the above products are taken out and rest of the parts are joined, 1- and 2-butene will be generated, thus, locating the position of double bonds in the alkenes.

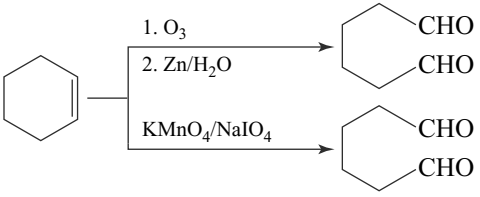
Another reagent for degrading 1,2-diols is the mixture of $NaIO_4$ and catalytic amount of $KMnO_4$ (*Lemieux reagent*), which gives the same information. In this method, permanganate hydroxylates alkene to give 1,2-diol and itself is reduced to manganate. The periodate then (i) cleaves the 1,2-diol (ii) oxidizes manganate to permanganate and the reaction continues. For example,



Terminal ═CH_2 is oxidized to CO_2 in this method.



Cleavage of cycloalkenes proceeds in the same manner.



Polymerization

Alkene molecules under specific condition may join together in a very large number. This reaction is termed as polymerization; the product is a polymer and the starting alkene is called the monomer. Thus, a polymer, here, may be defined as a long-chain molecule with repeating structural unit.

$$n\,CH_2{=}CH_2 \xrightarrow{\text{Catalyst}} \text{-}(CH_2{-}CH_2)\text{-}_n$$

Ethylene (monomer) → Polyethylene (polymer)

$$n\,F_2C{=}CF_2 \xrightarrow{\text{Catalyst}} \text{-}(CF_2{-}CF_2)\text{-}_n$$

Teflon

(For details, see chapter on *Polymers*.)

ANALYTICAL TESTS OF ALKENES

1. Alkenes decolourize bromine water or bromine in CCl_4.

$$H_2C{-}CH_2 + (Br_2 + CCl_4) \longrightarrow \underset{Br}{\overset{|}{-C}}{-}\underset{Br}{\overset{|}{C}}{-}$$

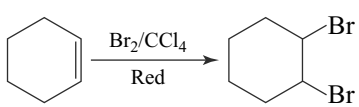
Red

2. Baeyer's reagent (1% alkaline $KMnO_4$).

$$CH_3{-}CH{=}CH_2 + MnO_4^- \longrightarrow CH_3{-}\overset{OH}{\overset{|}{C}}H{-}\overset{OH}{\overset{|}{C}}H_2 + MnO_2$$

Purple → Colourless + Brown

The above reactions are also given by cycloalkenes.



Colourless

PROBLEMS

Objective-Type Questions

1. When 2-methyl butan-1-ol is dehydrated to give an alkene, the preferred product is

(a) 2-methyl but-1-ene (b) but-1-ene
(c) but-2-ene (d) 2-methyl but-2-ene

2. Consider the following compounds.

(1) $CH_3CH_2CH_2CH_2OH$
(2) $CH_3CH_2CH(OH)CH_3$
(3) $(CH_3)_3COH$

These compounds are dehydrated by the treatment with sulphuric acid. The correct sequence of increasing order of the reactivity of these compounds towards dehydration is

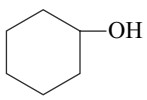
(a) 3, 1, 2 (b) 2, 1, 3
(c) 1, 3, 2 (d) 3, 2, 1

3. The major product obtained when 3-phenyl-1, 2 propanediol is heated with H_2SO_4 is

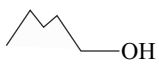
(a) $C_6H_5—CH_2—CO—CH_3$
(b) $C_6H_5—CH_2—CH_2—CHO$
(c) $C_6H_5—CH_2—C\equiv CH_2—CH_2—CH_3$

4. The product of the following reactions is

$$CH_2=CH—CHOOH + HBr \longrightarrow ?$$

(b) 

(c)

(d) 

6. The correct order of stability of diene is

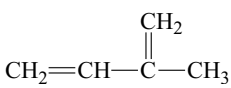
(a) cumulated > isolated > conjugated
(b) isolated > cumulated > conjugated
(c) conjugated > isolated > cumulated
(d) conjugated > cumulated > isolated

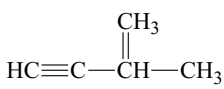
7. Consider the following sequence of the reactions and identify the final product.

$$H_2C=CH_2 \xrightarrow{HBr} (X) \xrightarrow[(aq.\ NaOH)]{Hydrolysis} (Y) \xrightarrow{aq.\ NaOH + I_2} (Z)$$

(a) H_3CCH_2I (b) H_3CCH_2OH
(c) H_3CCHO (d) CHI_3

8. An organic compound E(C_5H_8) on hydrogenation gives the compound F(C_5H_{12}). Compound E on ozonolysis gives HCHO and 2-ketopropanal. Identify the compound E.

(a) 

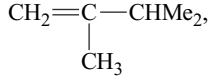
(b) 

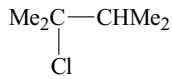
(c) $CH_3CH_2—CH=C=CH_2$
(d) $CH_2=CH—CH=CH_2$

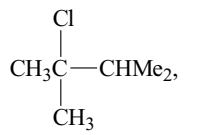
9. An organic compound A (C_4H_8) which when treated with H_2O/H_2SO_4 gives $C_4H_{10}O$ that cannot be resolved into optical isomers. What is A?

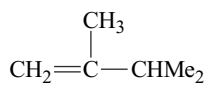
(a) Butene-1 (b) Cyclobutane
(c) Methyl cyclopropane (d) *trans*-Butene-2

10. An alkyl halide, X of formula $C_6H_{13}Cl$, on treatment with potassium tertiary butoxide gives two isomeric alkenes Y and Z (C_6H_{12}). Both of the alkenes on hydrogenation gives 2, 3-dimethyl butane. What are X, Y and Z?

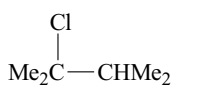
(a) 

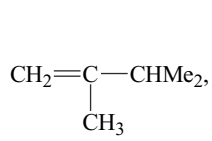


(b) 



(c) $Me_2C=CMe_2$, $CH_2=C—CHMe_2$,



(d) 

$(CH_3)_2C=CMe_2$

11. An organic compound 'A' has the molecular formula C_8H_{12} and on oxidation yields only $HOOC(CH_2)_6COOH$. The compound A is

(a) cyclo octyne (b) octyne-1
(c) octyne-2 (d) octyne-3

12. The major product obtained on treatment of $CH_3CH_2CH(F)CH_3$ with $CH_3O^{\ominus}/CH_3OH$ is

(a) $CH_3CH_2CH(OCH_3)CH_3$
(b) $CH_3CH=CHCH_3$
(c) $CH_3CH_2CH=CH_2$
(d) $CH_3CH_2CH_2CH_2OCH_3$

13. Which of the following is the most stable compound?

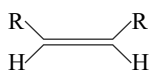
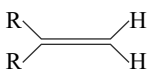
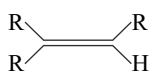
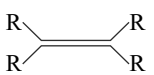
(a) *cis*-1, 2-Cyclohexanediol
(b) *trans*-1, 2-Cyclohexanediol
(c) *cis*-1, 3-Cyclohexenediol
(d) *trans*-1, 3-Cyclohexanediol

14. 3-Phenylpropene on reaction with HBr gives (as a major product)

(a) $C_6H_5CH_2CH(Br)CH_3$
(b) $C_6H_5CH(Br)CH_2CH_3$

(c) $C_6H_5CH_2CH_2Br$
(d) $C_6H_5CH(Br)CH{=}CH_2$

15. Which one of the following alkenes will react faster with H_2 under catalytic hydrogenation conditions?

(a) 
(b) 
(c) 
(d) 

16. The compound on reaction with $NaIO_4$ in the presence of $KMnO_4$ gives

(a) CH_3COCH_3
(b) $CH_3COCH_3 + CH_3COOH$
(c) $CH_3COCH_3 + CH_3CHO$
(d) $CH_3CHO + CO_2$

17. Alkyl halides react with dialkyl copper reagents to give

(a) alkenes (b) alkyl copper halides
(c) alkanes (d) alkenyl halides

18. Acid-catalysed hydration of alkenes except ethene leads to the formation of

(a) primary alcohol
(b) secondary or tertiary alcohol
(c) mixture of primary and secondary alcohols
(d) mixture of secondary and tertiary alcohols

19. The product of acid-catalysed hydration of 2-phenyl propene is

(a) 3-phenyl-2-propanol
(b) 1-phenyl-2-propanol
(c) 2-phenyl-2-propanol
(d) 2-phenyl-1-propanol

20. Which one of the following is responsible for depletion of the ozone layer in the upper strata of the atmosphere?

(a) Polyhalogens (b) Ferrocene
(c) Fullerenes (d) Freons

21. Reaction of HBr with propene in the presence of peroxide gives

(a) isopropyl bromide (b) 3-bromo propane
(c) allyl bromide (d) *n*-propyl bromide

22. 1-Chlorobutane on reaction with alcoholic potash gives

(a) 1-butene (b) 1-butanol
(c) 2-butene (d) 2-butanol

23. Which one of the following has the smallest heat of hydrogenation per mole?

(a) 1-Butene (b) *trans*-2-Butene
(c) *cis*-2-Butene (d) 1,3-Butadiene

24. The order of stability of three alkenes $R_2C{=}CR_2$, $R_2C{=}CHR$ and $RCH{=}CHR$ is

(a) $RCH{=}CHR > R_2C{=}CHR > R_2C{=}CR_2$
(b) $RCH{=}CHR < R_2C{=}CHR > R_2C{=}CR_2$
(c) $RCH{=}CHR > R_2C{=}CHR < R_2C{=}CR_2$
(d) $RCH{=}CHR < R_2C{=}CHR < R_2C{=}CR_2$

25. The treatment of propene with Cl_2 at 500–600°C produces

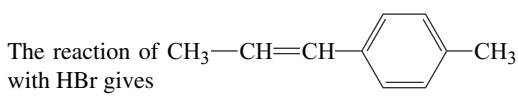
(a) 1,2-dichloropropane
(b) allyl chloride
(c) 2,3-dichloropropene
(d) 1,3-dichloropropene

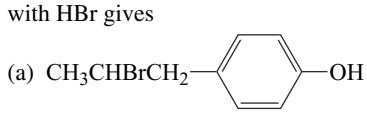
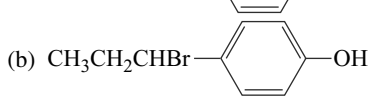
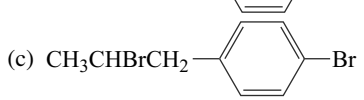
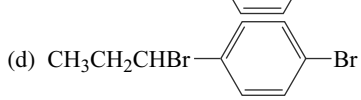
26. An alkene on treating with hot acidified $KMnO_4$ gives two molecules of ethanoic acid. The alkene is

(a) 1-butene (b) 2-butene
(c) 2-methylpropene (d) cyclobutene

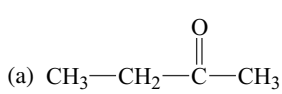
27. The major product formed when 2-bromobutane is treated with ethanolic KOH is

(a) 2-hydroxybutane (b) butanol
(c) 1-butene (d) 2-butene

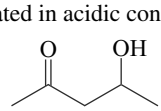
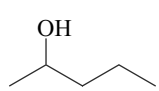
28. The reaction of  with HBr gives

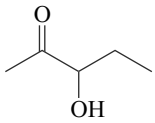
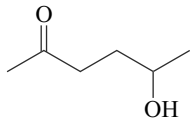
(a) 
(b) 
(c) 
(d) 

29. The product(s) obtained *via* oxymercuration ($HgSO_4 + H_2SO_4$) of 1-butyne would be

(a) 
(b) $CH_3{-}CH_2{-}CH_2{-}CHO$
(c) $CH_3{-}CH_2{-}CHO + HCHO$
(d) $CH_3{-}CH_2{-}COOH + HCOOH$

30. Which of the following will most readily be dehydrated in acidic condition?

(a) 
(b) 

(c)  (d) 

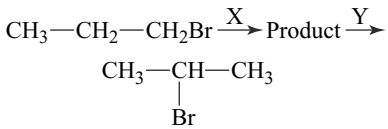
31. The reaction of propene with HOCl proceeds via the addition of

(a) H^+ in the first step
(b) Cl^+ in the first step
(c) OH^- in the first step
(d) Cl^+ and OH^- in a single step

32. In the presence of peroxide, hydrogen chloride and hydrogen iodide do not give anti-Markovnikov addition to alkenes because

(a) both are highly ionic
(b) one is oxidizing and the other is reducing
(c) one of the steps is endothermic in both the cases
(d) all the steps are exothermic in both the cases

33. Identify the set of reagents/reaction conditions 'X' and 'Y' in the following set of transformations.

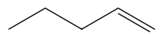
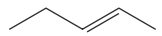
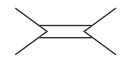
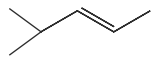


(a) X = dilute aqueous NaOH, 20°C; Y = HBr/acetic acid, 20°C
(b) X = concentrated alcoholic NaOH, 80°C; Y = HBr/acetic acid, 20°C
(c) X = dilute aqueous NaOH, 20°C; Y = $Br_2/CHCl_3$, 0°C
(d) X = concentrated alcoholic NaOH, 80°C; Y = $Br_2/CHCl_3$, 0°C

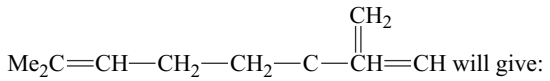
34. The nodal plane in the p-bond of ethane is located in

(a) the molecular plane
(b) a plane parallel to the molecular plane
(c) a plane perpendicular to the molecular plane which bisects the carbon–carbon σ-bond at right angle
(d) a plane perpendicular to the molecular plane which contains the carbon–carbon σ-bond

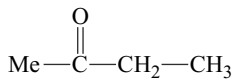
35. The alkene that can give acetone only on ozonolysis is

(a)  (b) 
(c)  (d) 

36. The ozonolysis of



will give:

(a) $Me_2C{=}O$
(b) HCHO
(c) 
(d) $CHO{-}CH_2{-}CH_2CO{-}CHO$

37. The addition of propene with HOCl proceeds via the addition of

(a) Cl^+ in the first step
(b) H^+ in the first step
(c) HO^- in the first step
(d) Cl^- and HO^- in a single step

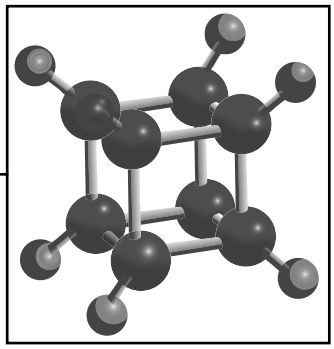
38. The addition of HBr is easiest with

(a) $Me_2C{=}CH_2$ (b) $ClCH{=}CHCl$
(c) $CH_2{-}CH_2{-}Cl$ (d) $Me{-}CH{=}CH_2$

Answers

1. (d)	2. (d)	3. (c)	4. (a)	5. (a)
6. (c)	7. (d)	8. (a)	9. (d)	10. (b)
11. (a)	12. (b)	13. (a)	14. (b)	15. (a)
16. (c)	17. (c)	18. (d)	19. (c)	20. (d)
21. (d)	22. (a)	23. (d)	24. (d)	25. (b)
26. (b)	27. (d)	28. (d)	29. (a)	30. (a)
31. (b)	32. (c)	33. (b)	34. (a)	35. (c)
36. (a, b, d)	37. (a)	38. (a)		

CHAPTER 11



Alkynes

Alkynes are hydrocarbons with carbon–carbon triple bonds. Their general formula is C_nH_{2n-2}. The C≡C is the functional group of the family.

$HC{\equiv}CH$	$CH_3{-}C{\equiv}CH$	$CH_3{-}C{\equiv}C{-}CH_3$
Ethyne (acetylene)	Propyne (methylacetylene)	2-Butyne (dimethyl acetylene)

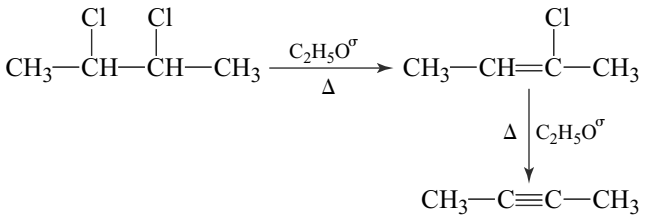
The simplest and the important alkyne is acetylene (ethyne). It is an important source of organic syntheses (on industrial scale). It is manufactured from water and calcium acetylide.

$$CaC_2 + 2H_2O \longrightarrow C_2H_2 + Ca(OH)_2$$

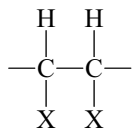
PREPARATION

Dehydrohalogenation of Vicinal Dihalides (1,2-Dihalides)

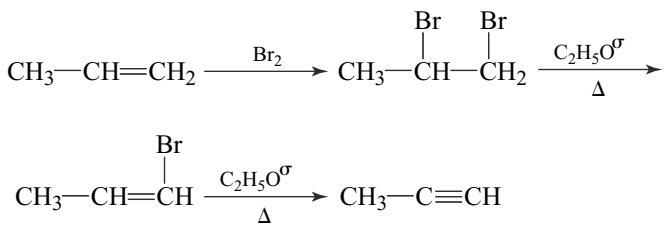
When a 1,2-dihalide is heated with a strong base ($C_2H_5O^{\ominus}$), alkyne is formed. The reaction takes place in two stages.



The reaction shows that halogen-bearing carbon atoms should have at least one H atom, i.e.,

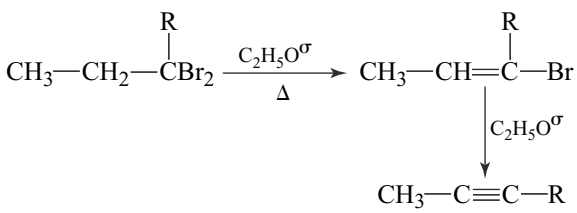


An alkene is easily converted into a vicinal dihalide on reaction with a halogen. Thus, this reaction can be a method of converting an alkene into an alkyne.

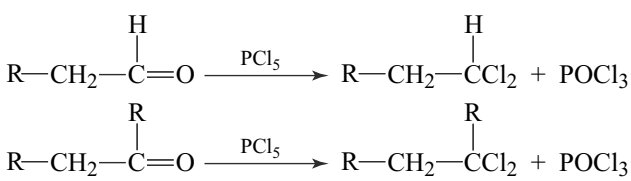


Dehydrohalogenation of Gem-Dihalides

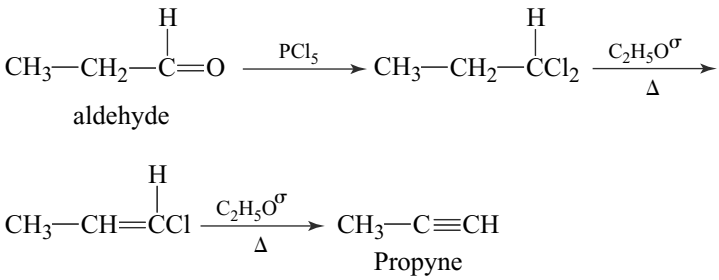
The gem-dihalides (1,1-dihalides), which have two H atoms on the adjacent carbon, give alkynes on heating with a strong base ($C_2H_5O^{\sigma}$, NH_2^{σ}, etc.). This reaction also takes place in two stages.



A gem-dihalide is easily prepared by the action of PCl_5 on an aldehyde or a ketone.

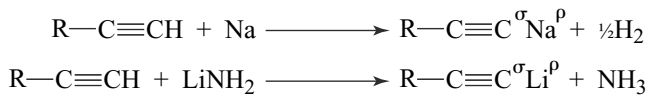


Thus, an aldehyde or a ketone can be converted into an alkyne by this reaction.

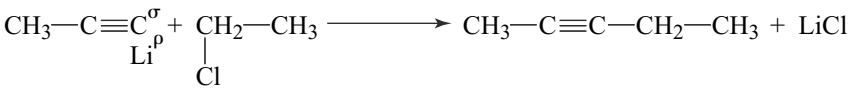


HIGHER ALKYNES

Terminal alkynes are acidic and react readily with Na or $NaNH_2$ or $LiNH_2$ to form salts, the acetylides.



This reaction, thus, generates a good nucleophile (R–C≡C$^{\sigma}$) that may react with a primary alkyl halide to form higher alkyne.



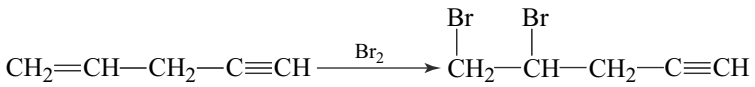
The reaction with secondary and tertiary alkyl halides is not satisfactory. It is because alkynide (the nucleophile) is also a strong base, which can cause elimination with 2° and 3° halides, decreasing yield of the alkyne.

PROPERTIES

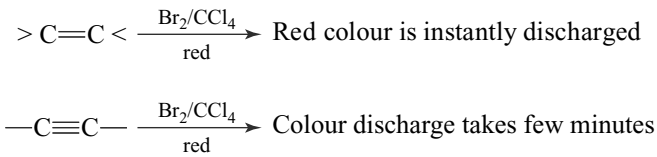
Physical properties of alkynes are similar to alkanes and alkenes. It is because of the force, here, between the molecules that is Van der Waal's type. Alkynes like other hydrocarbons are completely insoluble in water.

CHEMICAL REACTION

Alkynes have carbon–carbon triple bond (C≡C), one σ-bond and two π-bonds. The π-electrons are loosely held electrons. Alkynes, therefore, undergo addition reactions. However, the reaction rates of alkynes with electrophiles are slower than those of alkenes. It is shown by the selective bromination. Example,



Also, the red colour of bromine persists for a few minutes with most of the alkynes, i.e., a slow reaction.

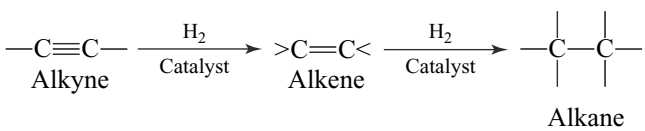


Important reactions given by alkynes include:

(i) Hydrogenation,
(ii) Electrophilic addition,
(iii) Nucleophilic addition and
(iv) Acidity of terminal alkynes.

Hydrogenation

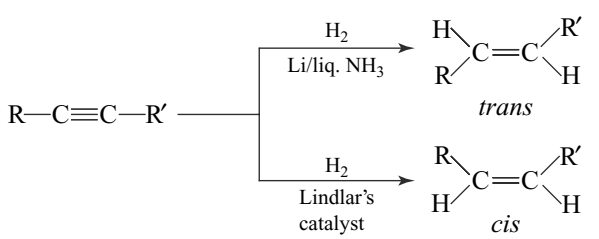
Hydrogenation, i.e., addition of hydrogen to alkynes, is a reduction reaction. It takes place in two stages: from alkyne to alkene and then from alkene to alkane.



By regulating reaction condition, the reaction can be stopped at the alkene stage. Also, *cis*- or *trans*-hydrogenated product can be produced by using suitable catalyst.

1. Reduction of alkyne with Na or Li in liquid NH_3 gives *trans*-alkene.
2. Use of Lindlar's catalyst almost gives *cis*-alkene.

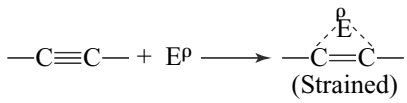
Lindlar's catalyst: $Pd/BaSO_4$ poisoned by quinoline.



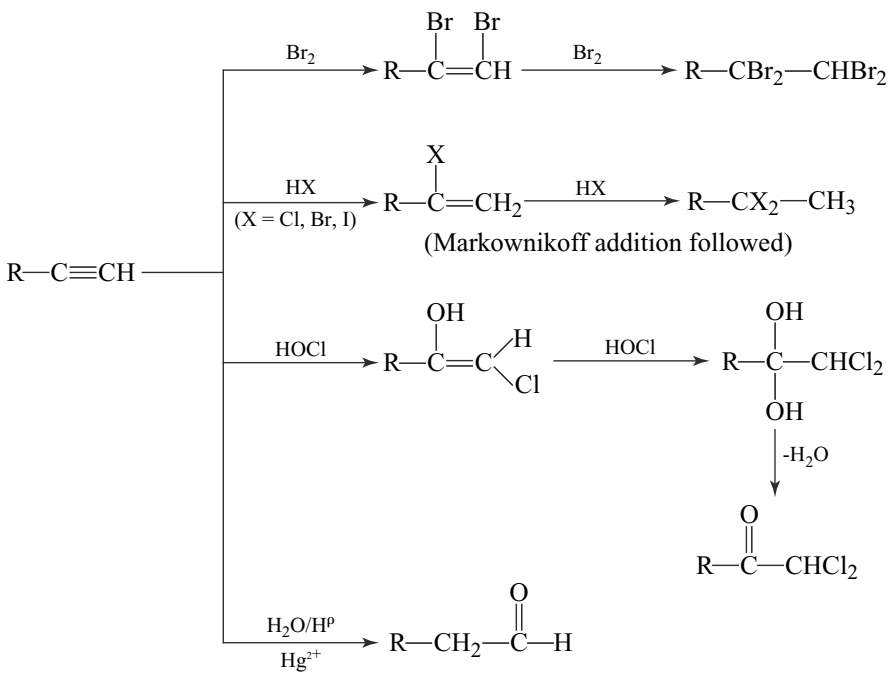
Electrophilic Addition

Electrophilic addition to alkynes takes place in two stages, alkyne ⟶ alkene and then the saturated final product. But the reaction with alkynes is found to be slower as compared to alkenes (compare decolourization of red colour of Br_2 above). Two reasons may be assigned to this process:

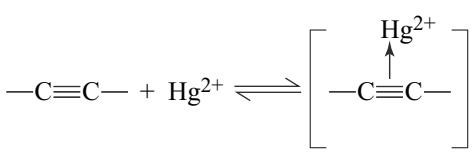
1. First, the π-electrons are tightly held between two sp-hybridized carbon nuclei. So, they are not easily available for combination with electrophiles.
2. Second, the cyclic intermediate formed initially is less stable because it is a highly strained arrangement.



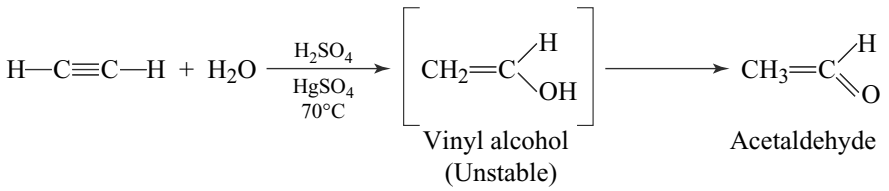
It seems probable that both the above factors, electronic and steric, contribute partly in decreasing reactivity of the alkynes towards electrophiles.



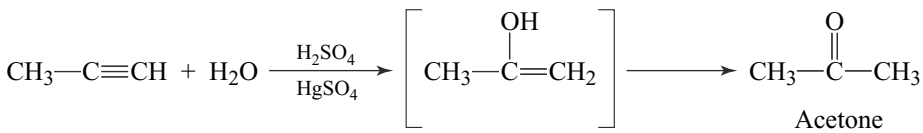
Hydration (addition of water) of alkynes requires not only the acid catalyst (H_2SO_4) but also mercuric ions (Hg^{2+}) or Cu^{+} or Ni^{2+}. It is suggested that the metal ion forms complex with triple bonds that assist further reaction.



This reaction proceeds as

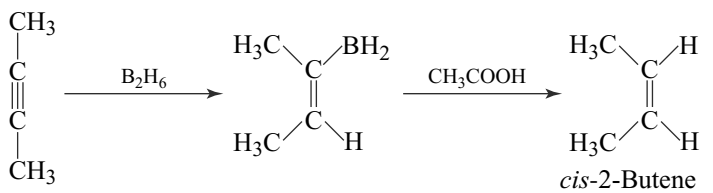


Addition of water to alkyl-substituted acetylene always follow Markownikoff's rule. A ketone is the final product.



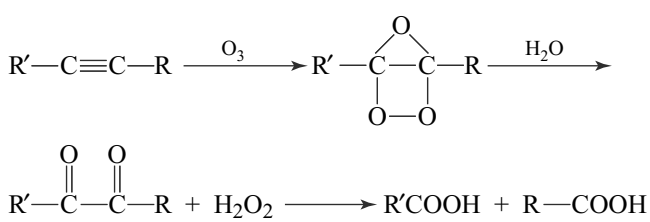
Hydroboration (Addition of B_2H_6)

Addition of boron hydride to carbon–carbon triple bond gives vinylborane. Vinylboranes are readily decomposed by acetic acid to give alkenes. The overall process is stereospecific, as a disubstituted alkyne gives only a *cis*-alkene.



Ozonization

Ozone reacts with alkynes to form ozonides. They are hydrolyzed by water to form 1,2-diketone and H_2O_2. H_2O_2 further oxidizes 1,2-diketone to form carboxylic acid.

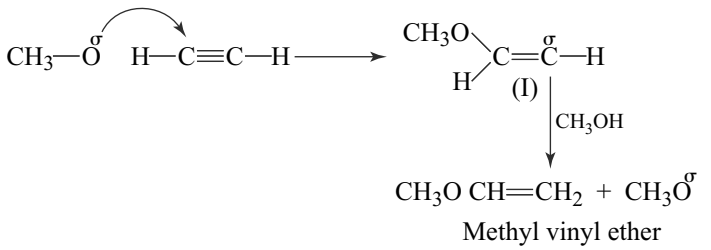


The identification of acids can locate the position of triple bond in the alkyne chain.

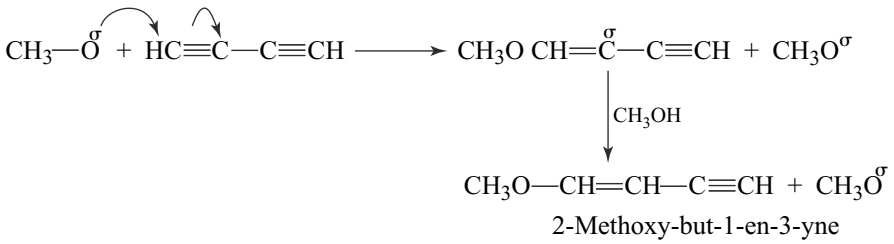
Nucleophilic Addition to C≡C

Unlike alkenes, alkynes also add nucleophiles readily. For example, methoxide ion (CH_3OH + NaOH) adds to C_2H_2 to form methylvinyl ether.

$$CH_3OH + NaOH \longrightarrow CH_3O^{\sigma} + Na^{\rho} + H_2O$$



The carbanion intermediate (I) is a very strong base and reacts rapidly with CH_3OH to form ether as the product and generates methoxide. The reaction also takes place with conjugated diynes and triynes. It is important to prepare ethers having unsaturated hydrocarbon units, e.g., formation of 1-methoxy-but-1-en-3-yne using 1,3-butadiyne.



Acidity of Alkynes

Terminal alkynes (i.e., 1-alkynes, R–C≡CH) behave as very weak acids. They form salt with strong bases like sodamide ($NaNH_2$) or KNH_2.

$$R—C\equiv CH + NaNH_2 \xrightarrow{\text{Liq. } NH_3} R—C\equiv C^{\sigma}Na^{\rho} + NH_3$$

Terminal alkynes also form salt with ammoniacal Ag^{ρ} and Cu^{ρ} that are insoluble. The silver salt is colourless whereas the copper salt is red in colour.

$$R—C\equiv CH + [Ag(NH_3)_2]^{\rho} \longrightarrow R—C\equiv C\,Ag + NH_3 + NH_4^{\rho}$$

R═H also — White ppt.

$$R—C\equiv CH \xrightarrow{CuCl/NH_4OH} R—C\equiv C\,.\,Cu$$

Red ppt.

Alkynes can be easily regenerated from the silver precipitate by the reaction with dilute acid or NaCN.

$$R{-}C{\equiv}CAg + HCl \longrightarrow R{-}C{\equiv}CH + AgCl \downarrow$$

$$R{-}C{\equiv}CAg + NaCN + H_2O \longrightarrow R{-}C{\equiv}CH + NaOH + AgCN \downarrow$$

This reaction can be used to:

1. Differentiate terminal alkynes from nonterminal alkynes. For example,

$$\underset{\text{1-Butyne}}{CH_3{-}CH_2{-}C{\equiv}CH} \xrightarrow{AgNO_3/NH_4OH} \underset{\text{Precipitate}}{CH_3{-}CH_2{-}C{\equiv}CAg}$$

$$\underset{\text{2-Butyne}}{CH_3{-}C{\equiv}C{-}CH_3} \xrightarrow{AgNO_3/NH_4OH} \text{No reaction}$$

Since 2-butyne has no acidic hydrogen, precipitate is not formed.

2. To separate an alkyne from alkene or alkane.

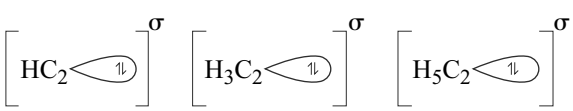
$$\left[\begin{array}{c} CH_3{-}CH_3 \\ + \\ CH{\equiv}CH \end{array}\right] \xrightarrow{AgNO_3/NH_4OH} \downarrow AgC{\equiv}CAg + CH_3{-}CH_3(g)$$

$$AgC{\equiv}CAg \xrightarrow{HNO_3} HC{\equiv}CH(g) + 2Ag^{\rho} + 2NO_3^{\sigma}$$

Cause of acidity in terminal alkynes

In acetylene, the three pairs of bonding electrons are very much concentrated between the two carbon nuclei. Thus, the C–H bond-pair electrons experience lesser repulsion and the bond-pair electrons are strongly held by the C nucleus (C is sp hybridized in C_2H_2).

A stronger acid has a weak conjugate base and vice versa. If C_2H_2 is more acidic than either C_2H_4 or C_2H_6 (or alkenes and alkanes in general), then the C_2H^{σ} ion must be a weaker base than either $C_2H_3^{\sigma}$ or $C_2H_5^{\sigma}$. The unshared pair of electrons in the above ions are housed in



sp-Hybrid sp^2-Hybrid sp^3-Hybrid

The s character in the hybrids of C are as Csp > Csp^2 > Csp^3, i.e., the electron pair in sp-hybrid orbital is most tightly held by the C nucleus. It has lesser donor ability and a weak base; so C_2H_2 is a stronger acid than C_2H_4 or C_2H_6.

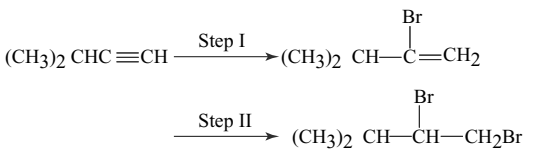
Analytical tests of alkynes

1. Discharges red colour of Br_2 (Br_2 in CCl_4).
2. Decolourizes $KMnO_4$ and forms dark brown MnO_2.
3. Terminal alkynes (–C≡H) form white silver acetylide with ammoniacal $AgNO_3$ and red precipitate of cuprous acetylide with $CuCl/NH_4OH$ (see reaction).

PROBLEMS

Objective-Type Questions

1. Which of the following sets of reagents can be used for Step I and Step II in the following reaction?

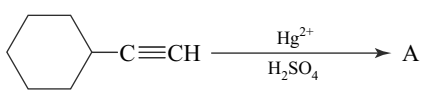


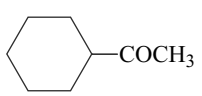
Step I	Step II
1. HBr	HBr and peroxide
2. HBr and peroxide	HBr
3. Br_2	HBr
4. Br_2	HBr and peroxide

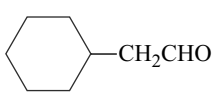
Select the correct answer using the codes given below.

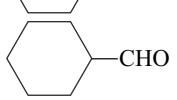
(a) 1 alone (b) 1, 2 and 4
(c) 2 and 4 (d) 3 and 4

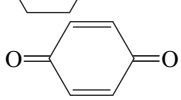
2. What is A in the following reaction?



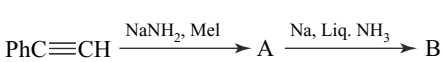
(a) 

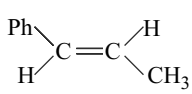
(b) 

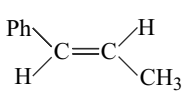
(c) 

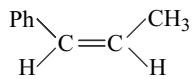
(d) 

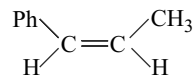
3. Identify A and B in the following scheme. They are



(a) PhC≡C—CH_3, 

(b) PhCH=CH_2, 

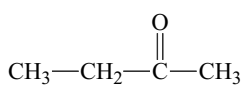
(c) PhC≡CCH_3, 

(d) PhCH=CH_2, 

4. When propyne reacts with $HgSO_4$ and H_2SO_4, the product is
(a) propane (b) propanol
(c) propanal (d) propanone

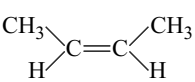
5. When 2-butyne is treated with dil. $H_2SO_4/HgSO_4$, the product is
(a) butanol-1 (b) butanal
(c) butanol-2 (d) 2-butanone

6. What is product formed when acetylene reacts with HOCl?
(a) CH_3COCl (b) $Cl_2CH–CHO$
(c) $ClCH_2–CHO$ (d) $ClCH_2–COOH$

7. The products obtained via oxymercuration (H_2SO_4/$HgSO_4$) of 1-butyne would give
(a) 

(b) $CH_3–CH_2–CHO + HCHO$
(c) $CH_3–CH_2–CH_2–CHO$
(d) $CH_3–CH_2–CHO + HCOOH$

8. When acetylene gas is passed through H_2SO_4 in the presence of $HgSO_4$, the product is a/an
(a) ketone (b) ether
(c) acetaldehyde (d) acetic acid

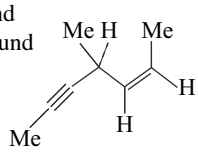
9. Which of the following is expected to have the lowest dipole moment?
(a) $CH_3–C≡C–CH_3$ (b) 

(c) $CH_3–CH_2–C≡CH$ (d) $CH_2=CH–C≡CH$

10. Propyne and propene can be distinguished by
(a) conc. H_2SO_4 (b) Br_2 in CCl_4
(c) dil. $KMnO_4$ (d) $AgNO_3$ in ammonia

11. Hydrogenation of the adjoining compound in the presence of poisoned palladium catalyst gives

(a) an optically active compound
(b) an optically inactive compound
(c) a racemic mixture
(d) a diastereomeric mixture



12. Hexyne-2 gives *trans*-2-hexane on reaction with

(a) $H_2/Pd/BaSO_4$ (b) $LiAlH_4$
(c) Li/NH_3 (d) Pt/H_2

13. The products in the following reaction

$$CH_3C{\equiv}CCH_2CH_3 \xrightarrow[\text{(ii) Oxidation}]{\text{(i) } O_3} \text{are}$$

(a) $CH_3–COCH_3 + CH_3–COCH_3$
(b) $CH_3COOH + CO_2$
(c) $CH_3COOH + CH_3–CH_2COOH$
(d) $CH_3–CHO + CH_3–CH_2–CHO$

14. Propyne when passed through a hot iron tube at 400°C produces

(a) methyl benzene (b) benzene
(c) dimethyl benzene (d) polypropene

15. The product 'A' in the following reaction is

$$CH_3—C{\equiv}C—CH_3 \xrightarrow[\text{(ii) } CH_3COOH]{\text{(i) } B_2H_6} \text{'A'}$$

(a) *trans*-2-butene (b) *cis*-2-butene
(c) butane (d) butanol-2

16. Terminal and nonterminal alkynes can be distinguished by

(a) Br_2 in CCl_4 (b) $KMnO_4$
(c) ammoniacal $AgNO_3$ (d) ammoniacal CuCl

17. An organic compound decolourizes Br_2 water and also gives red precipitate with $CuCl/NH_4OH$ solution. The compound is

(a) $CH_3–CH{=}CH_2$ (b) $CH_3–C{\equiv}CH$
(c) $CH_2{=}CH_2$ (d) $CH_3–C{\equiv}C–CH_3$

18. Identify the product A in the following reaction:

$$CH_3—C{\equiv}C—H \xrightarrow[\text{(ii) } CH_3COOH]{\text{(i) } B_2H_6} \underset{\text{(iii) } H_3O^{\oplus}}{\text{'A'}}$$

(a) $HC{\equiv}C–CH_2–CH_2–OH$
(b) $CH_3–C{\equiv}C–CH_2–OH$
(c) $CH_3–CH{=}CH–CH_2–OH$
(d) $CH_2{=}CH–CH_2–OH$

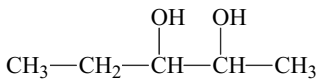
19. The products in the following reaction are

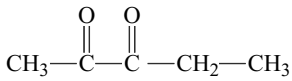
$$CH_3—CH_2—C{\equiv}C—H \xrightarrow[\text{(ii) } H_3O^{\oplus}]{\text{(i) } KMnO_4, KOH, H_2O}$$

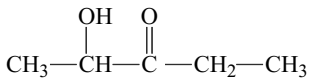
(a) $CH_3–CH_2–COOH + HCOOH$
(b) $CH_3–CH_2–CHO + CO_2$
(c) $CH_3–CH_2–COOH + CO_2$
(d) $CH_3–CH_2–CHO + HCOOH$

20. 2-Pentyne on reaction with dilute neutral solution of $KMnO_4$ (or permanganate) produces

(a) $CH_3–CHO + CH_3CH_2–CHO$

(b) 

(c) 

(d) 

21. Identify the product X in the reaction given below.

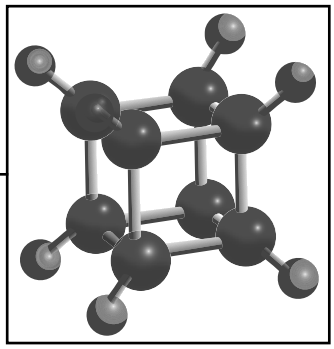
$$HC{\equiv}C—C{\equiv}CH \xrightarrow{CH_3OH/NaOH} X$$

(a) 1-Methoxy-2-buten-3-yne
(b) 2-Methoxy-1-buten-3-yne
(c) 1-Methoxy-1-buten-3-yne
(d) 1-Methoxy-2-buten-1-yne

Answers

1. (a)	2. (a)	3. (a)	4. (d)	5. (d)
6. (b)	7. (a)	8. (c)	9. (a)	10. (d)
11. (b)	12. (c)	13. (c)	14. (a)	15. (b)
16. (c,d)	17. (b)	18. (b)	19. (c)	20. (c)
21. (c)				

CHAPTER 12



Aliphatic Halogen Compounds

ALKYL HALIDES

Halogen derivatives of alkanes are known as alkyl halides. They are divided into mono, di, tri, etc., halides.

Monohalides

Monohalides contains only one halogen in an alkyl group, example

$CH_3—Cl$	$CH_3—\underset{\displaystyle Br}{\underset{\vert}{CH}}—CH_3$
Methyl chloride	Isopropyl bromide
C_2H_5Cl	$(CH_3)_3CCl$
Ethyl chloride	t-Butyl chloride

They are further divided as:

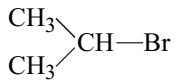
1. **Primary halide**
   Monohalides in which halogen bearing carbon is joined with two H atoms (or one C atom), that is $–CH_2–X$, are known as primary halides.

$CH_3—CH_2—Cl$ Ethyl chloride (chloro ethane)

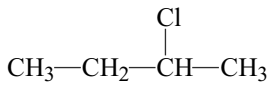
$CH_3—CH_2—CH_2—Br$ *n*-Propyl bromide (1-bromopropane)

$$CH_3—\underset{\displaystyle CH_3}{\underset{\vert}{C}}—CH_2—Br$$ Neopentyl bromide (2,2-dimethyl bromopropane)

2. **Secondary halide**
   Monohalides in which halogen bearing C is joined with only one H atom (or two C atoms), that is >CH–X, are known as secondary halides.

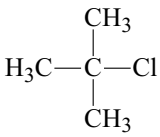


Isopropyl bromide
(2-bromo propane)

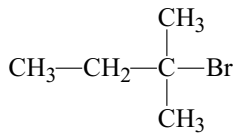


Sec. butyl chloride
(2-chloro butane)

3. **Tertiary halide**
   Monohalides in which halogen bearing C is joined with no H atom (or three C atoms), that is C—X are known as tertiary halides.



t-Butyl chloride
(2-methyl-2-chloropropane)



t-Pentyl chloride
(2-methyl-2-bromo butane)

Dihalides

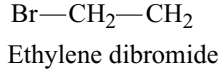
Dihalides contain two halogens in alkyl chain. They are divided as:

1. **Gem-dihalides**
   Gem-dihalides (gem means the same) contain both the halogen atoms on the same carbon. When two H atoms are removed from the same C atom, the group is called *alkylidene group*. Therefore, gem-dihalides are called alkylidene dihalides. For example,

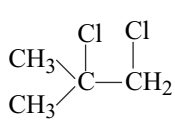
CH_3CHCl_2 Ethylidene dichloride (1,1-dichloroethane)

$CH_3CCl_2\,CH_3$ Isopropylidene dichloride (2,2-dichloropropane)

2. **Vicinal (vic) dihalides**
   When the two halogen atoms are on adjacent C atoms, the dihalide is called vic-dihalide. They are named as dihalides of the alkene from which they can be formed. For example,

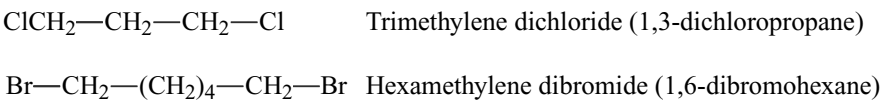


Ethylene dibromide
(1,2-dibromoethane)



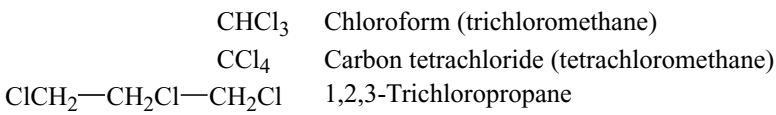
Isobutene chloride
(2-methyl-1,2-dichloropropane)

3. **Terminal (or α, ω) dihalides**
   A dihalide in which halogen atoms are on each of the terminal carbon atoms is called α-, ω- dihalide. Such compounds are named polymethylene dihalide.

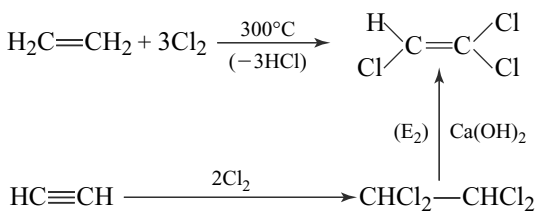


Polyhalides

They contain many halogen atoms in a chain.

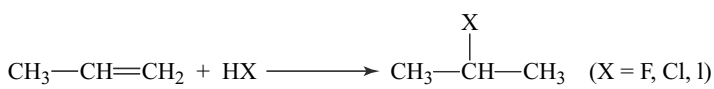


Carbon tetrachloride is widely used as a solvent and also as a cleaning solvent (though it is toxic). Triclene (trichloroethylene, BP 87°C) is widely used as dry cleaning solvent. It may be prepared as

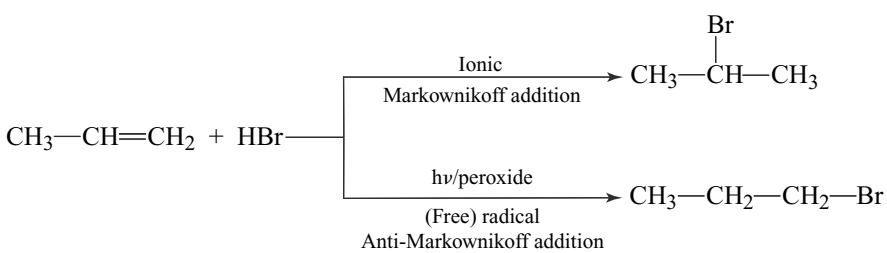


Preparation

1. **Addition of HX to alkene**
   This reaction proceeds as:



But addition of HBr is condition dependent. In ionic reaction, addition follows Markownikoff's rule, but in the presence of peroxide anti-Markownikoff addition takes place.



2. From alcohols

Reaction of alcohol with HX (X = Br and I) is satisfactory.

$$CH_3—CH_2—CH_2—OH + HBr \longrightarrow CH_3—CH_2—CH_2—Br + H_2O$$

$$CH_3—\underset{\displaystyle OH}{\underset{|}{CH}}—CH_3 + HBr \longrightarrow CH_3—\underset{\displaystyle Br}{\underset{|}{CH}}—CH_3 + H_2O$$

But primary alcohols react slowly with HCl, unless $ZnCl_2$ is added.

$$CH_3—CH_2—CH_2—OH + HCl \xrightarrow{ZnCl_2} CH_3—CH_2—CH_2—Cl + H_2O$$

Phosphorous halides also produce alkyl halide with alcohol.

$$3R—OH + PCl_3 \longrightarrow 3RCl + H_3PO_3$$

$$R—OH + PCl_5 \longrightarrow RCl + POCl_3 + HCl$$

Thionyl chloride also forms alkyl chloride with alcohols. This reaction is preferred as side products are gaseous and leaves no problem of separation of the product (alkyl halide).

$$R—OH + SOCl_2 \longrightarrow RCl + SO_2\uparrow + HCl\uparrow$$

3. Hundsdiecker reaction

Dry silver salt of a carboxylic acid upon heating with Br_2 in CCl_4 gives alkyl bromide. The alkyl bromide contains one carbon less than the carboxylic acid.

$$R—COOAg + Br_2 \xrightarrow[\Delta]{CCl_4} R—Br + AgBr + CO_2$$

Properties

The BPs and MPs of alkylhalides are higher than alkanes having the same number of carbon atoms. It is because the halogen has more electrons that results in greater Van der Waals' attraction. In a group of isomeric alkyl halides, the BP of primary halide is highest and that of the tertiary halide is the lowest.

Alkyl halides have extremely low water solubility.

Table 12.1

Name	Formula	BP (°C)
n-Butyl chloride	$CH_3(CH_2)_2—CH_2—Cl$	78
Iso-Butyl chloride	$CH_3—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH_2—Cl$	69
tert-Butyl chloride	$(CH_3)_3C—Cl$	51

The reactivity of the alkyl halides depends on the halogen atom. In general, reactivity increases in the order:

$$R—Cl < R—Br < R—I$$

It is because of the gradual decrease in the C–halogen bond strength.
The C–F bond is extremely strong, so alkyl fluorides are unreactive.

Reaction

Alkyl halides react with a variety of reagents. Important reactions are:

1. **Nucleophilic substitution (S_N1, S_N2)**
   It is the most important reaction of alkyl halides. The reactions may be summarized as follows:

   $$R—X + Y^{\sigma} \longrightarrow R—Y + X^{\sigma}$$

   $$Y^{\sigma} = Cl^{\sigma}, Br^{\sigma}, I^{\sigma}, HO^{\sigma}, R—O^{\sigma}, CH3COO^{\sigma}, CN^{\sigma}, R^{\sigma}, NH_2^{\sigma}, NO_2^{\sigma}$$

   $$R—X + HY \longrightarrow R—Y + HX$$

   $$HY = H_2O, R—OH, NH_3, \text{etc.}$$

   Details of nucleophilic substitution reactions are discussed under reaction mechanism (Chapter 5).

2. **Elimination reaction (E_1 and E_2)**
   The general reaction is

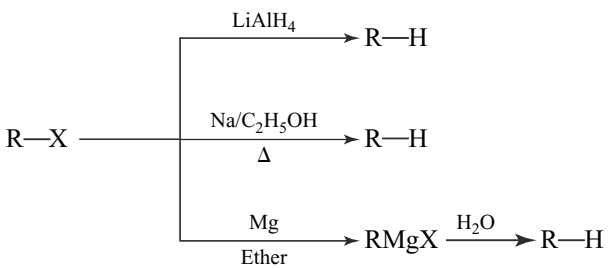
   $$R—CH_2—CH_2—X + Y^{\sigma} \longrightarrow R—CH=CH_2 + HY + X^{\sigma}$$

   See reaction mechanism for details (Chapter XX).

3. **Formation of Grignard reagents**
   It will be discussed separately ahead.

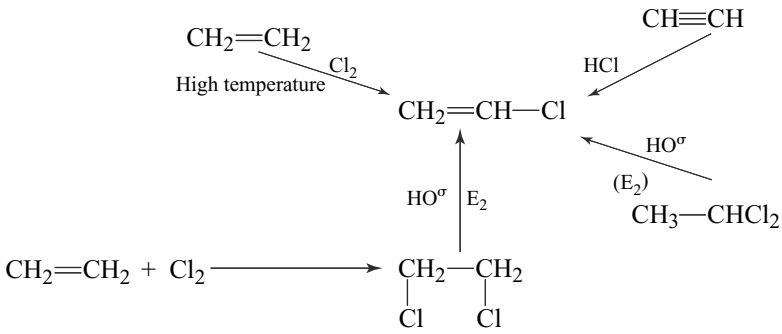
4. **Reduction**
   An alkyl halide can be reduced to the corresponding alkane by a variety of reagents.

   (a) $LiAlH_4$ (b) Na/C_2H_5OH (c) via Grignard reagent etc.



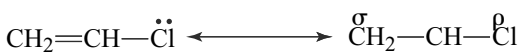
Vinyl halide

The most common and readily available is vinyl chloride. It can be prepared by a number of ways.



The commercial preparation follows high temperature chlorination of ethene.

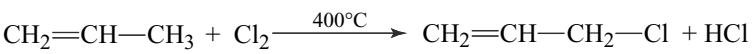
Vinyl halide is inert in S_N1 and S_N2 reaction (see Chapter 5). The reason of this inertness is conjugation of non-bonded pair of electron at the halogen with π electrons of C=C bonds.



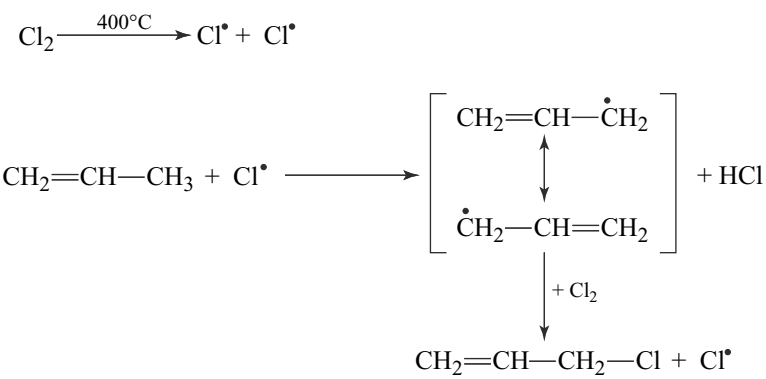
It makes C–Cl bond strong and inert in S_N1 and S_N2 reactions.

Allyl halide

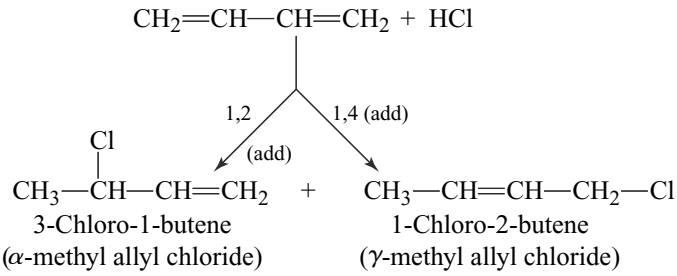
The most common allyl halide is allyl chloride. It may be prepared as:



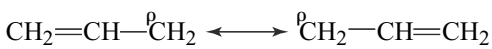
The reaction follows free radical mechanism.



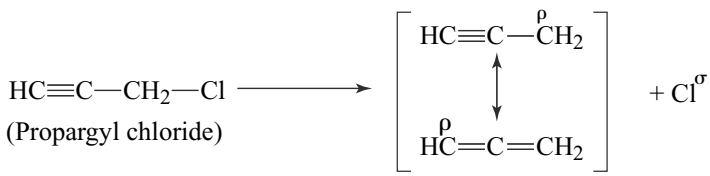
A general method for preparing allylic halide is by addition of HX to conjugated dienes. A mixture of 1,2 and 1,4 addition products are usually obtained.



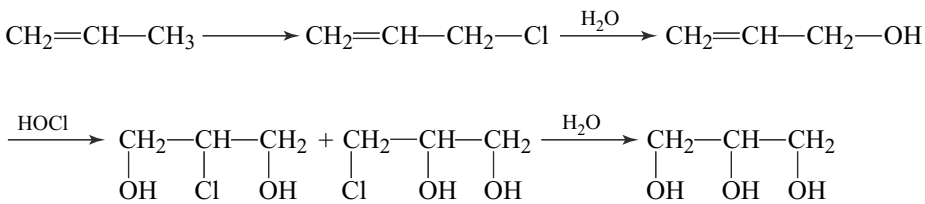
Unlike vinyl halides, allyl halides are very reactive (particularly in S_N1 reactions). It is because of conjugative stabilization of the allyl cation.



A triple bond has a comparable effect. For example, 3-chloro-1-propyne is quite labile.



Allyl chloride is an intermediate in the commercial preparation of glycerol (1,2,3-propanetriol) from propene.



Polyhalogen compounds

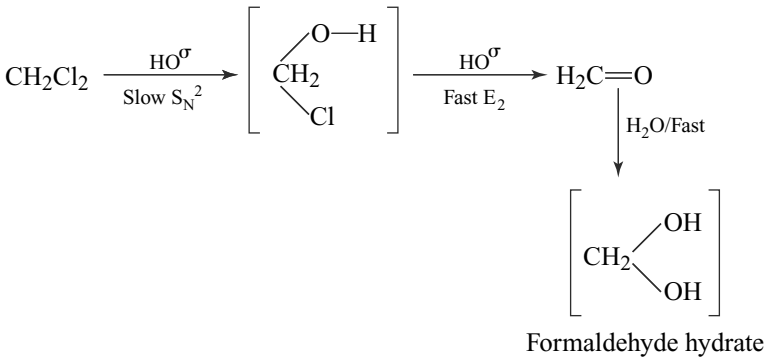
Chlorine compounds in this series are more important. For example,

CH_2Cl_2	$CHCl_3$	CCl_4
Methylene chloride	Chloroform	Carbon tetrachloride
bp 40°C	bp 61°C	bp 77°C

These substances are used as solvents.

Chemical reactivity of these substances is quite unusual.

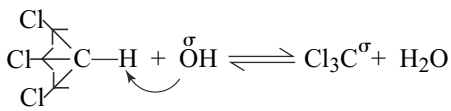
1. Methylene chloride reacts with hydroxide ion (S_N2 reaction) much slowly than methyl chloride.

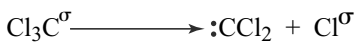


Formaldehyde hydrate

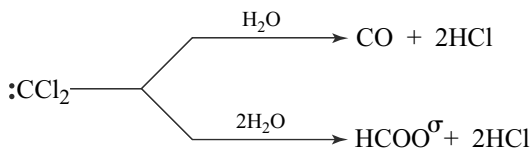
2. Carbon tetra chloride is even less reactive than methylene chloride.

3. Chloroform, however, is reactive towards hydroxide ion. The ultimate products are carbon monoxide, chloride ions and formate ion. It is because hydroxide ion attacks the $CHCl_3$ more rapidly at hydrogen than at carbon. This produces dichloro carbene that ultimately forms the products.





dichlorocarbene



The electrophilic nature of dichloro carbene (CCl_2, an electron-deficient species) is responsible for the above reactions.

Trihalo compounds

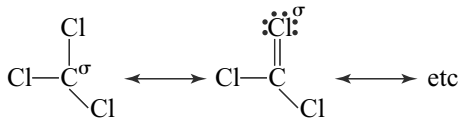
The compounds CHX_3 (X = Cl, Br, I) are common ones.

$CHCl_3$	$CHBr_3$	CHI_3
Chloroform	Bromoform	Iodoform
bp 60°C	bp 149°C	bp 119°C

Iodoform is a yellow crystalline solid. It is used as an antiseptic.

These trihalo derivatives are prepared by *haloform reaction* (see Chapter 6, *Name Reactions*).

Although F is mostly electronegative, $CHCl_3$ is found more acidic than CHF_3. It is because the anion CX_3 is more stable when X = Cl. Chlorine atom has vacant d-orbital in its valence shell. It facilitates delocalization of negative charge at C. As F has no d-orbitals in its valence shell, no such delocalization and consequent stabilization is achieved.



Organometallic compounds

Compounds in which metal and carbon are directly linked are known as *organometallic compounds*. For example,

CH_3Li	$(C_2H_5)_2Mg$	C_6H_5Li
Methyl lithium	Diethyl magnesium	Phenyl lithium

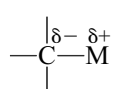
C_2H_5MgBr	C_6H_5MgBr
Ethylmagnesium bromide	Phenylmagnesium bromide

Potassium ethoxide and sodium acetate are not organometallic compounds as the metals K and Na are linked to oxygen.

$C_2H_5O^{\sigma}K^{\rho}$	CH_3COO^{σ}
Potassium ethoxide	Sodium ace

Almost all metals can form organometallics. Transition metals organometallics are very important as catalyst. Organic derivatives of less metallic elements like Si, B, Sb and As are also taken as organometallics. The nature of M–C bond ranges from ionic to polar covalent (C is always the negative centre).

$Me^{\sigma}Li^{\rho}$	RMgX
Ionic	Polar covalent



Grignard reagents

Alkyl (or aryl) magnesium halides are known as Grignard reagents. For example,

C_2H_5MgBr	C_6H_5MgBr
Ethyl magnesium bromide	Phenyl magnesium bromide

These compounds are named after Victor Grignard, who discovered them and developed their use as synthetic reagent, for which he got a Nobel Prize in 1912.

Properties

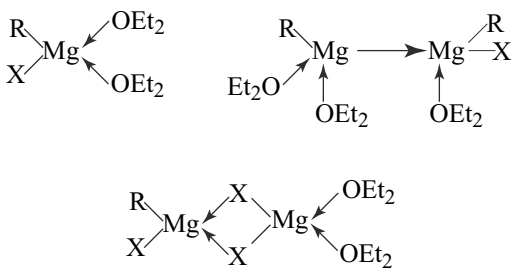
Grignard reagents are prepared in dry ether solution from Mg turnings and an alkyl halide (or aryl halide).

$$C_2H_5Br + Mg \xrightarrow{\text{Dry ether}} C_2H_5MgBr$$

A chloride reacts sluggishly. Also, they give precipitate of $MgCl_2$, which unlike $MgBr_2$ and MgI_2 is only slightly soluble in ether.

Structure

Grignard reagents, as prepared in ether solution, are very highly associated with the solvent (ether) through the O atom. The following structures have been proposed:



The crystalline Grignard reagents have been isolated as di-etherates, C2H5MgBr(OEt2)2. The X-ray analysis shows that the four groups (C_2H_5, Br and 2EtO) are arranged tetrahedrally around Mg atom.

Reaction

The Grignard reagents are highly polar compounds carbon being the negative pole.

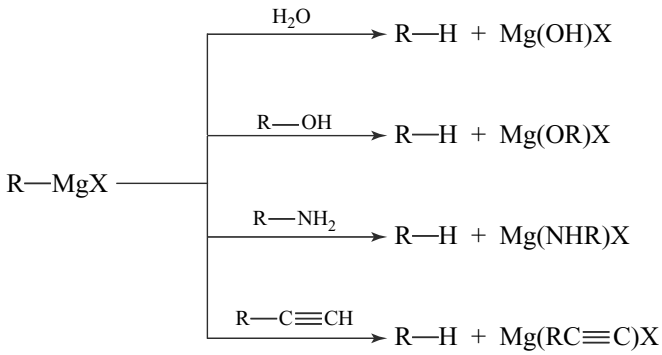
$$\overset{\delta-}{R}—\overset{\delta+}{Mg}—X$$

Thus, it is a source of a good nucleophilic (Rσ) or a strong base (Rσ). The reactions of RMgX fall broadly into two groups:

1. Reactions of RMgX with active hydrogen compounds
2. Addition reactions of RMgX to C=O, C≡N, etc. (that is to multiple bonds).

Reactions with active hydrogen compounds

Compounds that contain protonic hydrogen ($H^{\delta+}$) are taken as active hydrogen compounds, such as water, alcohol, acids, primary and secondary amines, terminal alkynes etc. Grignard reagents react with such compounds to give hydrocarbons. These reactions may be regarded as the neutralization of a strong base (Rσ of RMgX).

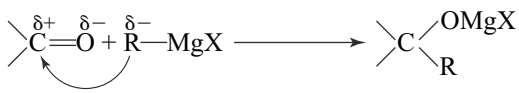


This type of reaction is useful in replacing a halogen bound to C by hydrogen. For example,

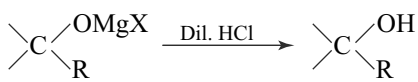
(Cyclobutyl bromide) Cyclobutane

Addition to C=O

The addition of a Grignard reagent to C=O generates a new C–C bond, an important reaction of synthetic utility (carbon–carbon double and triple bonds, being nonpolar, are inert to Grignard reagents). The general reaction is

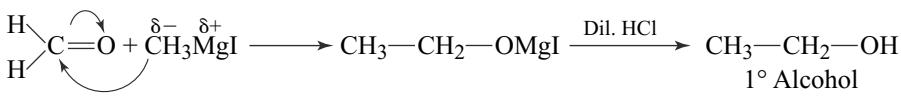


The addition product is decomposed by dil. acid (or even water or NH_4Cl) to alcohol.

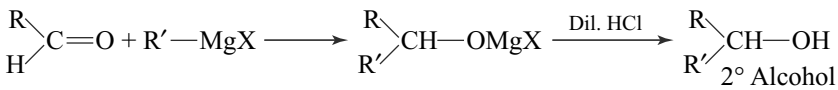


A wide range of alcohols containing more carbon than the carbonyl compound can be synthesized using this method.

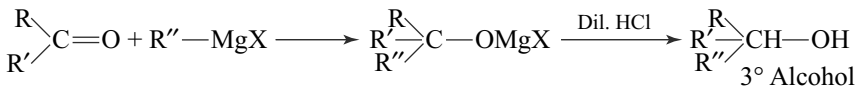
1. **Primary alcohol (1°)**
   Formaldehyde gives primary alcohol.



2. **Secondary alcohol (2°)**
   Other aldehydes give secondary alcohol.

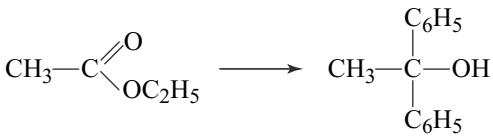


3. Tertiary alcohol (3°)
Ketones give tertiary alcohols.

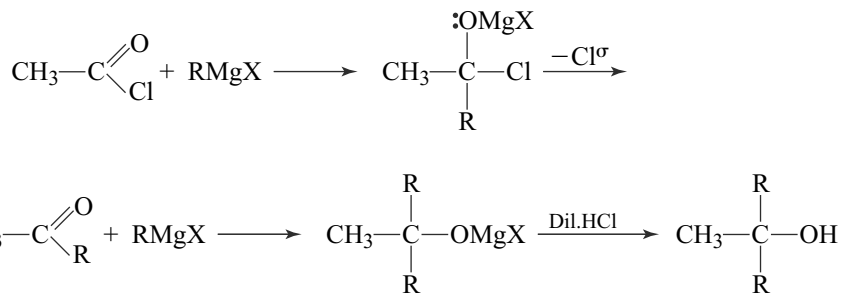


This reaction can give a 3° alcohol having all the three-alkyl groups differently.

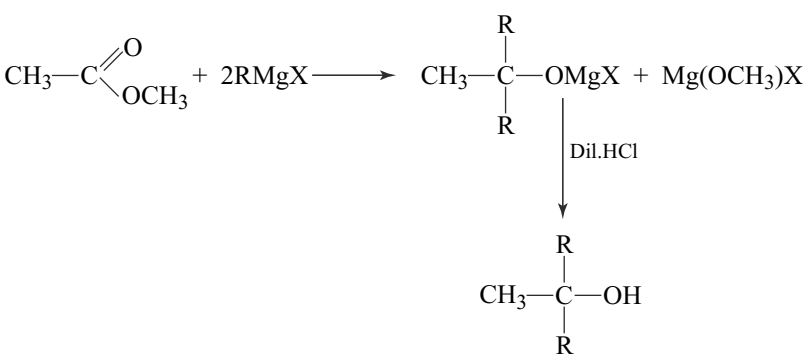
Problem How will you carry out the following?



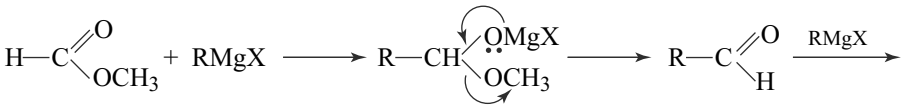
Acid chlorides, such as CH_3COCl, generally combine with two moles of Grignard reagent to give a tertiary alcohol.



Reaction of ester with Grignard reagents is similar to acid chlorides. These reactions are very useful for synthesis of tertiary alcohols with two similar alkyl groups.



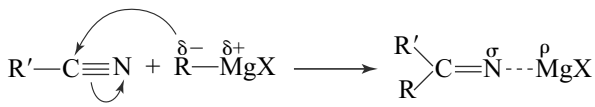
Ester of formic acid gives secondary alcohols.



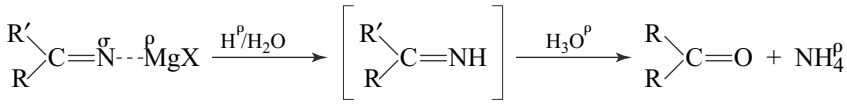
$$R_2CH—OMgX \xrightarrow{\text{Dil. HCl}} R_2CH—OH$$
2° Alcohol

Addition to C≡N

The nitrile group is polar, as nitrogen is more electronegative than carbon. Thus, RMgX adds to a nitrile.



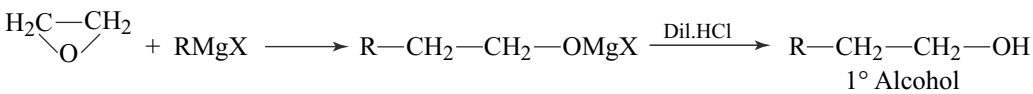
Hydrolysis of the addition product gives ketimines that are unstable in the reaction condition and rapidly hydrolyze to ketones.



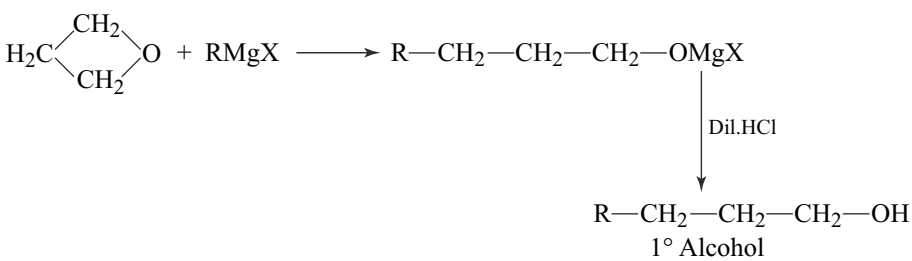
Thus, nitriles may also be used for the synthesis of tertiary alcohols.

Addition to small-ring cyclic ethers

Grignard reagents add to small-ring cyclic ethers (S_N2 displacement). The angle strain in three- and four-membered rings facilitates ring opening, (the strainless five- and six-membered cyclic ether are not attacked by Grignard reagents). The adducts are hydrolyzed by dil. acids to primary alcohols.



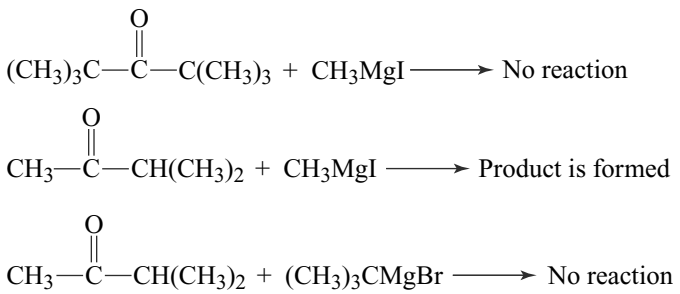
Chain length increases by two carbon atoms in the alcohol.



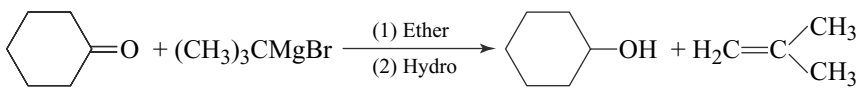
In this reaction, chain length increases by three carbon atoms in the alcohol.

Addition to hindered C=O group

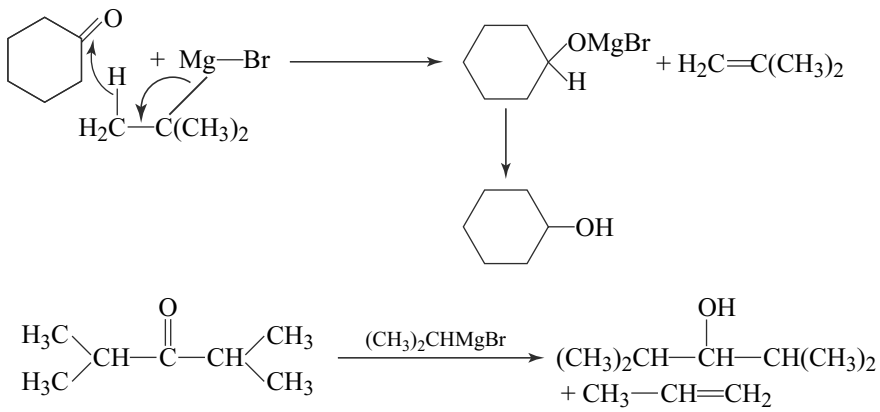
Extensive branching in the alkyl groups of either the carbonyl compound or the Grignard reagent fails addition reaction. The reason is steric hindrance. For example,



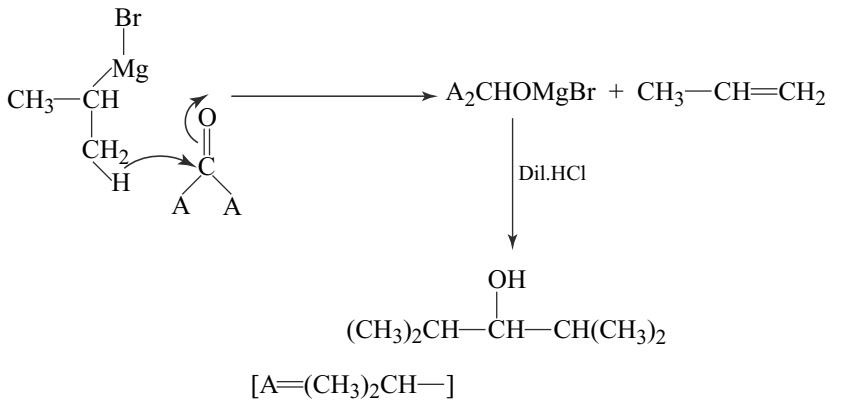
In this case, side reaction becomes important leading to abnormal product (due to reduction).



It proceeds by hydride transfer from the Grignard reagent to the ketone (i.e. reduction of the ketone).



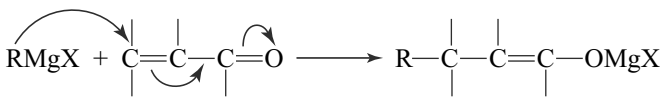
This reaction actually, is the reduction of the ketone to an alcohol by hydride shift from the reagent (Grignard reagent).



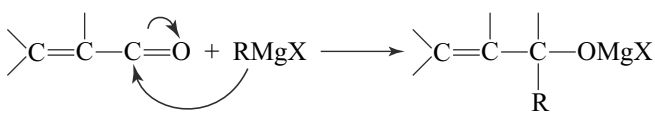
Addition to C=C bond

Grignard reagents are inert towards C=C or C≡C as these bonds are not polarized. However, if an electron-attracting group is present adjacent to C=C, it becomes polar and then addition of Grignard reagent can take place (as in Michael addition). The reaction products correspond to addition C=C as well as C = O (that is 1,4- and 1,2-addition, respectively).

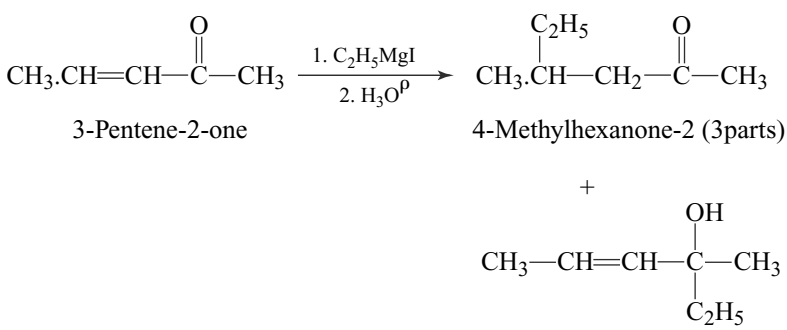
1,4-addition



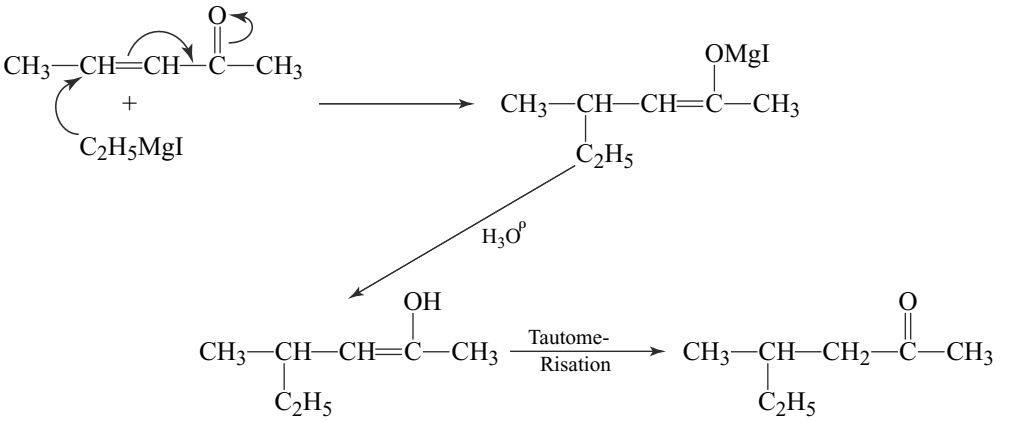
1,2-addition



Thus, ethyl magnesium iodide and 3-pentene-2-one react to give the following:

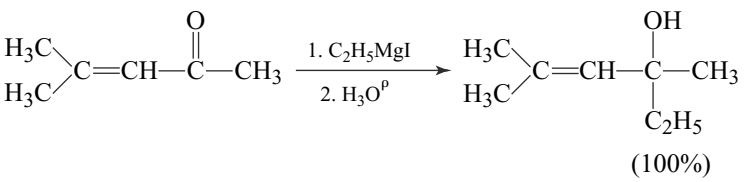


The formation of ketone takes place due to 1,4-addition and tautomerization after hydrolysis.



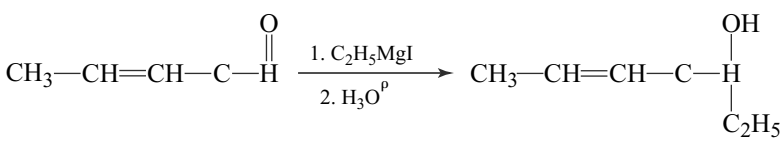
The ratio of the product in the above reaction is sensitive to steric hindrance.

1. Steric hindrance at C=C facilitates addition to C=O. For example,



(100%)

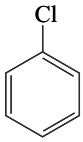
2. Also, decrease in steric hindrance at C=O gives similar result. For example,



(100%)

PROBLEMS

Objective-Type Questions

1. Which of the following reacts fast with $AgNO_3$?
(a) $CH_3CH{=}CHCl$ (b) $CH_2{=}CHCH_2Cl$
(c) $CH_3CH_2CH_2Cl$ (d) 

2. Which of the following has higher boiling point?
(a) (b)

(c) (d)

3. Alkyl halides are most often prepared from alcohols. Match list I and II and select the correct answer using the codes given below.

List I (Reactions)		List II (Alkyl halides)
(a) $H_3C(CH_2)_3OH$	$\xrightarrow[\Delta]{NaBr,\ H_2SO_4}$	1. $CH_3.CHBr(CH_2)_2CH_3$
(b) $(H_3C)_3COH$	$\xrightarrow[\text{Room temperature}]{\text{Conc. HCl}}$	2. Me_2CHCH_2Cl
(c) $H_3CCH(OH)(CH_2)_2CH_3$	$\xrightarrow{PBr_3}$	3. $(CH_3)_3C{-}Cl$
(d) Me_2CHCH_2OH	$\xrightarrow{SOCl_2}$	4. $CH_3(CH_2)_3Br$

Codes	(a)	(b)	(c)	(d)
(a)	4	3	1	2
(b)	4	3	2	1
(c)	3	4	1	2
(d)	3	4	2	1

4. What is the product of the following reaction?
$ClCH_2CH_2CH_2Br + KCN \longrightarrow ?$
(a) $ClCH_2CH_2CH_2CN$
(b) $CNCH_2CH_2CH_2Br$
(c) $CH_2{=}CH{-}CH_2Br$
(d) $ClCH_2CH{=}CH_2$

5. Ethylene oxide when treated with Grignard reagent yields
(a) tertiary alcohol
(b) cyclopropyl alcohol
(c) primary alcohol
(d) secondary alcohol

6. The intermediate product during the addition of HCl to propene in the presence of peroxide is
(a) $CH_3\overset{\oplus}{C}H{-}CH_2{-}Cl$
(b) $CH_3{-}\dot{C}H{-}CH_2{-}Cl$
(c) $CH_3{-}CH_2{-}\dot{C}H_2$
(d) $CH_3{-}CH_2{-}\overset{\oplus}{\dot{C}}H_2$

7. 1,2-Dibromopropane on reaction with X moles of $NaNH_2$ followed by treatment with ethyl bromide gives a pentyne. The value of X is
(a) two (b) four (c) one (d) three

8. The conversion of 2,3-dibromobutane to 2-butane with Zn and alcohol is
(a) α-elimination
(b) β-elimination
(c) both redox and β-elimination
(d) redox only

9. The order of reactivates of the following alkyl halides for a S_N2 reaction is
(a) R–F > R–Cl > R–Br > R–I
(b) R–F > R–Br > R–Cl > R–I
(c) R–Cl > R–Br > R–F > R–I
(d) R–I > R–Br > R–Cl > R–F

10. Which of the following represents the decreasing order of the dipole moment?
(a) CH_3Cl, CH_3Br, CH_3F
(b) CH_3Br, CH_3Cl, CH_3F

(c) CH_3Cl, CH_3F, CH_3Br
(d) CH_3Br, CH_3F, CH_3Cl

11. What is added to $CHCl_3$ to prevent it from forming phosgene gas?
(a) $CH_3—COOH$
(b) $CH_3—\overset{\overset{O}{\|}}{C}—CH_3$
(c) $CH_3—CH_2—OH$
(d) $CH_3—CHO$

12. The correct order of reactivity of PhMgBr with

$Ph—\overset{\overset{O}{\|}}{C}—Ph$, $CH_3—\overset{\overset{O}{\|}}{C}—H$, $CH_3—\overset{\overset{O}{\|}}{C}—CH_3$

is
(a) I > II > III (b) III > I > II
(c) II > III > I (d) II > I > III

13. Chloropicrin is obtained by the reaction of
(a) steam on carbon tetrachloride
(b) nitric acid on chlorobenzene
(c) chlorine on picric acid
(d) nitric acid on chloroform

14. The reaction of ROH with R′MgX produces
(a) RH (b) R′H
(c) R—R (d) R′—R′

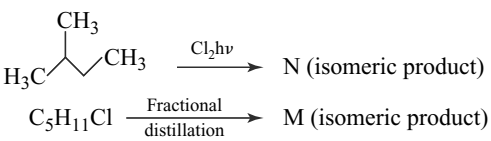
15. (CH3)3CMgCl on reaction with D2O produces
(a) $(CH_3)_3CD$ (b) $(CH_3)_3OD$
(c) $(CD_3)_3CD$ (d) $(CD_3)_3OD$

16. Which of the following will react with water?
(a) $CHCl_3$ (b) Cl_3CCHO
(c) CCl_4 (d) $ClCH_2CH_2Cl$

17. The molecule that has the highest dipole moment is
(a) CH_3Cl (b) CH_2Cl_2
(c) $CHCl_3$ (d) CCl_4

18. Which of the following is least reactive in a nucleophilic substitution reaction?
(a) $Me_3C—Cl$
(b) $CH_2=CH—Cl$
(c) $CH_3—CH_2Cl$
(d) $CH_2=CH—CH_2Cl$

19.



Give the value of the number N and M.
(a) 6, 6 (b) 4, 6
(c) 6, 4 (d) 3, 3

20. CH3–Br + Nu– CH3–Nu + Br^-. The decreasing order of the rate of the above reaction with nucleophiles (Nu^-) is

A = PhO^-, B = ACO^-, C = HO^-, D = $CH3O^-$
(a) D > C > A > B (b) D > C > B > A
(c) A > B > C > D (d) B > D > C > A

21. The compounds used as refrigerants are
(a) CH_2F_2 (b) CF_2Cl_2
(c) CF_4 (d) NH_3

22. When Cl_2 is passed through propene at 400°C, the product formed is
(a) polypropyl chloride
(b) allyl chloride
(c) vinyl chloride
(d) 1,2-dichloroethane

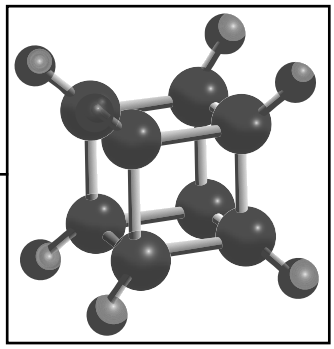
23. Triclene (trichloroethane) is used as a
(a) dehydrating agent
(b) chlorinating agent
(c) dry cleaning solvent
(d) solvent

24. Which of the following is true with respect to S_N2 reactivity?
(a) $CH_2Cl_2 > CH_3Cl$ (b) $CH_3Cl > CH_2Cl_2$
(c) $CCl_4 > CH_2Cl_2$ (d) $CH_2=CH_2Cl > CH_3Cl$

Answers

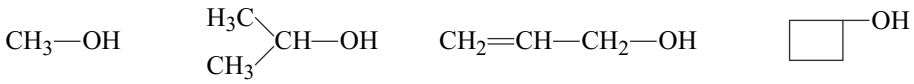
1. (c)	2. (b)	3. (a)	4. (a)	5. (c)
6. (a)	7. (d)	8. (c)	9. (d)	10. (c)
11. (c)	12. (c)	13. (d)	14. (b)	15. (a)
16. (b)	17. (a)	18. (b)	19. (c)	20. (b)
21. (b,d)	22. (b)	23. (c)	24. (b)	

CHAPTER 13



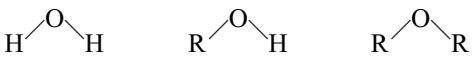
Alcohols and Ethers

An alcohol is a hydroxy derivative of an aliphatic hydrocarbon (acyclic or cyclic). It is obtained by the replacement of hydrogen (or hydrogens) by the –OH group (or groups).



Methyl alcohol | Isopropyl alcohol | Allyl alcohol | Cyclobutyl alcohol

Alcohols (R–OH) and ethers (R–O–R) may also be taken as derivatives of water.



Water | Alcohol | Ether

CLASSIFICATION

Alcohols may be classified in two different ways.

Classification on the basis of the number of –OH groups

An alcohol that has only one –OH group is known as monohydric alcohol. Dihydric and trihydric alcohols contain two and three –OH groups, respectively. Alcohols containing many –OH groups are called polyhydric alcohols.

Table 13.1

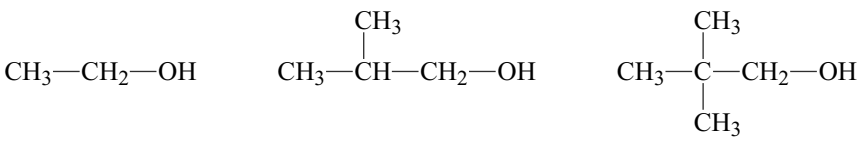
Monohydric alcohol	Dihydric alcohol	Trihydric alcohol	Polyhydric alcohol
$CH_3—OH$ Methyl alcohol	$H_2C—OH$ $\vert$ $H_2C—OH$ Ethylene glycol	$H_2C—OH$ $\vert$ $HC—OH$ $\vert$ $H_2C—OH$ Glycerol (1,2,3-propanetriol)	$H_2C—OH$ $\vert$ $(CH—OH)_4$ $\vert$ $H_2C—OH$ Sorbitol hexahydric alcohol
$(CH_3)_2CH—OH$ Isopropyl alcohol			
$(CH_3)_3C—OH$ tert-Butyl alcohol			

Classification on the basis of the nature of C atom bearing the –OH group

It is important for monohydric alcohols. Monohydric alcohols have the general formula C_nH_{2n+1}. OH and are generally denoted as R–OH. They are classified as, primary (1°), secondary (2°) and tertiary (3°) alcohols.

Primary alcohol (1°)

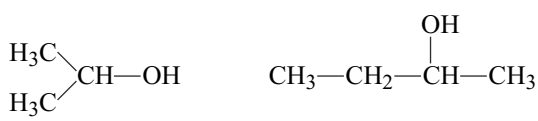
A primary alcohol has $–CH_2–OH$ group, that is the –OH-bearing C is joined with two H atoms (or one C atom).



Ethyl alcohol | Isobutyl alcohol | Neopentyl alcohol

Secondary alcohol (2°)

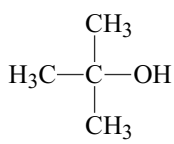
A secondary alcohol contains the group>CH–OH, that is the –OH-bearing C is joined with only one H atom (or two C atoms).



Isopropyl alcohol | Secondary butyl alcohol

Tertiary alcohol (3°)

A tertiary alcohol has >C–OH group, that is the –OH bearing carbon has no H atom (or is joined with three C atom).



Tert-butyl alcohol

DISTINCTION AMONG 1°, 2° AND 3° ALCOHOLS

Many reagents can be used to distinguish 1°, 2° and 3° alcohols.

Lucas reagent

A solution of $ZnCl_2$ in conc. HCl is known as the Lucas reagent. It is a common laboratory reagent. It forms alkyl halide, with alcohols, differing in speed of the reaction, which is used to make distinction.

Table 13.2

Reagents $ZnCl_2$ + conc. HCl	**3° Alcohol**	**2° Alcohol**	**1° Alcohol**
The alcohol is treated with Lucas reagent, ($ZnCl_2$ + conc. HCl)	An oily layer (of R_3C–Cl) separates out immediately.	A secondary alcohol takes several minutes to form oily layer (R_2CH–Cl).	A primary alcohol forms oily layer only on heating.

$$R_3C—OH + HCl \xrightarrow{\text{Rapid}} R_3C—Cl + H_2O$$

$$R_2CH—OH + HCl \xrightarrow[\text{minutes}]{\text{Takes}} R_2CH—Cl + H_2O$$

$$R—CH_2—OH + HCl \xrightarrow[\text{On heating}]{\Delta} R—CH_2—Cl + H_2O$$

Thus, the reactivity of alcohols follows the order

Tertiary alcohol > Secondary alcohol > Primary alcohol

Victor–Meyer Test

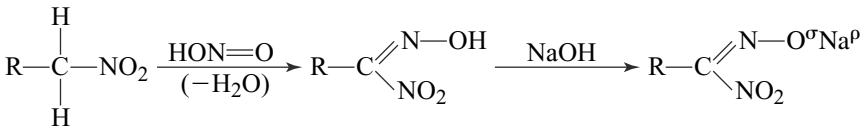
It is a coloured reaction. The test follows three steps: (i) the alcohol is converted to the corresponding nitroalkane, (ii) nitroalkane is treated with HNO_2 and (iii) the solution is finally made alkaline.

$$\underset{\text{Alcohol}}{R—OH} \xrightarrow{PBr_3} \underset{\text{Alkyl bromide}}{R—Br} \xrightarrow{AgNO_2} \underset{\text{Nitroalkane}}{R—NO_2}$$

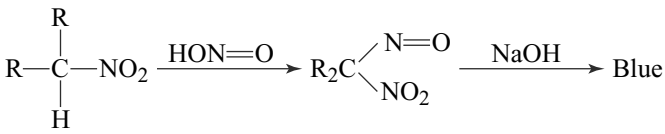
Table 13.3

Test	**1°**	**2°**	**3°**
The nitroalkane is treated with HNO_2, ($NaNO_2$ + HCl) and the solution is finally made alkaline, NaOH.	Red colour	Blue colour	Colourless

The colours are due to the reaction of the nitroalkane with HNO_2 and NaOH.

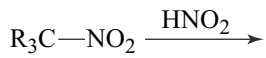


Nitro alkane (1° alcohol) — Nitrolic acid — Red



Nitro alkane (2° alcohol) — Pseudo-nitrol

Both the above reactions are due to the presence of H atom at the carbon atom that bears NO_2 group.

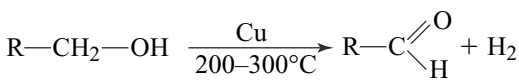


Nitro alkane (3° alcohol) — No, reaction, it is because NO_2 group bearing *carbon has no hydrogen atom.*

Dehydrogenation

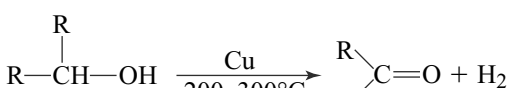
Alcohols dehydrogenate over hot copper. The products are different with 1°, 2° and 3° alcohols. It is used for distinction.

1. A primary alcohol forms an aldehyde.



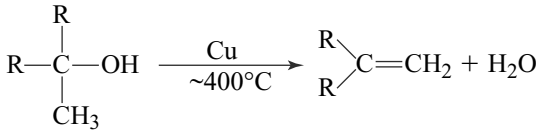
1° Alcohol (vapour) — Aldehyde

2. A secondary alcohol gives a ketone.



2° Alcohol (vapour)

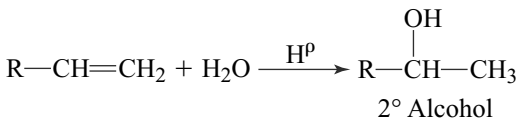
3. Tertiary alcohols undergo dehydration (loss of H_2O) rather than dehydrogenation (loss of H_2).



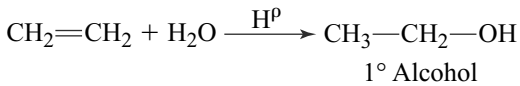
PREPARATION OF ALCOHOLS

Hydration of alkenes

Hydration of alkenes gives alcohols. The reaction is acid catalyzed. The addition follows Markownikoff's rule.



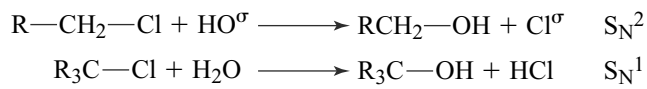
Therefore, this method cannot produce primary alcohol, except CH_3–CH_2–OH.



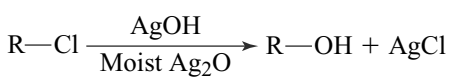
(See Chapter 10 for details.)

Hydrolysis of alkyl halides

Alkyl halides are hydrolyzed by aq. NaOH or KOH to alcohols. The reaction is either S_N1 or S_N2 depending on the alkyl halides (see Chapter 5, *Reaction Mechanism*, for details of S_N1 and S_N2 reactions).



Moist silver oxide is a good reagent to replace Cl by –OH. Elimination is not a side reaction.



Grignard synthesis of alcohols

All three types of alcohols (1°C, 2°C and 3°C) can be prepared using proper reagents with Grignard reagents. (see Grignard Reagents for details).

Hydroboration of alkenes

Alkenes add B_2H_6. The direction of addition is 'anti-Markownikoff'. Addition compound is decomposed by alkali solution to primary alcohol.

$$R—CH=CH_2 \xrightarrow{B_2H_6} (R—CH_2—CH_2)_3B \xrightarrow[HO^{\sigma}]{H_2O} R—CH_2—CH_2—OH$$

(See Chapter 10 for hydroboration.)

Reduction of carbonyl compounds

Carbonyl compounds (aldehydes, ketones, carboxylic acids, esters) can be reduced to alcohols.

$$R—\underset{H}{\overset{O}{\overset{\|}{C}}} \xrightarrow{2H} RCH_2—OH \quad (1° \text{ Alcohol})$$

$$R—\overset{O}{\overset{\|}{C}}—R \longrightarrow R_2CH—OH \quad (2° \text{ Alcohol})$$

$$R—\underset{OR'}{\overset{O}{\overset{\|}{C}}} \xrightarrow{2H} R—CH_2—OH \quad (1° \text{ Alcohol})$$

(For details, see chapters on aldehydes, ketones and carboxylic acids.),

ETHYL ALCOHOL AND METHYL ALCOHOL

These are industrially important alcohols. They are manufactured in a number of ways.

Methyl alcohol (Methanol)

1. By destructive distillation of wood.
2. From water gas: This method is now mostly used for the manufacture of methanol. The yield of the reaction is high and the product is about 99 per cent pure.

$$C + H_2O \xrightarrow{\sim 1300°C} CO + H_2$$

$$CO + 2H_2 \xrightarrow[\text{High P/300°C}]{ZnO—Cr_2O_3} CH_3—OH$$

3. From natural gas: In this method, CH_4 is oxidized over Cu catalyst at high pressure and around 250°C to methanol. Methane for this reaction is obtained from natural gas.

$$2CH_4 + O_2 \xrightarrow[\substack{P\sim 100\ atm.\\ 250^\circ C}]{Cu\ (catalyst)} 2CH_3—OH$$

Methyl alcohol is highly toxic. Even small dose affects optic nerves causing blindness. A slightly large dose is fatal, (that is may cause death).

Ethyl alcohol (Ethanol)

It is mostly manufactured (in India) by the fermentation of sugars in the presence of yeast.
The main sources of sugars are molasses (waste from sugarcane factories) and starch from grains.

CH_3CH_2–OH from Molasses

Molasses is diluted and acidified to a pH of about 4 (the wart). The wart is mixed with yeast and kept at around 35°C in large tanks. The reactions are

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow[(from\ yeast)]{Invertase} \underset{Glucose}{C_6H_{12}O_6} + \underset{Fructose}{C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow[(from\ yeast)]{Zymase} 2CH_3CH_2—OH + 2CO_2$$

From starch

Mash (starchy substance) is treated with malt (containing diastage). Diastage converts starch into maltose.

$$\underset{Starch}{C_6H_{10}O_5} + n/2H_2O \xrightarrow[(from\ malt)]{Diastage} \underset{Maltose}{n/2C_{12}H_{22}O_{11}}$$

Maltose is put to fermentation. The reactions are

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow[yeast]{Maltase} \underset{Glucose}{2C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow[(from\ yeast)]{Zymase} 2CH_3CH_2—OH + 2CO_2$$

The ultimate solution obtained by any of the above methods on distillation gives ethanol, which is around 95 per cent pure. It is known as *Rectified spirit*.

Absolute alcohol

The rectified spirit contains ~95 per cent alcohol and the rest is water. It is refluxed with quick lime. It gives 99.5 per cent pure alcohol. The last traces of water are removed by distilling alcohol (99.5 per cent) with Ca or Mg metal. Alcohol so obtained is almost pure (100 per cent) and is called *Absolute alcohol*.

Methylated spirit

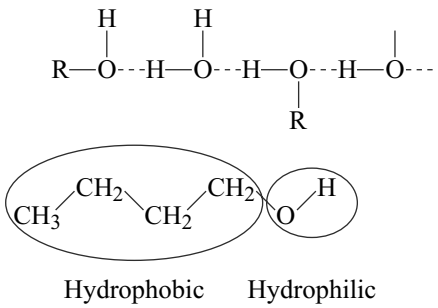
Ethyl alcohol is consumed by human beings. To make it unfit for human consumption, ethyl alcohol is mixed with methyl alcohol (toxic). It is called methylated spirit.

Power alcohol

A mixture of alcohol, petrol and benzene is known as power alcohol. It may be used as motor fuel.

PROPERTIES

Lower alcohols are highly miscible (soluble) with water. It is due to the presence of highly polar group –OH (hydroxyl), which can enter into intermolecular H-bonding with water. But with the increase in the carbon atoms (that is alkyl part), water solubility decreases. An alcohol has both the *hydrophilic* (water loving, due to –OH group) and the *hydrophobic* (water hating, that is alkyl part) moieties. Thus, with the increase in the molecular mass, the hydrophobic nature of alcohol increases. It reduces the solubility.



Another factor affecting solubility is chain branching. The solubility increases with the increase in the branching. It is seen in the four butyl alcohols. The solubility of *n*-butyl alcohol is 8 g in 100 g of water, whereas t-butyl alcohol is completely miscible with water (see Table 1 below).

Branching also affects volatility. The highly branched t-butyl alcohol has lower BP than that of *n*-butyl alcohol.

The effect of branching on MP is opposite. It is because of the crystal packing that is improved by branching.

Table 13.4

Name	Formula	MP(0°C)	BP(0°C)	Solubility g/100 g water
Methyl alcohol	$CH_3—OH$	–98	64.5	∝
Ethyl alcohol	$CH_3—CH_2—OH$	–115	78.0	∝
n-Butyl alcohol	$CH_3—CH_2—CH_2—CH_2—OH$	–90	118	8.0
Isobutyl alcohol	$(CH_3)_2CH—CH_2—OH$	–108	108	10.0
s-Butyl alcohol	$CH_3CH_2—\underset{\displaystyle OH}{\underset{\vert}{CH}}—CH_3$	–114	100	12.5
t-Butyl alcohol	$(CH_3)_3C—OH$	–25	83	∝

CHEMICAL REACTIONS

The functional group in alcohols is the hydroxyl group (–OH). Thus, an alcohol has the following sites of reactions:

1. Reactions of the O–H bond.
2. Reactions of the C–OH bond.
3. Reactions of the alkyl group.

Reaction of O–H bond

Acidic and Basic Properties

Alcohols, such as water, are amphoteric. It behaves acidic to strong bases or highly electropositive metals (Na).

$$C_2H_5—OH + Na^{\rho}NH_2^{\sigma} \longrightarrow C_2H_5O^{\sigma}Na^{\rho} + NH_3$$

$$C_2H_5—OH + Na \longrightarrow C_2H_5O^{\sigma}Na^{\rho} + \tfrac{1}{2}H_2$$

The order of acid strength is

Primary alcohol > Secondary alcohol > Tertiary alcohol

Thus, t-butyl alcohol is less acidic than ethyl alcohol.
The anions (that is, conjugate bases of alcohols) are known as alkoxide ions.

CH_3O^{σ}	$C_2H_5O^{\sigma}$	$(CH_3)_2CH–O^{\sigma}$	$(CH_3)_3C–O^{\sigma}$
Methoxide	Ethoxide	Isopropoxide	t-Butoxide

The base strength of alkoxides is

$$R_3C—O^{\sigma} > R_2CH—O^{\sigma} > RCH_2—O^{\sigma}$$

(Conjugate base of a weak acid is a strong base.)
Alcohols are bases in the presence of strong acids,

$$R—OH + HBr \rightleftharpoons R—\overset{\rho}{\underset{H}{O}}H + Br^{\sigma}$$

Ester Formation

(See Chapter 5, *Reaction Mechanism* for details.)

Ether Formation

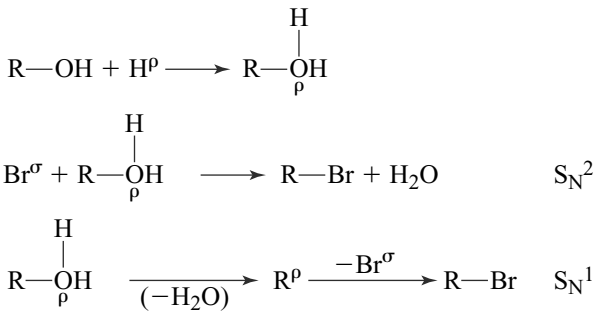
It will be explained in this chapter, later on.

Reactions of the C–OH bond

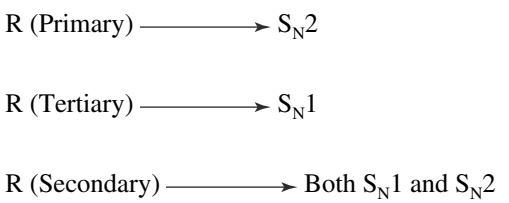
Halide Formation

It is an important reaction of an alcohol in which C–O bond of the alcohol is broken. Different reagents can be used for this purpose.

1. *Hydrogen halides*
   Hydrogen halides replace –OH of an alcohol by X. The reaction proceeds better in the presence of a strong acid (H_2SO_4).



The S_N2 or S_N1 route depends on R.

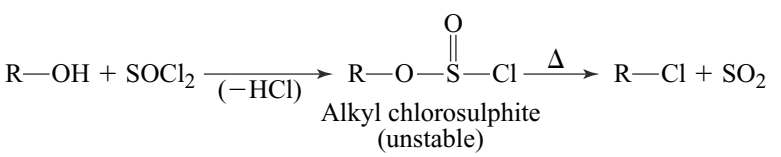


The reactivity of HX is

$$HI > HBr > HCl$$

(See *Lucas Test* in this chapter.)

2. *Thionyl chloride, $SOCl_2$*
   It is very useful for the preparation of alkyl chlorides. The overall reaction is



This reaction is synthetically advantageous as the side products (SO_2 and HCl) are gases and the method does not require separation of the main product, that is R–Cl.

3. *Phosphorous halides*

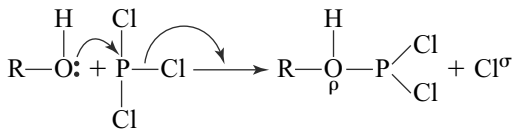
Phosphorous tri- and penta-halides (PX_3 and PX_5) are excellent reagents for converting an alcohol to alkyl halides.

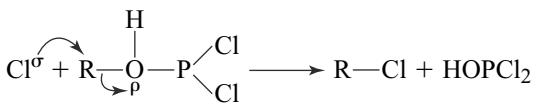
$$3R{-}OH + PCl_3 \longrightarrow 3R{-}Cl + H_3PO_3$$

$$R{-}OH + PCl_5 \longrightarrow R{-}Cl + POCl_3 + HCl$$

But these reactions need separation of R–Cl from the product mixture. This is a disadvantage compared to $SOCl_2$.

The reaction with PCl_3 is thought to proceed as

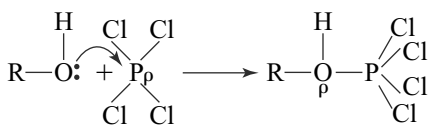


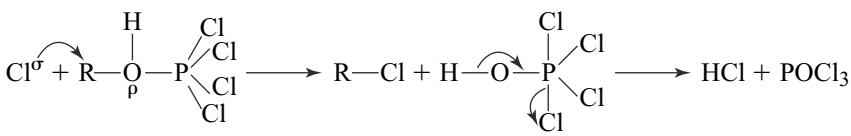


Repetition of these steps ultimately gives R–Cl and H_3PO_3.

PCl_5 reacts in the following way to give R–Cl.

$$2PCl_5 \rightleftharpoons PCl_4^{\sigma} + PCl_6^{\sigma}$$

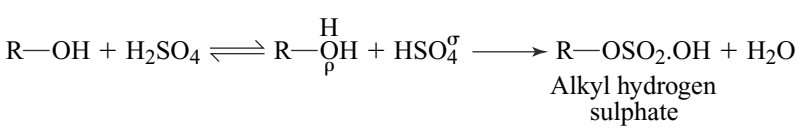




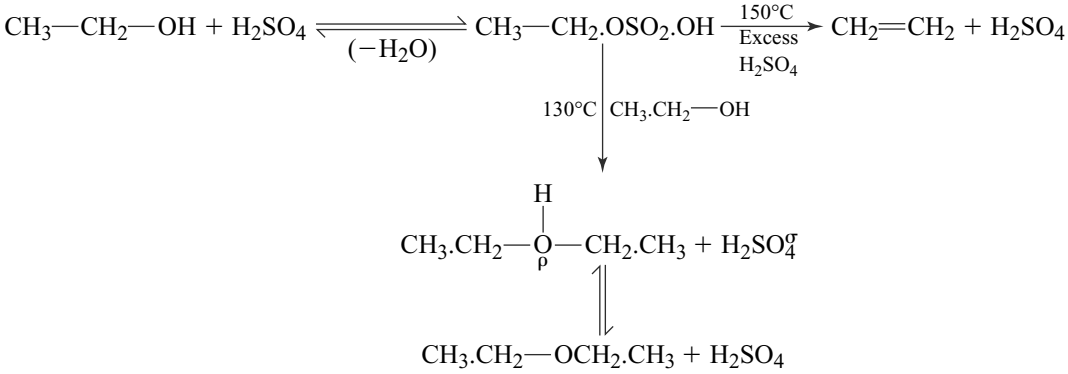
4. *Dehydration of alcohols*

Dehydration of alcohols may form either an alkene or ether. It depends on temperature. The most common dehydrating agent is conc. H_2SO_4 or conc. H_3PO_4 (or Al_2O_3).

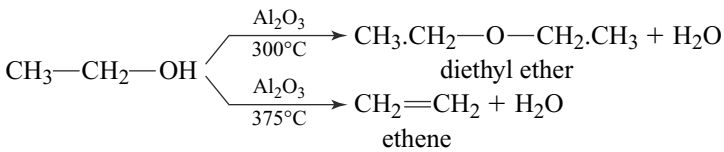
Alcohols first form alkyl hydrogen sulphate with conc. H_2SO_4.



Alkyl hydrogen sulphate may form alkene or ether depending upon the temperature and the amounts of alcohol and H_2SO_4.



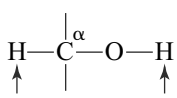
Most alcohols also dehydrate over Al_2O_3 (or silica gel) at high temperature giving alkene or ether.



Tertiary alcohols dehydrate with conc. H_2SO_4 at lower temperatures (than 1° alcohols). Such dehydrations are explained in the chapter on alkenes (Chapter 10).

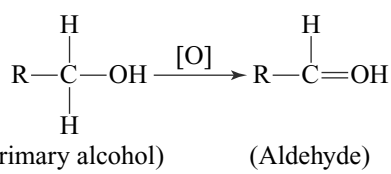
5. *Oxidation of alcohols*

Oxidation of alcohols involves replacement of α-H and the H of the O–H bond, that is

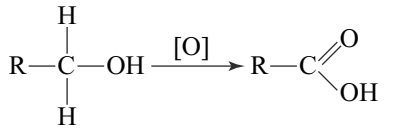


The product contains C=O group. The actual oxidation product depends on the nature of alcohol:

(a) A primary alcohol may form an aldehyde (by losing only one α-H atom)

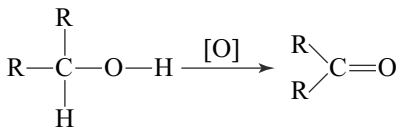


or a carboxylic acid (by losing both the α-H atoms).



(Primary alcohol) (Carboxylic acid)

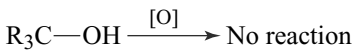
(b) A secondary alcohol forms a ketone (by losing its only α-H atom).



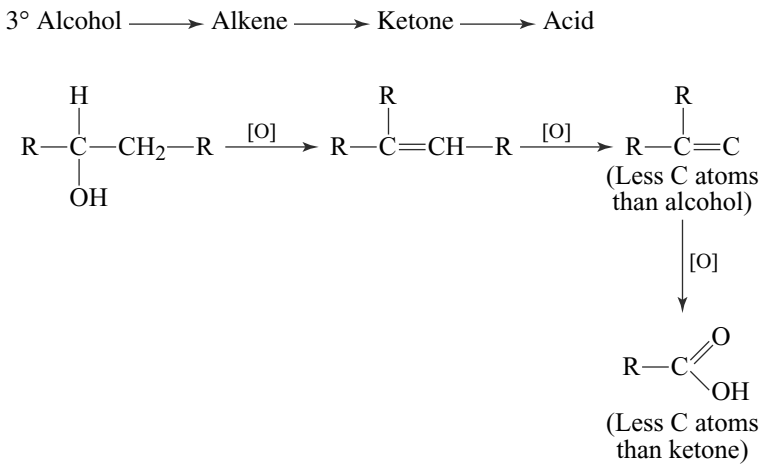
(Sec. alc.)

The oxidation of secondary alcohol beyond the ketone stage is difficult and always proceed with the cleavage of C–C bonds.

(c) A tertiary alcohol is not oxidized in the condition where 1° and 2°alcohols are oxidized.



However, they are oxidized in drastic condition (acidic reagent) and then only with the cleavage of C–C bond. The oxidation follows the sequence given below.



As the oxidation products of alcohols (1°, 2° and 3°) are different and easily recognizable, this method can be used to distinguish between alcohols. Oxidation of alcohols may be carried out by many reagents.

(a) The $Na_2Cr_2O_7 + H_2SO_4$ combination is common. The laboratory reagent chromic acid may also be used. The overall reaction is

$$(CH_3)_2CH—OH + 2H_2CrO_4 + 6H^{\rho} \longrightarrow (CH_3)_2C{=}O + 2Cr^{3\rho} + 8H_2O$$

(b) $KMnO_4$ in non-polar solvent or acidic (or basic). In acid, $HMnO_4$ is oxidant.

$$\underset{(1^\circ\text{ Alcohol})}{R.CH_2—OH} + \underset{\text{Purple}}{KMnO_4} \xrightarrow{CCl_4} R—COO^{\sigma}K^{\rho} + \underset{\text{Brown}}{MnO_2} + KOH$$

$$R—COO^{\sigma}K^{\rho} \xrightarrow{H_3O^{\rho}} R—COOH$$

Thus, 1° alcohol decolourizes $KMnO_4$.
In basic medium, the oxidation is believed to proceed as

$$R_2C(H)(OH) + HO^{\sigma} \rightleftharpoons R_2CHO^{\sigma} + H_2O$$

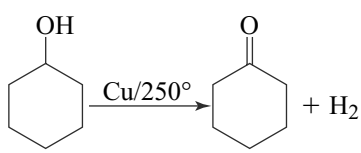
$$R_2C(H)(O_{\sigma}) + MnO_2^{\sigma} \longrightarrow R_2C{=}O + HMnO_2^{2\sigma} \xrightarrow{HO^{\sigma}} MnO_2 + MnO_4^{\sigma}$$

Thus, $KMnO_4$ is not decolourized by a 2° alcohol.

(c) Aldehydes are easily oxidized to carboxylic acids. Thus, to oxidize 1° alcohol to the aldehyde stage, specific reagents are used, example pyridinium chlorochromate, $C_5H_5NH^{\rho}CrO_3Cl^{\sigma}$ (Sarett reagent). This reagent does not affect C=C in the alcohol also.

$$CH_3.CH{=}CH.CH_2—OH \xrightarrow[HCl]{CrO_3/C_5H_5N} CH_3.CH{=}CH—C(=O)H$$

(d) Catalytic dehydrogenation is usual industrial method for the oxidation of primary and secondary alcohols to aldehydes and ketones, respectively (see distinction between alcohols).



$$\underset{R'}{\overset{R}{\diagdown}}CH—OH \xrightarrow{Cu/300^\circ} \underset{R'}{\overset{R}{\diagdown}}C{=}O + H_2$$

$$R.CH_2—OH \xrightarrow{Cu/300^\circ} R—\overset{O}{\overset{\|}{C}}—H$$

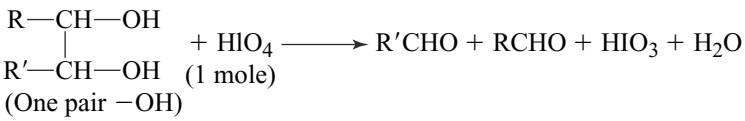
(e) Hypohalite (X_2 + NaOH, X = Cl, Br, I) is used for the selective oxidation of alcohols (see haloform reaction).

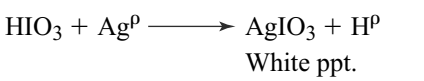
(f) Periodic acid (HIO_4) and lead tetracetate [$Pb(CH_3COO)_4$] as oxidant

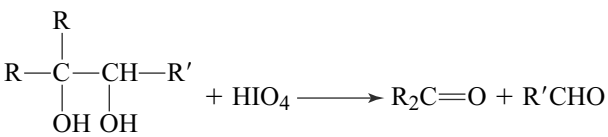
These reagents oxidize vicinal polyols with the cleavage of C–C bonds. The oxidation has analytical importance.

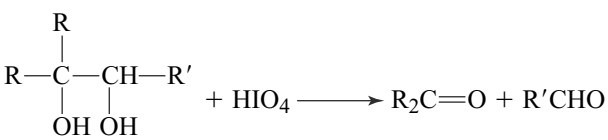
Periodic Acid (HIO_4)

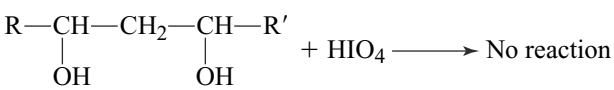
Periodic acid oxidizes 1,2-diols (or polyols having –OH groups at adjacent carbon atoms only), to carbonyl compounds with the cleavage of C–C bond. Quantitatively, 1 mole periodic acid is consumed per pair of –OH groups. Periodic acid itself is reduced to HIO_3. It may be indicated by the formation of white precipitate (of $AgIO_3$) upon addition of silver nitrate solution.







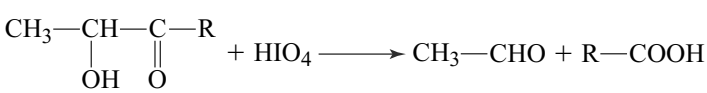


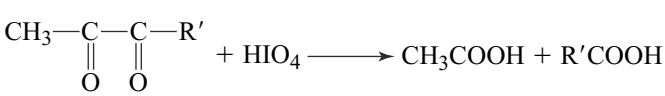


(The –OH groups are not at the adjacent carbon atoms.)

This reaction is also important for locating the position of –OH groups in the molecules as the carbonyl groups are generated at the original carbons bearing the –OH groups.

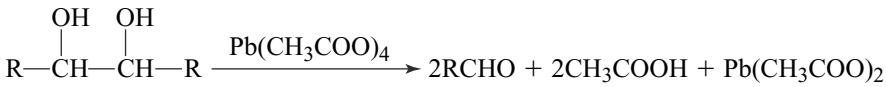
Ketohydroxy compounds as well as α-diketones may also be cleaved by HIO_4





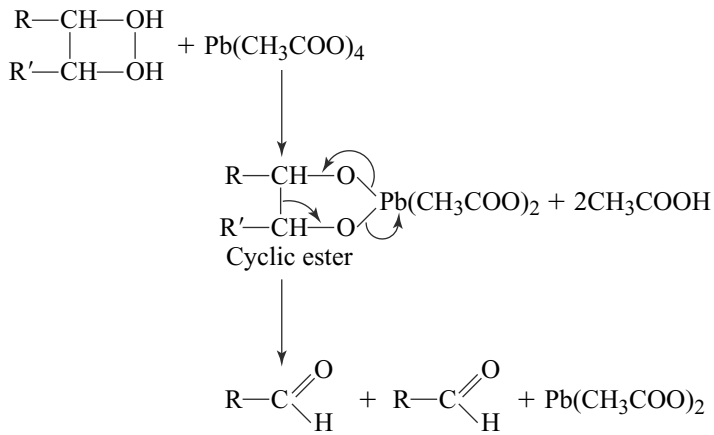
Lead Tetracetate $Pb(ACO)_4$

This reagent also oxidizes 1,2-diols with the cleavage of C–C bond. The products are aldehydes.



(R groups may be different also)

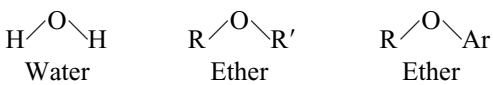
The reaction is believed to proceed through a five-membered cyclic ester intermediate, as



This reaction can also be used to locate the position of –OH groups in the molecule.

ETHERS

Ethers may be taken as dialkyl (or aryl) derivatives of water



Ethers are either simple ethers or mixed ethers. In a simple ether, both alkyl groups are similar, while a mixed ether contains two different alkyl groups.

$C_2H_5—O—C_2H_5$ Simple ether

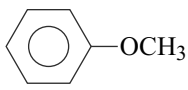
$CH_3—O—C_2H_5$ Mixed ether

Ethers are much more volatile than alcohols of the same molecular weight. It is because ethers, unlike alcohols, lack H-bonding. Thus, diethyl either ($C_2H_5OC_2H_5$) boils at 35°C (body temperature), which is 48–83°C below the boiling points of the isomeric butyl alcohols (see alcohols). Some important ethers are given below:

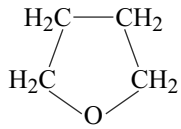
$CH_3.CH_2OCH_2.CH_3$ — Diethyl ether (Bp 35°C)

$CH_3—O—CH=CH_2$ — Methyl vinyl ether (Bp 8°C)

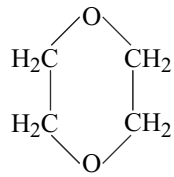
$HO—CH_2.CH_2.OCH_2.CH_2—HO$ — Diethyleneglycol (Bp 245°C)



Methyl phenyl ether (anisole) Bp 155°C

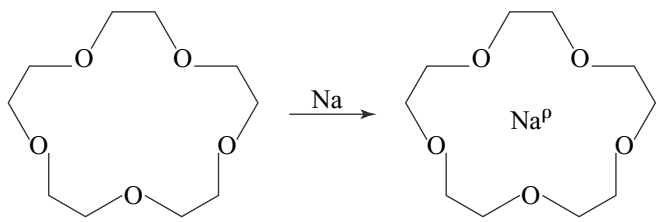


Tetrahydrofuran Bp 65°C



1,4-Dioxane Bp 101°C

Cyclic ethers containing many (four, five, six or more) oxygen atoms are known as crown ethers.



Crown ether — Complex with Na^{ρ}

They form complexes with metal ions, which are known as inclusion compounds. In the complexes, crown ether is the 'host' and the species it binds with is the 'guest'. The crown ethers can allow inorganic salts to dissolve in non-polar solvents, for example $KMnO_4$ is soluble in non-polar solvent in the presence of crown ether as K^+ complexes with ether.

PREPARATION

Williamson's synthesis

This process involves the reaction of an alkyl halide with sodium alkoxide (RO^sNa^r). The reaction is a typical SN^2 displacement.

$$RO^{\sigma} + \overset{\delta+}{R'}—\overset{\delta-}{X} \longrightarrow [R—\overset{\delta-}{O}\cdots R'\cdots \overset{\delta-}{X}] \longrightarrow R—O—R' + X^{\sigma}$$

Important points

1. Both simple and mixed ethers may be produced by this reaction.
2. It is an important laboratory method.
3. Alkoxides are strong bases; therefore, elimination is competing reaction.
4. Ethers containing highly branched alkyl group are better prepared by using primary halide and the alkoxide of the branched alcohol. For example, isopropyl methyl ether is better obtained by the use of

methyl iodide and isopropoxide ion. The use of methoxide and isopropyl iodide produces alkene (by E^2 reaction)

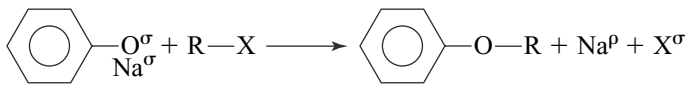
$$(CH_3)_2CHO^{\sigma} + CH_3—I \xrightarrow{S_N2} (CH_3)_2CH.OCH_3 + I^{\sigma}$$

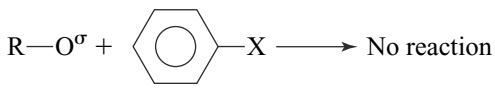
$$(CH_3)_2CH—I + CH_3O^{\sigma} \xrightarrow{E^2} CH_3—CH{=}CH_2 + CH_3OH + I^{\sigma}$$

Another such reaction may include the preparation of ethyl t-butyl ether.

$$(CH_3)_2C—O^{\sigma} + CH_3.CH_2—Cl \longrightarrow (CH_3)_3C.OCH_2.CH_3 + Cl^{\sigma}$$

5. Aryl halides are of low reactivity (see *Aryl Halides* in Chapter 7).
Therefore, alkyl aryl ethers can be prepared only by reacting sodium phenoxide with alkyl halide.





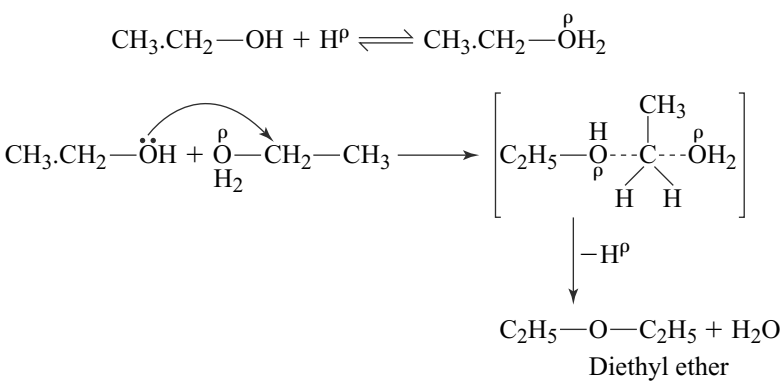
Dehydration of alcohols

Partial dehydration of alcohols under the influence of conc. H_2SO_4 or H_3PO_4 gives ethers.

$$\underset{\text{(Excess)}}{R—OH} \xrightarrow[\Delta]{\text{Conc. } H_2SO_4} \underset{\text{(Ether)}}{R—O—R} + H_2O$$

Mechanistically, the reaction is a nucleophilic substitution.
Primary alcohols follow S_N2 route, whereas secondary and tertiary alcohols follow S_N1 mechanism.

S_N2 reaction



S_N1 reaction

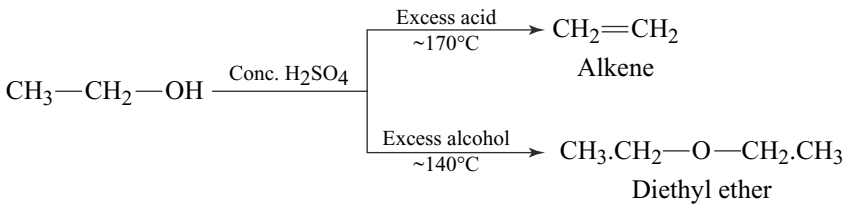
$$R_3C{-}OH + H^{\oplus} \rightleftharpoons R_3C{-}\overset{\oplus}{O}H_2 \longrightarrow R_3C^{\oplus} + HO_2$$

$$R_3C{-}\ddot{O}H + \overset{\oplus}{C}R_3 \longrightarrow R_3C{-}\overset{H}{\underset{\oplus}{O}}{-}CR_3 \xrightarrow{-H^{\oplus}} R_3C{-}O{-}CR_3$$

Ether

Important points

1. Ethers having highly branched alkyl groups are strained molecules. Thus, in the dehydration of t-butyl alcohol tert in tert-butyl has been changed to t-butyl throughout the text to maintain consistency. Please check., di-t-butyl ether is not formed. It is because of steric crowding between the alkyl groups.
2. This method can produce simple ethers only.
3. Formation of alkene is an important side reaction, but it can be avoided by keeping low temperature and using excess of alcohol.



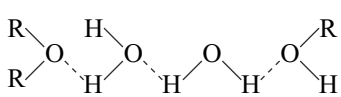
Ethers can also be prepared by dehydrating alcohol over heated alumina (Al_2O_3).

$$2R_2CH{-}OH \xrightarrow[\Delta]{Al_2O_3} R_2CHOCHR_2 + H_2O$$

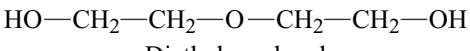
PROPERTIES

Ethers have polar C–O bonds. Thus, ethers have some dipole moment.

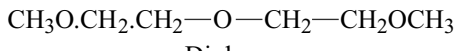
Lower ethers (up to C = 3) are soluble in water due to intermolecular H–bonding with water.



Ethers are used as solvents, example diethyl ether. Some ethers are very useful as high boiling solvents, e.g.,

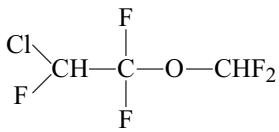


Diethyleneglycol
(Bp 245°C)

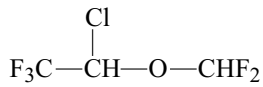


Diglyme
(Bp 161°C)

Diethyl ether is also used as an inhalation anaesthetic. However, it has slow effect and unpleasant recovery period. Therefore, diethyl ether is now replaced by ethrane and isoflurane.



Ethrane

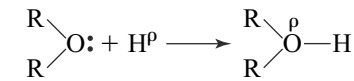


Isoflurane

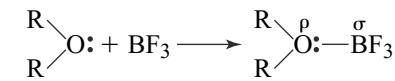
REACTIONS

Ethers as Base

Ethers have lone pair of electrons at O atom. So, they behave as a base (in both Bronsted and Lewis sense).



(Bronsted base)

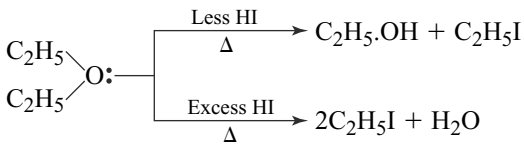


(Lewis base)

Reactions involving C–O bond

Ethers are very much less reactive. The C–O bond in ethers breaks only in drastic condition in the presence of HX.

On heating with HX, ethers react as



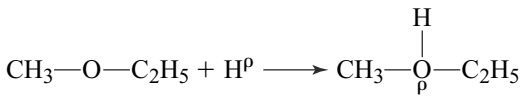
Reactivity of HX in the above reaction is

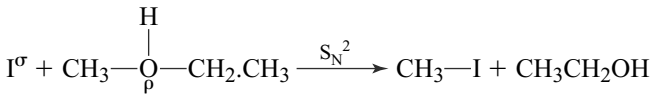
$$HI > HBr > HCl$$

Mechanistically, the above reaction is acid-catalysed nucleophilic displacement. Some important aspects of the reaction are:

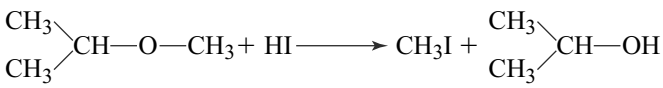
Mechanistically, the above reaction is acid-catalysed nucleophilic displacement. Some important aspects of the reaction are:

1. S_N2 mechanism is followed when alkyl groups are primary. In primary and secondary alkyl group containing ethers, the lower alkyl group converts into alkyl iodide. Steric factor may be responsible for this.

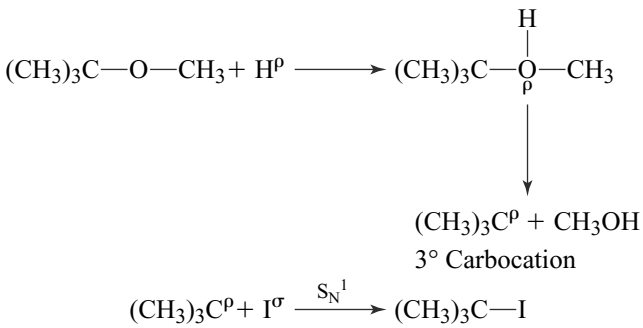




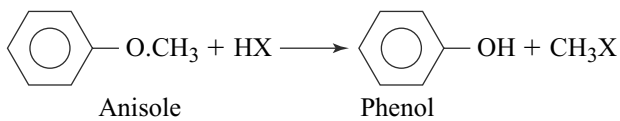
Similarly,



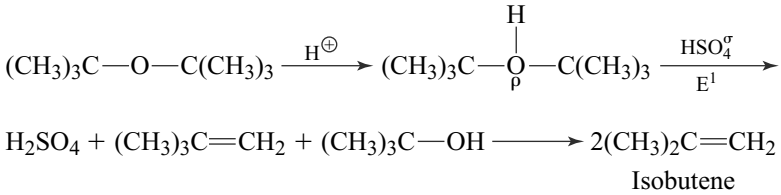
2. If one of the alkyl groups is tertiary, the reaction follows S_N1 mechanism giving a tertiary alkyl iodide. It is because 3°C carbocation is much more stable than 1°C carbocation.



3. In alkyl aryl ethers, the alkyl–oxygen bond (O–R), not the aryl–oxygen bond (C_6H_5–O), breaks. It is due to low reactivity of aryl–oxygen bond. Thus, anisole forms phenol and methyl halide on reaction with HX.



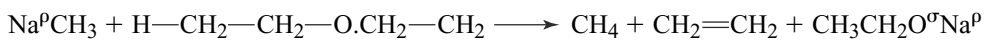
4. Highly branched ether, di-t-butyl ether, dehydrates with H_2SO_4 to isobutene.



$$H_2SO_4 + (CH_3)_3C{=}CH_2 + (CH_3)_3C{-}OH \longrightarrow \underset{\text{Isobutene}}{2(CH_3)_2C{=}CH_2}$$

Reaction with alkali metal alkyls ($CH^-_3Li^+$)

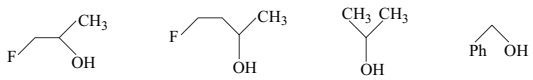
Ethers are not acidic and do not usually react with bases. However, very strong bases, such as alkali metal alkyls, react with many types of ethers destructively.



PROBLEMS

Objective-Type Questions

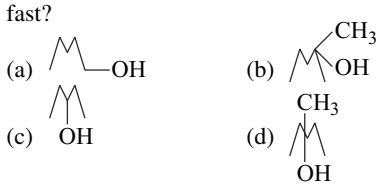
1. The order of reactivity of the following alcohols towards conc. HCl is



(I) (II) (III) (IV)

(a) I > II > III > IV (b) I > III > II > IV
(c) IV > III > II > I (d) IV > III > I > II

2. Which of the following alcohols undergo dehydration fast?



3. HBr reacts the fastest with
(a) 2-methyl-propan–1-ol
(b) propan-1-ol
(c) propan-1-ol
(d) 2-methyl propan-2-ol

4. Lucas reagents is used to distinguish among primary, secondary and tertiary
(a) alkyl halides (b) alcohols
(c) aliphatic amines (d) aromatic amines

5. The reagent, anhydrous $ZnCl_2$ and conc. HCl is used to identify the type of
(a) nitroalkane (b) alkyl amine
(c) alkyl halides (d) alcohols

6. Ease of dehydration of alcohol is
(a) pri > sec > tert (b) sec > pri > tert
(c) tert > sec > pri (d) tert > pri > sec

7. List the hydrogen halide acids in decreasing order of reactivity in the following reaction:
$R{-}OH + HX \longrightarrow RX + H_2O$
(a) HI > HF > HBr > HCl
(b) HI > HCl > HBr > HF
(c) HI > HBr > HCl > HF
(d) HBr > HI > HCl > HF

8. Which one of the following is more reactive than the rest towards a mix of anhydrous $ZnCl_2$ and conc. HCl?
(a) 2-Methyl-propan-2-ol
(b) Methanol
(c) Butan-1-ol
(d) Butan-2-ol

9. An alcohol $C_5H_{11}OH$ on dehydration gives an alkene, which on oxidation yields a mixture of a ketone and an acid. The alcohol is
(a) $CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_3$
(b) $(CH_3)_3CCH_2OH$
(c) $CH_3CH_2CH(OH)CH_2CH_3$
(d) $CH_3{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_2{-}CH_2{-}CH_3$

10. The major organic product in the reaction
$CH_3{-}O{-}CH(CH_3)_2 + HI \longrightarrow$ Product is

(a) $ICH_2OCH(CH_3)_2$

(b) $CH_3OC(CH_3)_2$ with I below the C

(c) $CH_3I + (CH_3)_2CHOH$

(d) $CH_3OH + (CH_3)_2CHI$

11. The general molecular formula, which represents the homologous series of alkanols is

(a) $C_nH_{2n}O$ (b) $C_nH_{2n+1}O$

(c) $C_nH_{2n+2}O$ (d) $C_nH_{2n}O_2$

12. The compound that reacts the fastest with Lucas reagent at room temperature is

(a) 1-butanol (b) 2-butanol

(c) 2-methylpropanol (d) 2-methylpropan-2-ol

13. The order of reactivity of alcohols towards hydrogen halide is

(a) benzyl > 3° > 2° > 1°

(b) benzyl < 3° < 2° < 1°

(c) 3° > 2° > 1° > benzyl

(d) 3° > 2° > benzyl > 1°

14. The reactivity of alcohols towards active metals is

(a) 3° > 2° > 1° (b) 3° < 2° < 1°

(c) 3° < 1° < 2° (d) 2° < 3° < 1°

15. Lucas reagent is

(a) anhydrous $AlCl_3$ with conc. HCl

(b) anhydrous $ZnCl_2$ with conc. H_2SO_4

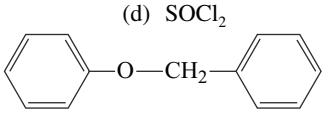
(c) anhydrous $ZnCl_2$ with conc. HCl

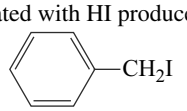
(d) anhydrous $CaCl_2$ with conc. HCl

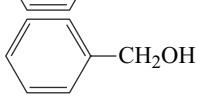
16. Which of the following reagents is most effective in replacing –OH group in an alcohol by –Cl group?

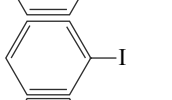
(a) HCl gas (b) Conc. HCl

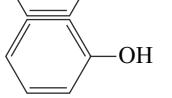
(c) SOCl (d) $SOCl_2$

17. The ether  when treated with HI produces

(a) 

(b) 

(c) 

(d) 

18. 1-Propanol and 2-propanol can be best distinguished by

(a) oxidation with alkaline $KMnO_4$ followed by reaction with Fehling solution

(b) oxidation with acidic dichromate followed by reaction with Fehling solution

(c) oxidation by heating with copper followed by reaction with Fehling solution

(d) oxidation with concentrated H_2SO_4 followed by reaction with Fehling solution

19. Identify the correct order of the boiling points of the following compounds:

$CH_3–CH_2–CH_2–CH_2–OH$ (1)

$CH_3–CH_2–CH_2–CHO$ (2)

$CH_3–CH_2–CH_2–COOH$ (3)

(a) 1 > 2 > 3 (b) 3 > 1 > 2

(c) 1 > 3 > 2 (d) 3 > 2 > 1

20. The compound which will give red colour in Victor–Meyer's test is

(a) propanol-2 (b) butanol-1

(c) butanol-2 (d) t-butyl alcohol

21. Grignard reagent on reaction with a ketone forms

(a) primary alcohol (b) secondary alcohol

(c) tertiary alcohol (d) carboxylic acid

22. Which of the following set of reagents can convert $R–CH_2–CH_2–OH$ into $R–CH_2–CH_2–COOH$?

(a) PBr_3, KCN, H_3O^+ (b) PBr_3, KCN, H_2/Pt

(c) HCN, PBr_3, H_3O^+ (d) KCN, H_3O^+

23. The correct order of the boiling points for primary (1°), secondary (2°) and tertiary (3°) alcohol is

(a) 1° > 2° > 3° (b) 3° > 2° > 1°

(c) 2° > 3° > 1° (d) 2° > 1° > 3°

24. A fruity smell is obtained by the reaction of ethanol with

(a) PCl_5 (b) $CH_3–COOH$

(c) $CH_3–COOH_3$ (d) $CH_3–CHO$

25. *n*-Propyl alcohol and isopropyl alcohol can be chemically distinguished by which of the following reagent?

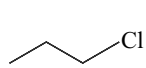
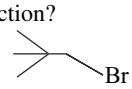
(a) Reduction

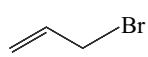
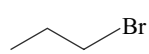
(b) Oxidation with acidic $K_2Cr_2O_7$

(c) PCl_5

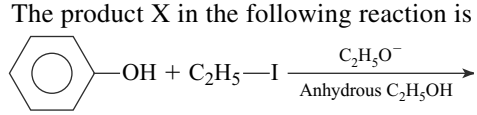
(d) $SOCl_2$

26. Which of the following alkyl halides is the most reactive in the Williamson's reaction?

(a)  (b) 

(c)  (d) 

27. The product X in the following reaction is

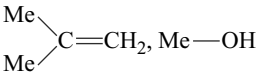


(a) C_6H_5–OC_6H_5 (b) C_6H_5I
(c) C_2H_5–O–C_2H_5 (d) C_6H_5–OC_2H_5

28. The product A in the reaction given below is

$$Me_3C—O—Me \xrightarrow{HI/\Delta} A$$

(a) $Me_3C—OH$, CH_3I

(b)  , Me—OH

(c) $Me_3C—I$, Me—OH

(d) $CH_3—I$, ,

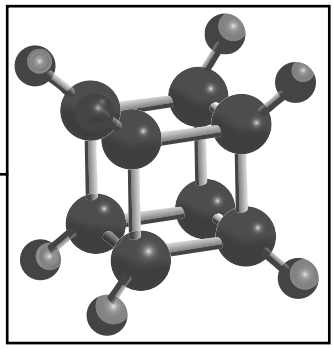
29. When ethanol is heated with conc. H_2SO_4 at various temperature, the products are

(a) $C_2H_5—OSO_2OH$ (b) $CH_3—CH_3$
(c) $(C_2H_5)_2O$ (d) $CH_2=CH_2$

Answers

1. (c)	2. (b)	3. (d)	4. (b)	5. (d)
6. (c)	7. (c)	8. (a)	9. (a)	10. (c)
11. (c)	12. (d)	13. (a)	14. (b)	15. (c)
16. (d)	17. (a,d)	18. (c)	19. (b)	20. (b)
21. (c)	22. (a)	23. (a)	24. (b)	25. (b)
26. (c)	27. (c)	28. (c)	29. (a,c,d)	

CHAPTER 14



Aldehydes and Ketones

The carbonyl group (—C(=O)—) is a very important functional group. It constitutes many classes of organic compounds, that is aldehydes, ketones, carboxylic acid, acid chloride and acid amide. The chemistry of carbonyl compounds is virtually the backbone of synthetic organic chemistry. In this chapter, aldehydes and ketones are discussed.

ALDEHYDES

Aldehydes contain aldehydic (or formyl) group, —C(=O)H joined with an alkyl or aryl group.

$CH_3—C(=O)H$

Acetaldehyde

$C_6H_5—C(=O)H$

Benzaldehyde

As the –CHO group is monovalent, it always constitute the terminal of a chain.

$$^{4}CH_3—^{3}CH_2—^{2}CH(^{1}CHO)—CH_3$$

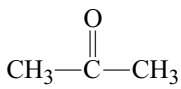
2-Methyl butanal

The simplest member, formaldehyde, H—C═O, contains two hydrogen atoms (not an alkyl group) attached to the carbonyl group. For this reason, it shows special properties.

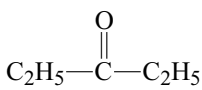
KETONES

The carbonyl group in a ketone is joined with two carbon atoms (that is two alkyl or aryl groups). When the two alkyl groups are the same, the ketone is called a simple ketone, but when they are different, a mixed ketone results.

Simple Ketones

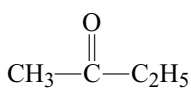


Acetone (dimethyl ketone)

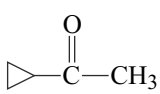


Diethyl ketone

Mixed Ketones

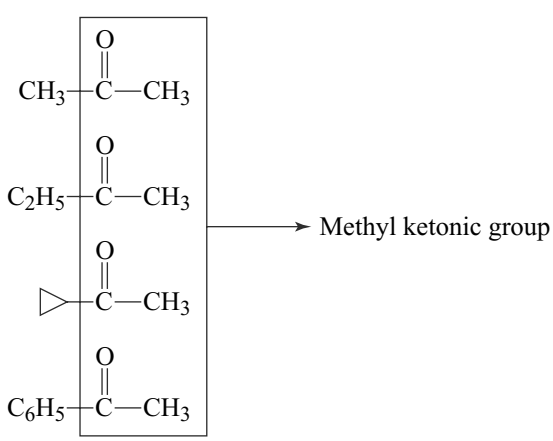


Ethyl methyl ketone



Cyclopropyl methyl ketone

All methyl ketones possess a special property (they undergo haloform reaction), which is not shown by other ketones.



Preparation of Aldehydes

Oxidation of Primary alcohols

Primary alcohols may be oxidized to aldehydes by $K_2Cr_2O_7 + H_2SO_4$, $KMnO_4$ and CrO_3. The most common oxidant is $K_2Cr_2O_7 + H_2SO_4$.

Aldehydes are further oxidized to carboxylic acid by the same oxidant in the reaction mixture. But the aldehydes can be easily removed by distillation as they always have a lower boiling point than that of the alcohol from which they are prepared.

$$\underset{\text{BP} = 78^\circ\text{C}}{CH_3—CH_2—OH} \xrightarrow[H_2SO_4]{Na_2Cr_2O_7} \underset{\text{BP} = 20^\circ\text{C}}{CH_3—CHO}$$

$$\underset{\text{BP} = 97^\circ\text{C}}{CH_3—CH_2—CH_2—OH} \xrightarrow[H_2SO_4]{Na_2Cr_2O_7} \underset{\text{BP} = 49^\circ\text{C}}{CH_3—CH_2—CHO}$$

When the aldehyde has lower volatility, pyridinium chlorochromate, $C_5H_5NH^{\rho}CrO_3.Cl^{\sigma}$, (PCC), the *Sarett's reagent*, is used for oxidation. The reaction is carried out in CH_2Cl_2 (solvent),

$$R—CH_2—OH \xrightarrow{PCC/CH_2Cl_2} CH_3—CHO$$

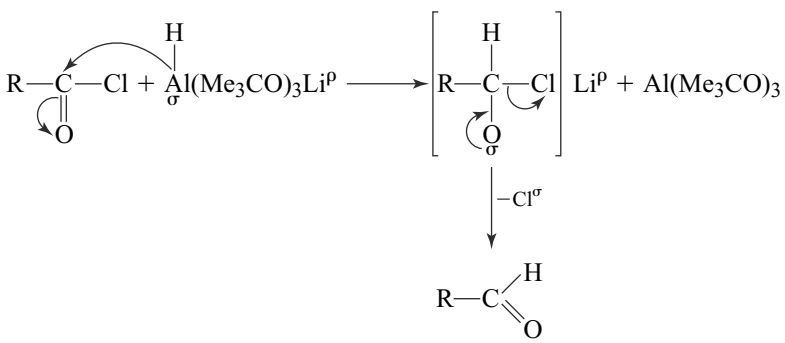
Reduction of acid chlorides (Rosenmund Reduction)

Acid chlorides are reduced with H_2 over a palladium catalyst to the aldehyde. The reduction of aldehyde to the corresponding alcohol is checked by poisoning the catalyst with sulphur.

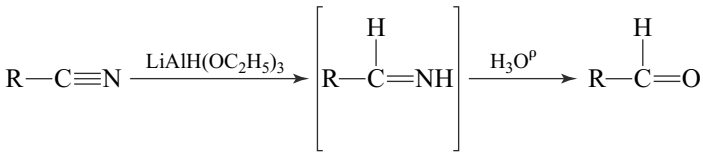
$$R—COOH \xrightarrow[(-HCl,\ SO_2)]{SOCl_2} R—COCl \xrightarrow[H_2]{Pd(BaSO_4)\ (s)} R—C(=O)H + HCl$$

Another reagent for the above reduction is lithium tri-tert-butoxy aluminium hydride, $Li[AlH(Me_3CO)_3]$. The reagent is specific for the reduction of >C=O group without affecting other functional groups. It is milder than $LiAlH_4$ as a reducing agent. Therefore, reduction of acid chloride is stopped at the aldehyde level (not proceeding up to alcohol level).

The reaction is believed to proceed as

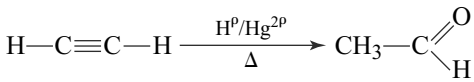


This reagent also reduces RCN and N,N-dialkyl amides, $R—\overset{O}{\overset{\|}{C}}=N(R')_2$, to aldehydes.



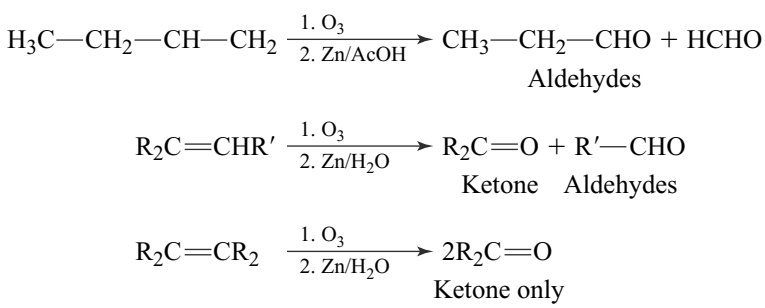
Hydration of alkynes

This method can produce acetaldehyde only. (The reaction is explained in Chapter 11, *Alkynes*.)



Oxidative cleavage of alkenes

For this purpose, ozonolysis is the preferred reaction, as O_3 does not oxidize the aldehyde produced rapidly. Also, the number of alkyl groups at the double bond determines whether aldehydes or ketones are produced. (See Chapter 10, *Alkenes*.)



Hydroboration of alkynes

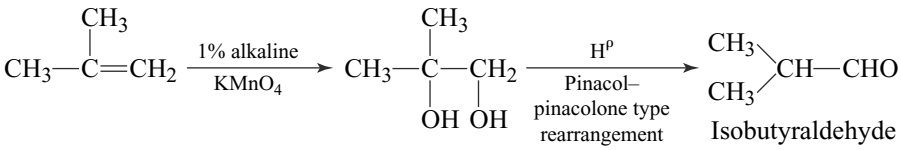
(Discussed in Chapter 11, *Alkynes.*)

Cleavage of glycols

The 1,2-diols undergo C–C bond cleavage with HIO_4 or lead tetracetate to give carbonyl compounds (discussed in Chapter 13, *Alcohols*).

Hydroxylation of alkene followed with rearrangement

For example,



This reaction is used to produce isobutyraldehyde in large scale.

Wacker Process for CH_3CHO

Ethylene is oxidized in the presence of $PdCl_2$–$CuCl_2$ in acidic solution to CH_3CHO. It is a cyclic reaction and believed to proceed as

$$C_2H_4 + PdCl_2 + H_2O \longrightarrow CH_3CHO + Pd + 2HCl$$

$$Pd + 2CuCl_2 \longrightarrow PdCl_2 + 2CuCl$$

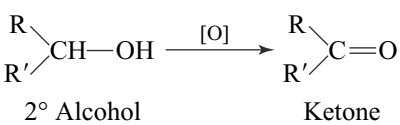
$$2CuCl + 2HCl + \tfrac{1}{2}O_2 \longrightarrow 2CuCl_2 + H_2O$$

$$\overline{C_2H_4 + \tfrac{1}{2}O_2 \longrightarrow CH_3.CHO}$$

Preparation of Ketones

Oxidation of secondary alcohols

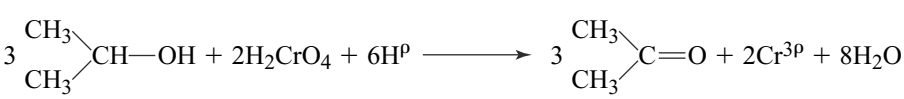
Secondary alcohols may be oxidized to ketones by using variety of reagents.



Common reagents are

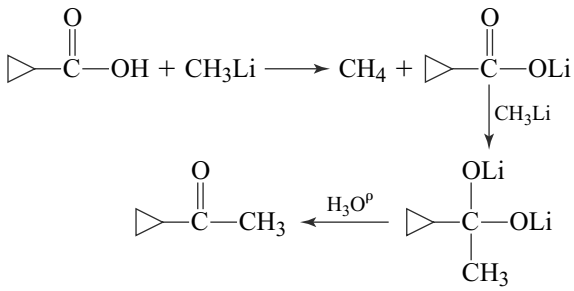
1. $Na_2Cr_2O_7 + H_2SO_4$
2. $CrO_3 + CH_3COOH$
3. Sarett's reagent
4. $KMnO_4$

The overall reaction with chromic acid may be written as:

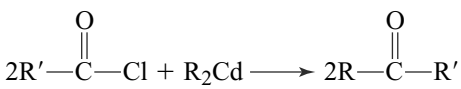


Conversion of carboxylic acid and derivatives by Organo-Li and -Cd compounds

Reaction of lithium alkyl with carboxylic acids may be used for the preparation of ketones.

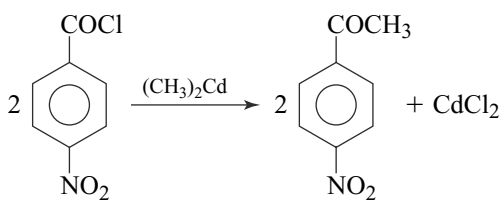


More useful is organocadmium compound, which reacts with acid chloride to form ketone.



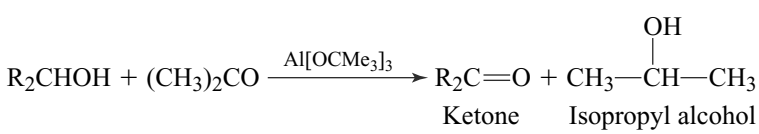
Two important aspects of this reaction are

1. Organocadmium compounds containing primary and aryl groups only are stable enough to be used. It is a limitation.
2. Organocadmium compounds have low reactivity. Therefore, they do not react with many functional groups like >C=O, –CN and –COOR. Thus, the presence of these groups in the acid chloride does not affect the synthesis of ketones. For example,



Ketones by Oppenauer oxidation

Secondary alcohols are oxidized to ketones when refluxed with aluminium isopropoxide, $Al[OCH(CH_3)_2]_3$ or aluminium tert-butoxide, $Al[OC(CH_3)_3]_3$ in excess of acetone solution. This reaction is known as *Oppenauer oxidation*. This oxidation takes place at the expense of acetone, which is reduced to isopropyl alcohol.

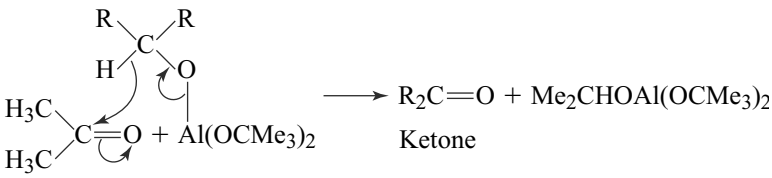


Mechanism

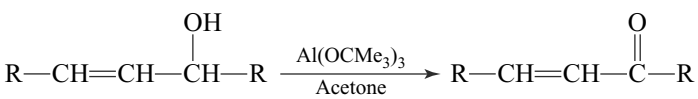
1. First, the aluminium derivative of the alcohol to be oxidized is formed by exchange reaction with $Al(OCMe_3)_3$.

$$R_2CHOH + Al(OCMe_3)_3 \rightleftharpoons R_2CHOAl(OCMe_3)_2 + Me_3C - OH$$

2. Second, oxidation proceeds as

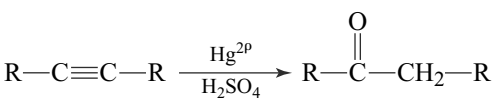


Cyclohexanone may also be used in place of acetone. Unsaturated secondary alcohols may be oxidized to ketones without affecting the double bond.



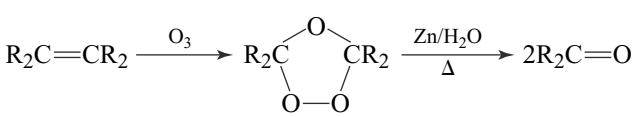
Hydration of alkynes

Alkynes of the type R–C≡CH or R–C≡C–R undergo hydration in the presence of Hg^{2+} and H_2SO_4 to give ketones (for details see Chapter 11, *Alkynes*).



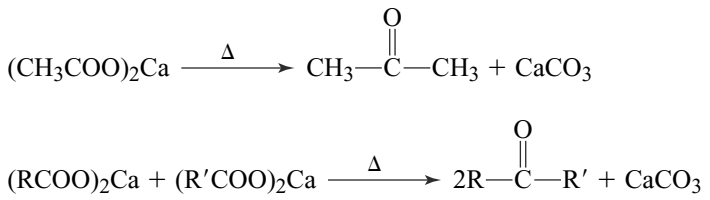
Oxidative cleavage of alkenes

Alkenes of the type $R_2C{=}CR_2$ when cleaved by O_3, ketones are formed (for details see Chapter 10, *Alkenes*).



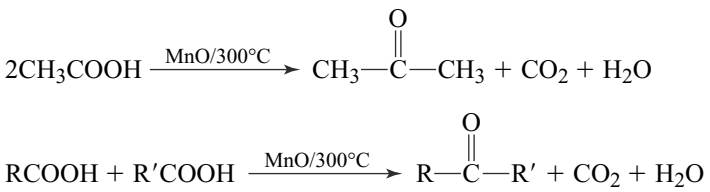
Thermal decomposition of Ca salt of carboxylic acids

Ketones are obtained when Ca salts of fatty acids, (other than formic acid) are heated alone. Mixed ketones are formed when salts of two fatty acids are heated.



Catalytic decomposition of fatty acids

Vapours of fatty acids are decomposed over MnO catalyst to give ketones.

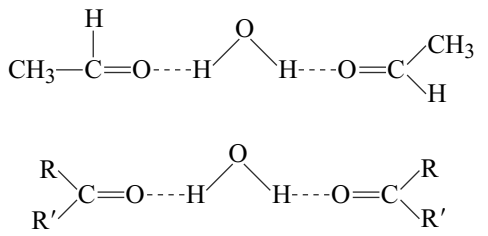


PROPERTIES AND REACTIONS

The carbonyl group (>C=O) is polar in nature (C and O differ in electronegativity) It has large effect on its properties.

Solubility

Lower members (up to C_4) are soluble in water due to intermolecular H-bonding with water.



However, higher and lower aldehydes and ketones are soluble in organic solvents (ether, benzene and methanol).

Boiling Points

The polar nature of the carbonyl group makes aldehydes and ketones having higher BP than those of non-polar hydrocarbons or less polar ethers of comparable mass.

Compounds		Molecular mass	BP (°C)
Pentane	$CH_3(CH_2)_3CH_3$	72	36
Diethyl ether	$C_2H_5–OC_2H_5$	74	35
Butanal	$CH_3(CH_2)_2CHO$	72	76
Butanone	$CH_3CH_2COCH_3$	72	80

However, alcohols of comparable mass have higher BP than aldehydes and ketones. It is because in alcohols, molecules are associated through intermolecular H-bonding, which is not possible in aldehydes and ketones:

Compounds	Molecular mass	BP (°C)
Butanal	72	76
Butanone	72	80
Butan-1-ol	74	118

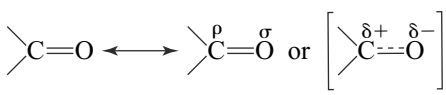
Reactions

Aldehydes and ketones undergo a wide variety of reactions. There are two sites of reactions in aldehydes and ketones:

1. The polar carbonyl ($>\overset{\delta+}{C}=\overset{\delta-}{O}$) group and
2. The alkyl group (or groups) joined to the carbonyl group.

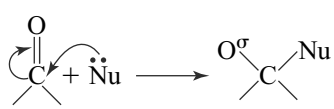
Reactions of carbonyl group

The carbonyl group is polar as O atom is more electronegative than C atom. It is best represented by the dipolar resonance form with O negative and C positive.

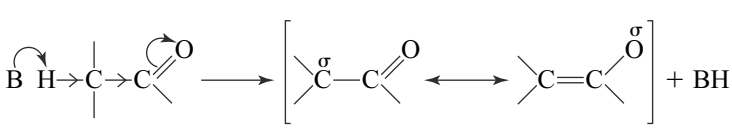


The positive nature of the carbonyl carbon makes carbonyl group electron-attracting (–I effect) as a whole. The polar nature of C = O group works in two ways towards its reactions.

1. The C of the C=O group is attacked by a nucleophile.



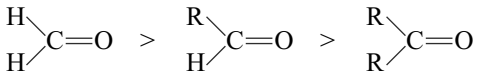
2. The electron-attracting effect of >C=O makes the α-H atom acidic. It is, thus, taken up by a base to give resonance-stabilized carbanion.



It is the first step in many condensation reactions (example aldol and Claisen condensation).

Reactivity

The reactions of aldehydes and ketones are influenced by both the electronic and the steric factors. The overall reactivity of aldehydes and ketones is



(All these factors are explained in detail in the Chapter 5, *Reaction Mechanism*.)

REACTIONS OF >C=O GROUP

The important reactions are as follows:

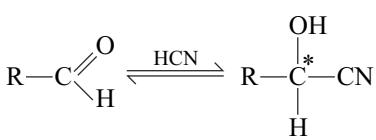
1. Nucleophilic addition
2. Reduction
3. Oxidation
4. Condensation with NH_3 and NH_3 derivatives

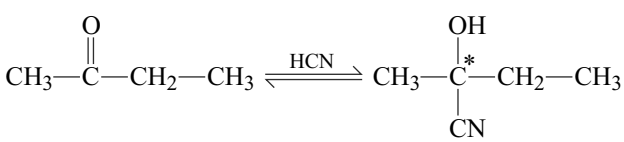
Nucleophilic addition

Addition of HCN

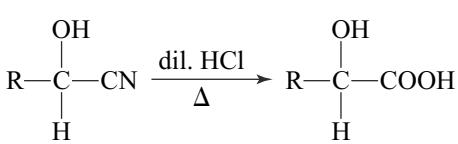
HCN adds to aldehydes and ketones to form cyanohydrine. The reaction is catalysed by HO^{σ}.

Cyanohydrins of aldehydes and mixed ketones always create chiral centre



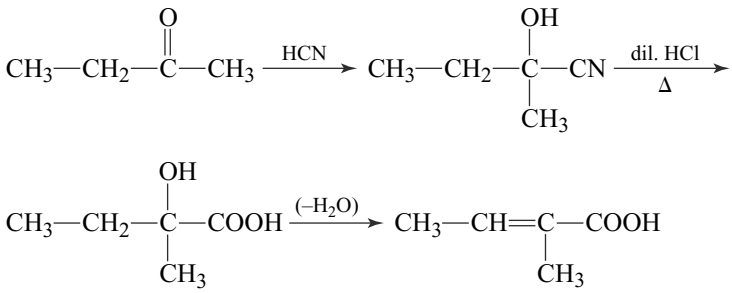


Cyanohydrins are easily hydrolyzed by acid (HCl and H_2SO_4) to α-hydroxy acids.



α-Hydroxy acid

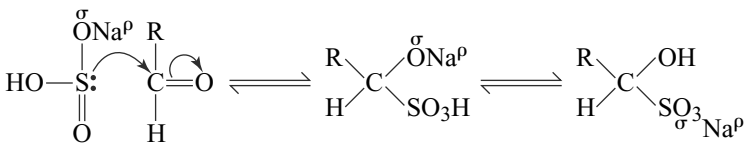
Many α-hydroxy acids may undergo dehydration to α,β-unsaturated acids. For example,



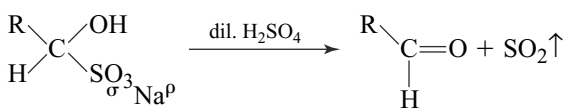
α,β-Unsaturated acid

Addition of $NaHSO_3$

Sodium bisulphite ($NaHSO_3$) adds to aldehydes and reactive ketones (that is which have no bulky alkyl groups) to give crystalline precipitate. The reaction is reversible.



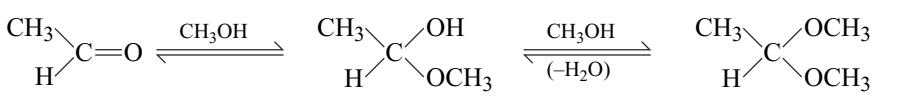
The addition product can be decomposed easily with dilute acid to the carbonyl compound. It is, therefore, used in separation and purification of aldehydes in particular.



Aldehyde

Addition of alcohols

Alcohols add to aldehydes to form hemiacetal and acetal, example

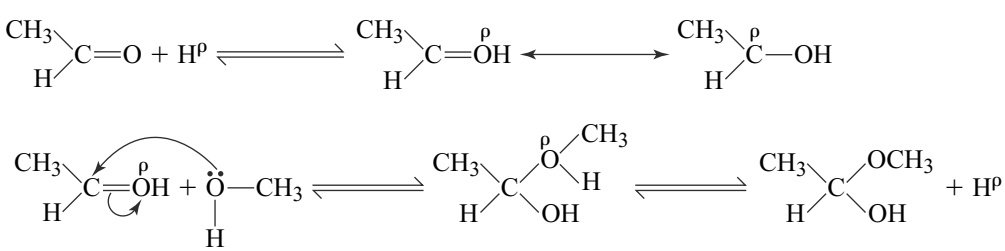


Hemiacetal
(1-Methoxy ethanol)

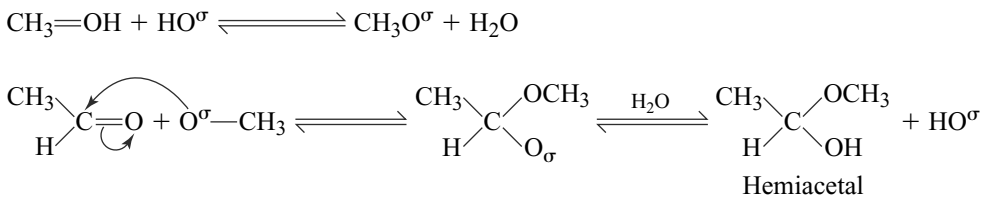
Acetal
(1,1-Dimethoxy ethane)

Hemiacetal formation may be catalysed by both acids and bases.

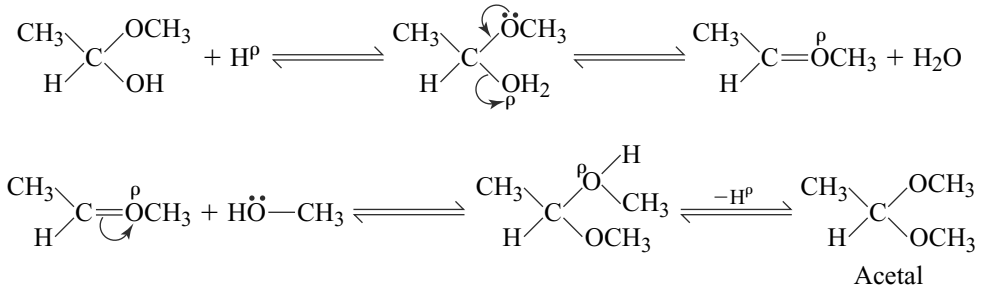
Acid catalysis



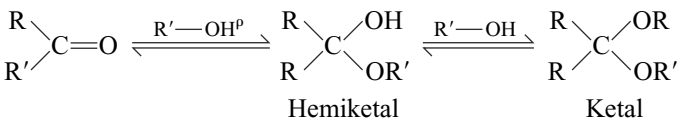
Base catalysis



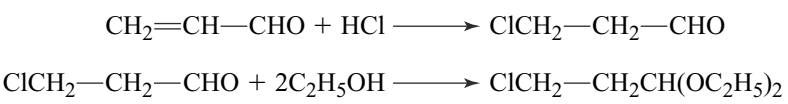
In contrast to hemiacetal formation, acetal formation is catalysed by acids only.

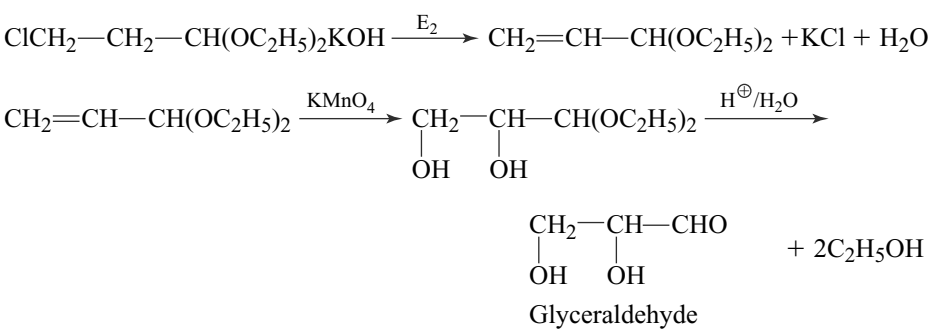


The reaction between a ketone and an alcohol proceeds in the same way to form hemiketal and ketal.

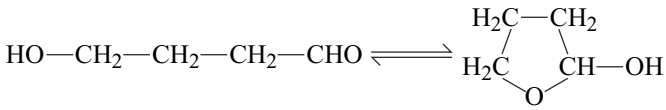


Acetals and ketals are stable to bases. Therefore, the carbonyl group may be protected by preparing these derivatives. The carbonyl group is regenerated by reaction with acids. This behaviour is synthetically very useful [example synthesis of glyceraldehydes from acrolein (CH_2=CH–CHO)].





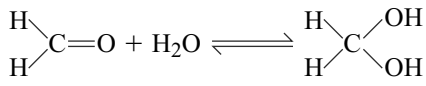
Hemiacetal formation may take place in an intramolecular manner when five- or six-membered ring can be formed from a hydroxyaldehyde.



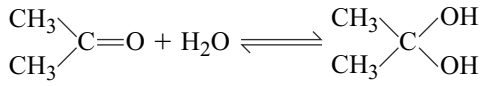
This type of reaction is very important in carbohydrate chemistry.

Addition of water (Formation of Hydrate)

Aldehydes and ketones may add H_2O to form gem-diols (gem means same), which are too unstable to be isolated. The addition is very much affected by steric factor.



99%



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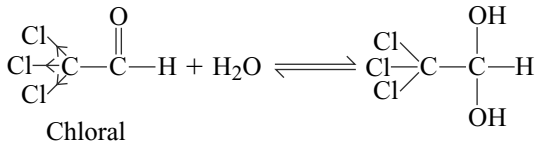
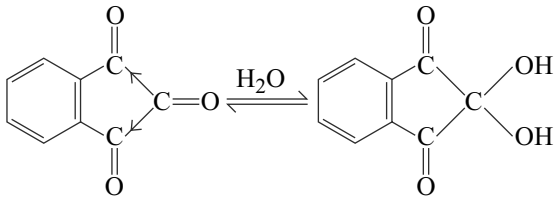
When carbonyl compounds contain strong electron-attracting groups, the gem-diols are stable enough to be isolated. For example,

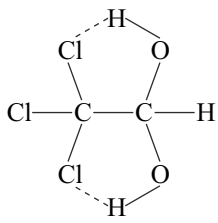


Chloral Chloral hydrate



(Ninhydrine) (Hydrate)

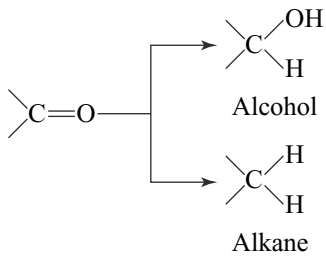
These hydrates achieve stability through intramolecular H-bonding.



Chloral hydrate (H-bonded)

Reduction

The >C=O group of aldehydes and ketones may be reduced to the alcohol level or the hydrocarbon level.



The products depend upon reducing agents used.

FORMATION OF ALCOHOLS

Many reducing agents can be used for this purpose:

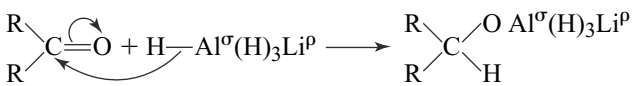
1. Catalytic hydrogenation (industrial process) using H_2 and metal catalysts Ni, Pd or Pt under high pressure.

   This reagent combination reduces C=C also.

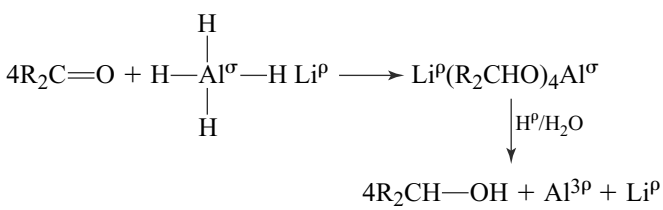
$$CH_3—CH=CH—CHO \xrightarrow[\Delta]{H_2/Ni} CH_3.CH_2.CH_2.CH_2.OH$$

2. Lithium aluminium hydride ($LiAlH_4$) and sodium borohydride ($NaBH_4$) are very important reducing agents. $LiAlH_4$ reduces C=O groups of aldehydes and ketones to alcohols.

   The reduction is a hydride (H^-) transfer reaction.



All four hydrogens on aluminium can be utilized in the above way. The product of reduction is decomposed by dil. acid. Thus, the stoichiometric reaction is



An aldehyde gives 1°C alcohol.

$$4RCHO + LiAlH_4 \longrightarrow (RCH_2O)Al^{\sigma}Li^{\rho} \xrightarrow[H_2O]{H^{\rho}} RCH_2{-}OH + Al^{3\rho} + Li^{\rho}$$

This reagent can reduce other polarizable groups like C≡N, C=N, N=O and even C_6H_5–CH=$\overset{|}{C}$– also. Thus, it is less selective for C=O group reduction.

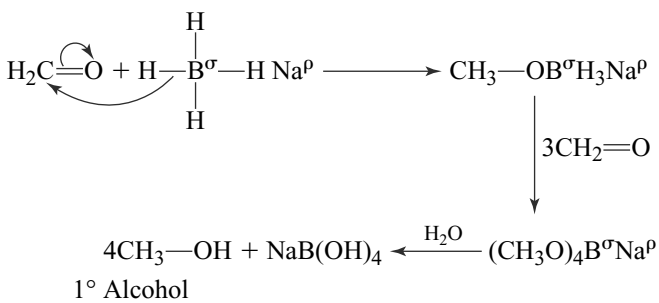
$$\underset{\text{Cinnamaldehyde}}{C_6H_5{-}CH{=}CH{-}CHO} \xrightarrow[\text{Ether}]{LiAlH_4} \underset{\text{3-Phenyl propanol-1}}{C_6H_5{-}CH_2{-}CH_2{-}CH_2{-}OH}$$

Another important limitation of $LiAlH_4$ is that it can only be used in organic solvents (ether), and not in water, as $LiAlH_4$ is decomposed by water or acid.

$$LiAlH_4 + 4H_2O \longrightarrow LiOH + Al(OH)_3 + 4H_2$$
$$LiAlH_4 + 4H^+ \longrightarrow Li^{\rho} + Al^{3\rho} + 4H_2$$

Sodium borohydride, $NaBH_4$, is a milder reducing agent than $LiAlH_4$. It does not reduce other polarizable groups and can be used in water medium also ($NaBH_4$ is stable in water).

The reduction with $NaBH_4$ proceeds similar to $LiAlH_4$.



$$C_6H_5{-}CH{=}CH{-}CHO \xrightarrow{NaBH_4/H_2O} C_6H_5{-}CH{=}CH{-}CH_2.OH$$

3. *Meerwein–Ponndorf–Verley reduction*

Reducing agent in this method is aluminium isopropoxide in isopropyl alcohol, which reduces a ketone to secondary alcohol (it is a hydride transfer reaction).

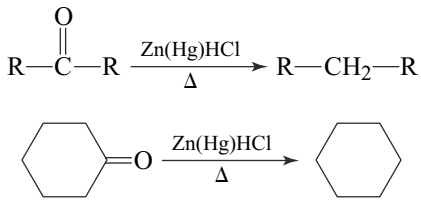
$$\begin{matrix} R \\ R \end{matrix}\!\!>\!C{=}O + (CH_3)_2CH{-}OH \underset{}{\overset{Al(OCHMe_2)_3}{\rightleftharpoons}} \begin{matrix} R \\ R \end{matrix}\!\!>\!CH{-}OH + (CH_3)_2C{=}O$$

Acetone is an important byproduct in this reaction. The C=C is not reduced in this method.

Reduction of >C=O to >CH_2 (that is formation of alkane)

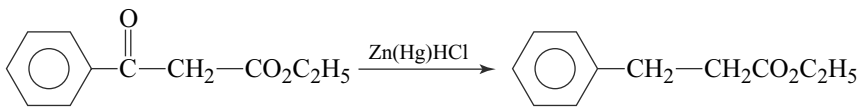
Clemmensen reduction

Reagent of this method is zinc amalgam and conc. HCl.



Cyclohexanone Cyclohexane

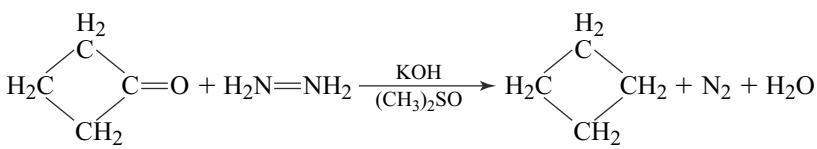
The method is important for those carbonyl compounds in which base sensitive groups are present. For example,



(–$COOC_2H_5$ group is sensitive to base, i.e. it may hydrolyze).

Wolff–Kishner reduction

Reagent of this method is hydrazine ($H_2N–NH_2$) and KOH. This method is important for those carbonyl compounds in which R group is stable to base but not to acid.



Cyclobutanone Cyclobutane

(The cyclic ketone is sensitive to acid, the ring may open by protonation of C=O group).

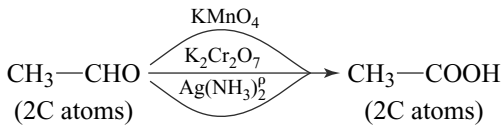
Oxidation

Aldehydes are easily oxidized, whereas ketones are resistant to oxidation.

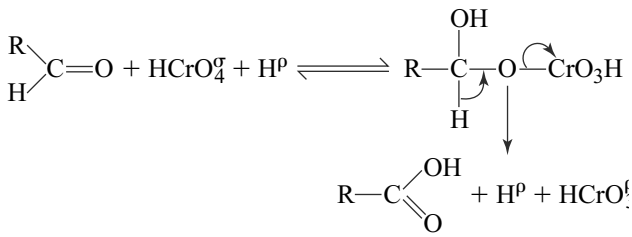
ALDEHYDES

Aldehydes are easily oxidized to carboxylic acids having the same number of carbon atoms.

The usual oxidants are potassium permanganate and acidic dichromate ($K_2Cr_2O_7$ + conc. H_2SO_4).



Oxidation of aldehydes by chromic acid proceeds through chromate ester.



Aldehydes can also be oxidized by milder reagents. Two such important reagents are (a) Tollen's reagent and (b) Fehling's solution.

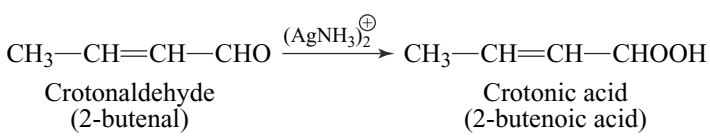
Tollen's reagents

Ammoniacal silver nitrate solution is known as Tollen's reagent. The Ag^{ρ} ions oxidize aldehydes to carboxylic acid and are themselves reduced to metallic Ag. deposits on the sides of the test tube and look like a mirror. The test is, therefore, called silver mirror test.

$$R—CHO + 2Ag(NH_3)_2OH \longrightarrow 2Ag + RCOONH_4 + 3NH_3 + H_2O$$

Important points

1. This reaction is used to distinguish an aldehyde from a ketone as ketones are not oxidized by this reagent.
2. Tollen's reagent does not affect C=C. Therefore, it may be used for the synthesis of α,β-unsaturated acids from α,β-unsaturated aldehydes (these are produced easily through aldol condensation).



Fehling's solution

A mixture of $CuSO_4$ solution and strongly alkaline solution of Roschelle salt (sodium potassium tartarate) is known as Fehling's solution. This reagent forms red precipitate of Cu_2O with aldehydes.

$$R—CHO + 2Cu^{2\rho} + 5HO^{\sigma} \longrightarrow \underset{\text{Red}}{Cu_2O} + RCOO^{\sigma} + 3H_2O$$

Benzaldehyde does not give this reaction

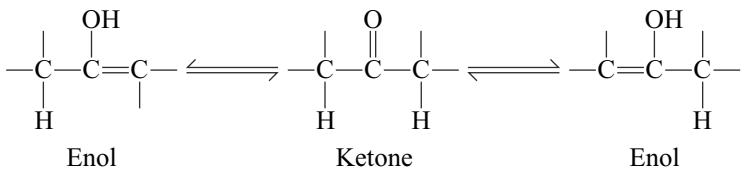
When Cu^{2+} is present with citrate ions, the solution is known as *Benedict's reagent*. It also gives red precipitate of Cu_2O with aldehydes.

KETONES

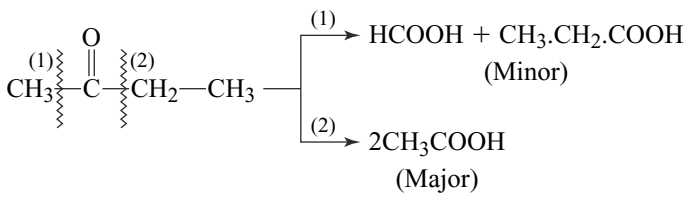
Oxidation of ketones proceed with the cleavage of C–C bonds and only under drastic condition (except for the haloform reaction). The products are carboxylic acids having lesser number of C atoms (than the ketone).

Different aspects of the oxidation

1. The oxidation is believed to involve, C=C of enol of the ketone. Thus, if ketone has H on both sides of C=O group, oxidation may occur on either side (giving mixture of acids).

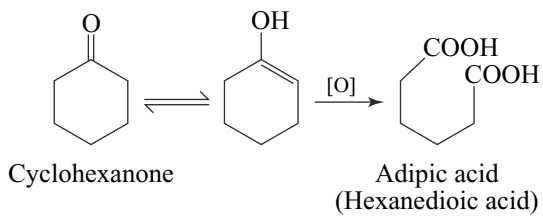


2. In the oxidation of mixed ketones, the C=O group mainly remains with the smaller alkyl group.



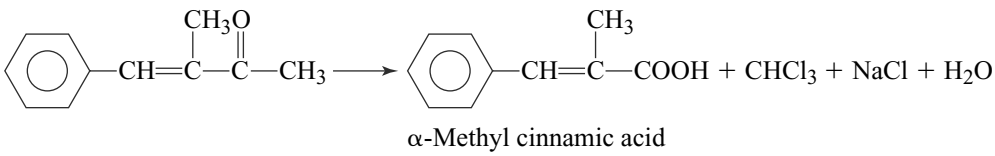
As mixture of acids is obtained, it is not a reaction of synthetic utility.

3. Oxidation is utilized mostly to prepare dicarboxylic acids, from cyclic ketones, having the same number of C atoms.



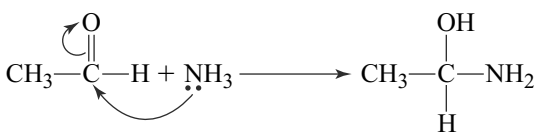
4. Methyl ketones undergo easy oxidation, in the haloform reaction (see haloform reaction). With iodine and NaOH, methyl ketones form yellow precipitate of iodoform (CHI_3). Thus, methyl ketones are identified by this reaction.

An additional advantage of the reaction is that hypohalite ($NaOH + X_2 \longrightarrow NaOX$) does not attack C=C.

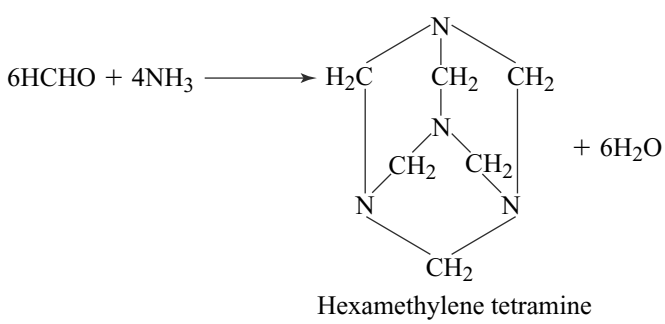


Reaction of aldehydes and ketones with NH_3 and its derivatives

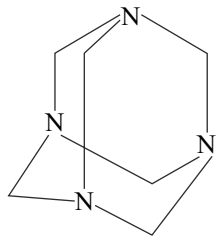
Acetaldehyde adds NH_3 quickly and forms a crystalline compound.



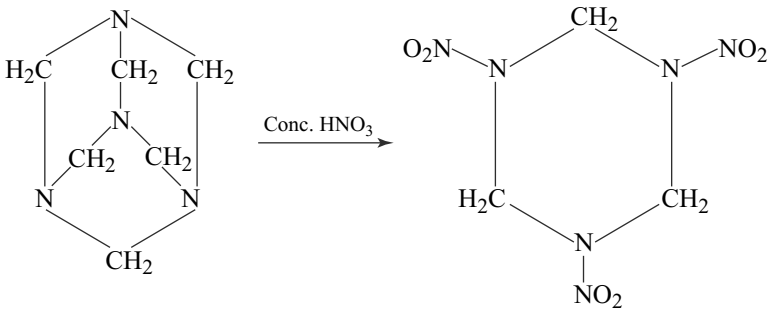
Formaldehyde also reacts with NH_3 but in a different way. The product is a white solid hexamethylenetetramine (Urotropine). It has complex cyclic structure.



Conformational structure may be represented as:

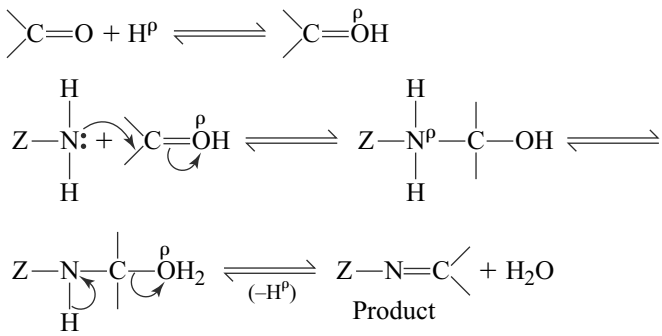


Hexmethylenetetramine reacts with conc. HNO_3 to give highly explosive substance cyclonite (RDX).

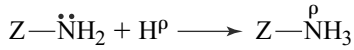


Hexahydro-1,3,5-trinitrosym-triazine

Amines and many other NH_3 derivatives condense with aldehydes and ketones, but dehydration follows to form stable compounds. Reactions in which two molecules combine and then H_2O is generally split out are known as condensation reactions. Acids (or bases) catalyse such reactions.
The reaction with NH_3 derivatives ($Z–NH_2$) proceeds as:

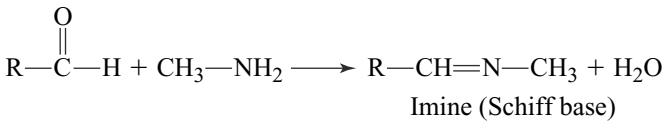


The reaction requires an optimum pH, otherwise the nucleophile is destroyed by the reaction.



Reaction with R–NH_2 (1°C amine)

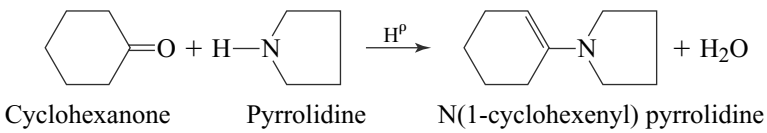
Aldehydes and ketones react with R–NH_2 to produce substituted imines, which are called *Schiff's base*.



Schiff's bases are quite stable and isolable.

Reaction with R_2NH (2° amine)

2° Amines form enamines with aldehydes and ketones. The product dehydrates to form C=C as N has no H atom.



Reaction with some other NH_3 derivatives

Many NH_3 derivatives form crystalline products, which are analytically important. They are

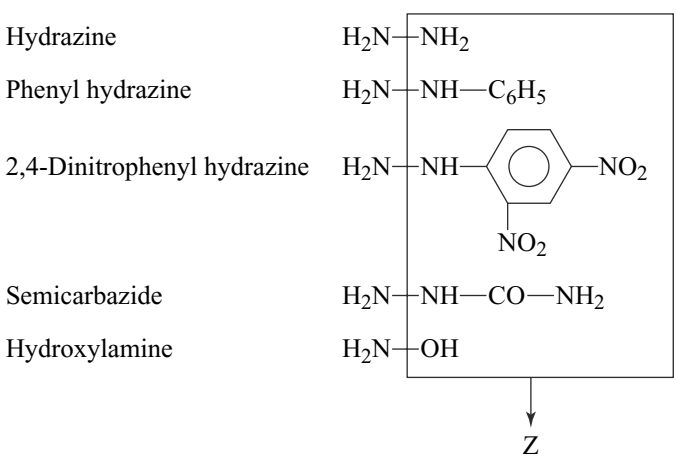
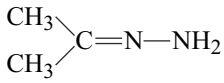
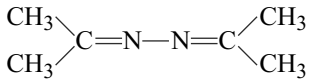
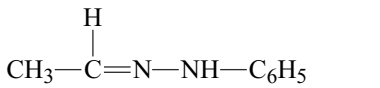
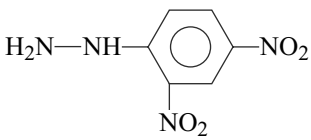
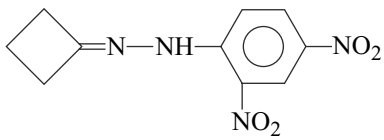
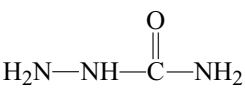
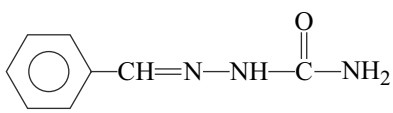


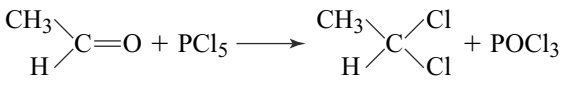
Table 14.1 Condenstation products of carbonyl compounds

Reagent	Product	Class of product
$H_2N—NH_2$ Hydrazine	 Acetone hydrazone	Hydrazone
	 Acetone azine	Azine
$H_2N—NH—C_6H_5$ Phenyl hydrazine	 Acetaldehyde phenylhydrazone	Substituted hydrazone[1]
 2,4-Dinitro phenyl hydrazine	 Cyclobutanon 2,4-dinitro phenyl hydrazone	Substituted hydrazone[1]
 Semicarbazide	 Benzaldehyde semicarbazone	Semicarbazone[1]
$H_2N—OH$ Hydroxylamine	$H_2C=N—OH$ Formaldoxime	Oxime[1]

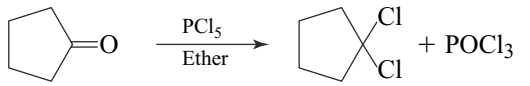
Note:

1. Both NH_2 groups in hydrazine may condense to give azine.
2. The products marked 1 are solids. These are good derivatives for the isolation and characterization of aldehydes and ketones.

The carbonyl oxygen may be replaced by chlorine atoms on reaction with PCl_5, giving gem-dichloro derivative.



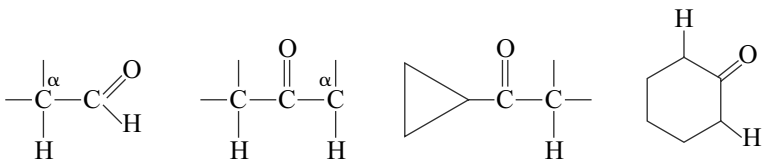
1,1-Dichloro ethane



Cyclopentanone 1,1-Dichloro cyclopentane

Reductions due to acidity of α-H-atom

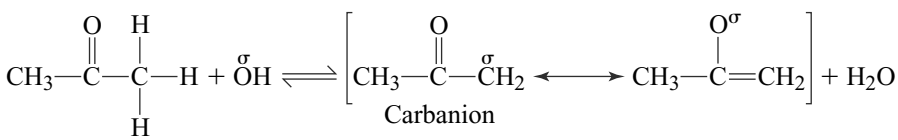
Many aldehydes and ketones have hydrogen atoms on the carbon α to the carbonyl group.



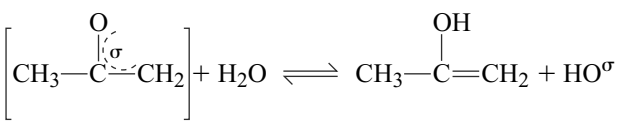
(α-H atom) (α-H atom) (α-H atom)

The hydrogen α to the carbonyl group has acidic nature (C=O group electron-attracting) and can be removed as proton to give a carbanion, which is resonance stabilized. It is catalysed by a base. The product of this change may be an enolate anion or an enol. It is known as enolization. Acids may also catalyse enolization.

Base-catalysed enolization

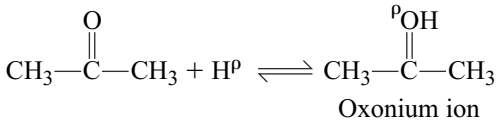


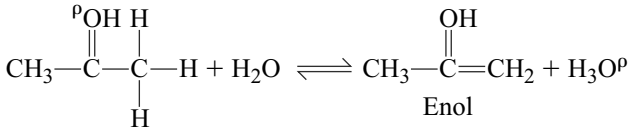
Carbanion



Acid-catalysed enolization

The carbonyl compound (acetone) first forms oxonium ion. In the second step, removal of an α-proton (with H_2O or other proton acceptor) forms enol.



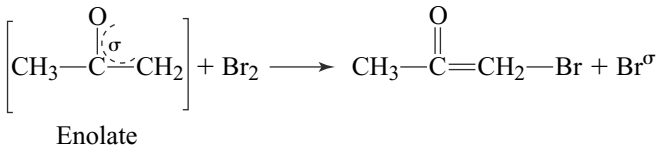


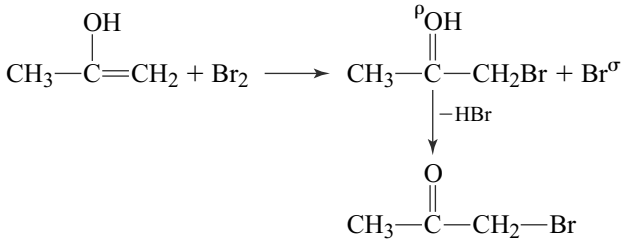
Unlike base-catalysed reaction, here enol is formed directly.

The acidity in α-H atoms includes many very important synthetic reactions.

Haloform reaction (see Chapter 6, *Name Reaction*).

This reaction proceeds with halogenation of the carbonyl compound (methyl ketones). Both the enolate and the enol can combine rapidly with halogen to give α-halo derivative.



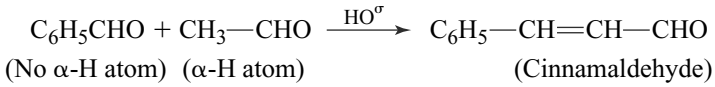


Aldol condensation (see Chapter 6, *Name Reaction*)

This reaction is of great synthetic utility as C–C bond is generated in this condensation. Aldehydes having no α-H atom undergo *Cannizzaro's reaction* (see Chapter 6, for details).

Claisen–Schmidt condensation

Aldehydes having no α-H atom (HCHO and benzaldehyde) may condense with aldehydes and ketones having α- H atom in the presence of basic catalyst. The product is α,β-unsaturated aldehydes or ketones. This reaction is known as Claisen–Schmidt condensation.



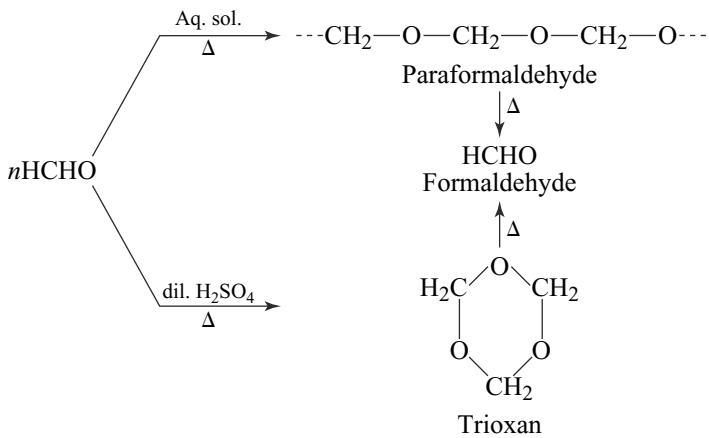
Side reactions to give self-condensation, $CH_3CHO + CH_3CHO$, is important. It can be prevented by careful control of the condition.

Polymerization

Like many other unsaturated organic molecules, aldehydes undergo polymerization reactions. The products depend on conditions and reagents.

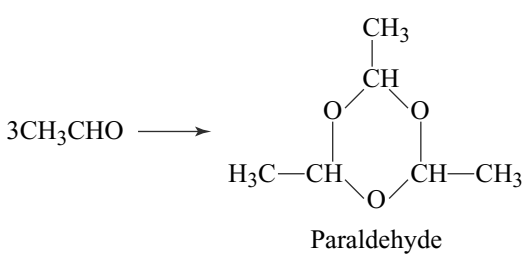
Polymers of formaldehyde (Methanal)

1. An aqueous solution of formaldehyde when evaporated to dryness, a white crystalline solid separates. It is a long chain polymer called paraformaldehyde (MP 121–123°C). It gives formaldehyde on heating.
2. On warming formaldehyde with dil. H_2SO_4, a cyclic trimer, 1,3,5-trioxan is obtained (MP 61–62°C). It also gives formaldehyde on heating.

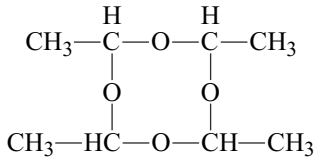


Polymers of acetaldehyde (Ethanal)

1. Acetaldehyde undergoes rapid polymerization in the presence of a trace of conc. H_2SO_4, to a trimer called paraldehyde (BP128°C). It is used as a steep-inducing drug. On reaction with dil. acid, paraldehyde regenerates acetaldehyde.

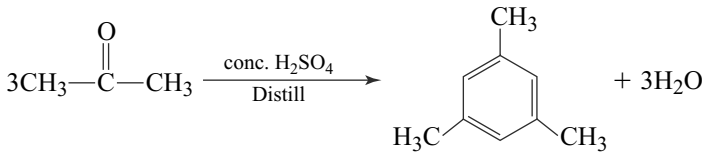


2. When acetaldehyde is treated with a few drops of conc. H_2SO_4 (or dry HCl) at a low temperature (0°C), a tetramer is formed. It is called metaldehyde (MP 246°C). It also gives acetaldehyde when distilled with dil. acid. It has the structure.



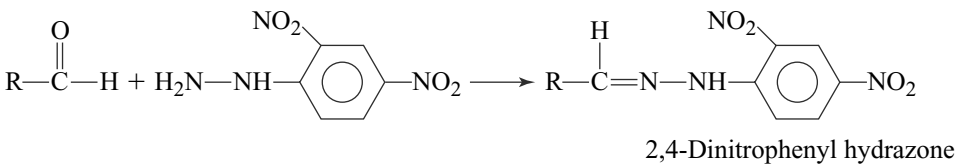
Metaldehyde

Acetone (propanone) behaves differently. It undergoes condensation when distilled with conc. H_2SO_4. The product is 1,3,5-trimethyl benzene with three molecules of water. It is the conversion of an aliphatic compound into aromatic one.

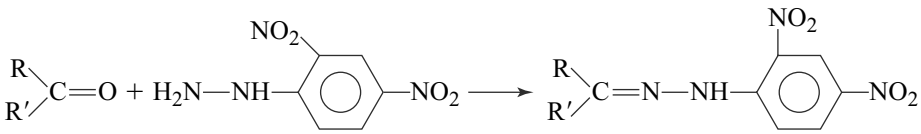


CHARACTERIZATION OF ALDEHYDES AND KETONES

1. The reagent 2,4-dinitrophenyl hydrazine gives insoluble orange or red solid with both aldehydes and ketones.

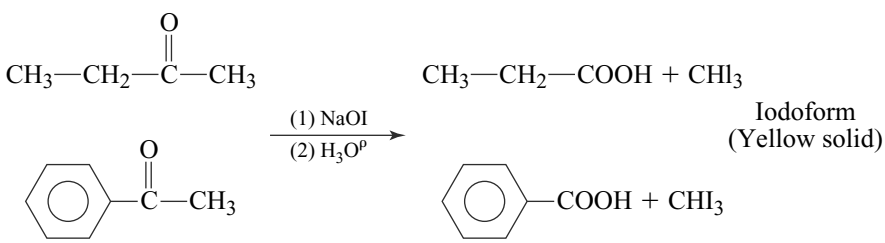


2,4-Dinitrophenyl hydrazone



This reaction, thus, characterizes (tests) the carbonyl compounds as an aldehyde or a ketone.

2. Methyl ketones are further characterized by haloform (specially iodoform) reaction. Methyl ketones form yellow solid, iodoform (CHI_3), when treated with NaOI (sodium hypoiodite) or I_2 and NaOH.



DISTINCTION BETWEEN ALDEHYDES AND KETONES

Aldehydes are very easily oxidized by mild oxidizing agents but not the ketones. This behaviour is used for distinction between aldehydes and ketones.

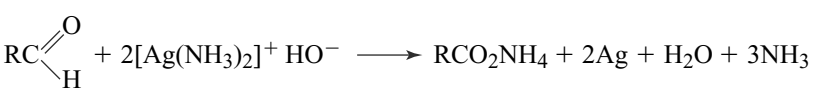
Table 14.2

Reagent	Aldehydes	Ketones
1. Schiff's reagent	Gives magenta colour	X
2. Tollen's reagent	Forms silver mirror	X
3. Fehling's reagent	Gives red precipitate of Cu_2O	X

Note:

1. **Schiff's reagent:** Aqueous solution of Rosaniline hydrochloride [Magenta colour (reddish purple)] is decolourized by passing SO_2 gas. The colourless solution is called Schiff's reagent. Aldehydes restore magenta colour to Schiff's reagent. It is a very sensitive test.
2. **Tollen's reagent:** Ammoniacal silver nitrate is known as Tollen's reagent. It contains complex Ag^+ ions. The Ag^+ ion (weak oxidizing agent) oxidizes aldehydes (reducing agents) to carboxylic acid and metallic Ag is formed.

   Liberated silver deposits at the walls of the test tube. It looks like a mirror. So, the test is called silver mirror test. The reaction is



$$RC(=O)H + 2[Ag(NH_3)_2]^+ HO^- \longrightarrow RCO_2NH_4 + 2Ag + H_2O + 3NH_3$$

3. **Fehling's solution:** A mixture of an aqueous solution of $CuSO_4$ and strongly alkaline solution of Rochelle salt (sodium potassium tartarate) is known as Fehling's solution. Aldehydes forms red precipitate of Cu_2O with Fehling's solution.

$$R{-}CHO + 2Cu^{2\rho} + 5HO^{\sigma} \longrightarrow Cu_2O + RCOO^{\sigma} + 3H_2O$$

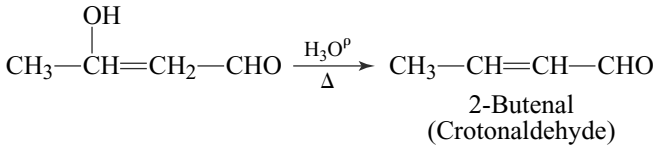
$CuSO_4$ and alkaline solution of citric acid (known as *Benedict's solution*) also gives red solid Cu_2O. That is, aldehydes are oxidized by weak oxidizing agents like Ag^+ or Cu^{2+} ions.

Unsaturated Carbonyl Compounds

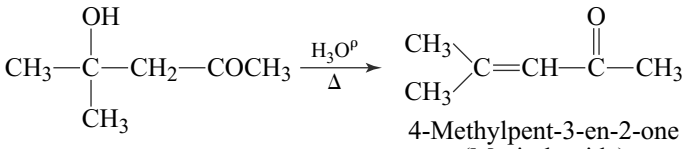
A double bond (C=C) close to carbonyl group imparts exceptional properties to the carbonyl compounds. Two distinct situations are of interest, that is,

1. α,β-Unsaturated aldehydes and ketones
2. Cumulated double bond (Ketenes)

   α,β-unsaturated aldehydes or ketones are generally obtained by dehydration of aldol addition products.



2-Butenal
(Crotonaldehyde)



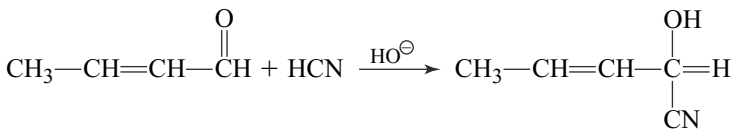
4-Methylpent-3-en-2-one
(Mesityl oxide)

This class of compounds may undergo usual addition and condensation reactions given by carbonyl compounds, such as:

1. Addition of HCN to form cyanohydrine.
2. Condensation with NH_3 derivatives.
3. Addition of Grignard reagents.

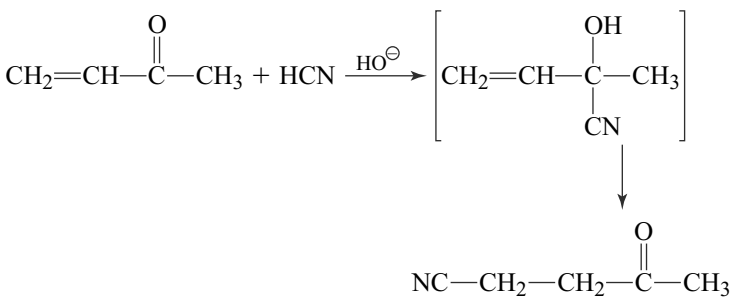
But 1,2- or 1,4-addition may also take place. It is highly affected by steric hindrance, example

(a)

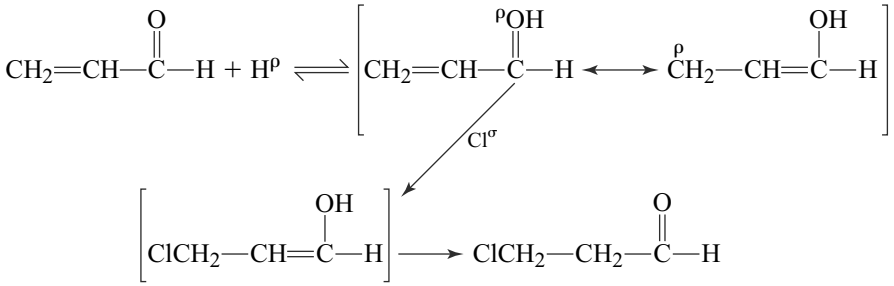


(1,2-Addition)

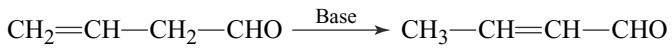
But with a ketone, 1,4-addition product is formed. It proceeds to give an enol intermediate, which is unstable with respect to the β-cyano ketone.



(b) Addition of HX to α,β-unsaturated aldehydes and ketones occurs at 1,4-and halogen goes to β-carbon atom. The 1,2- addition product is unstable. For example, addition of HCl to acrolein proceeds as

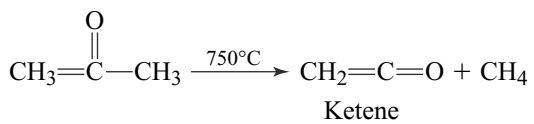


β,γ-unsaturated aldehydes and ketones are difficult to prepare. They rearrange readily to the α,β-isomers, especially in the presence of a base.



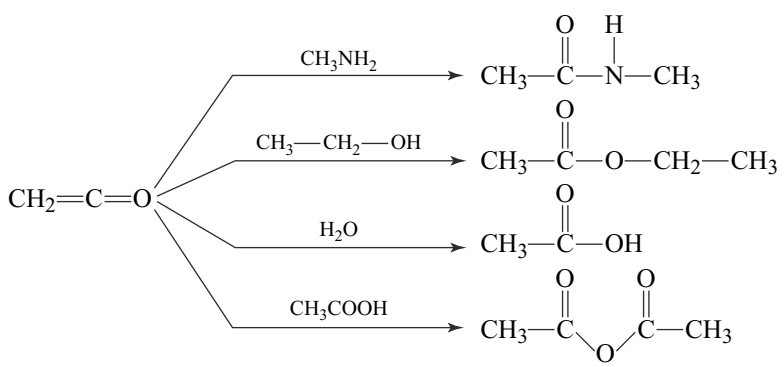
KETENES

Chemical substances with cumulated carbonyl and C=C (that is >C=C=O) are called ketenes. It may be prepared in the laboratory by pyrolysis of acetone.

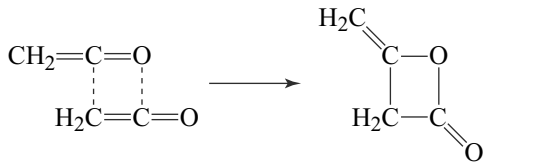


Ketene

Ketene is a very useful acetylating agent for RNH_2 and R–OH. It gives many addition reactions (thus, there is no problem of product separation).



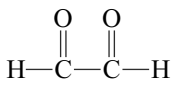
Ketene readily dimerizes to give diketene, a β-lactone.



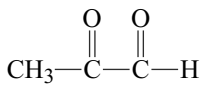
Diketene
(Vinylaceto-β-lactone)

DICARBONYL COMPOUND

1,2-Dialdehydes: The structures of some common and important members of this class are given below:



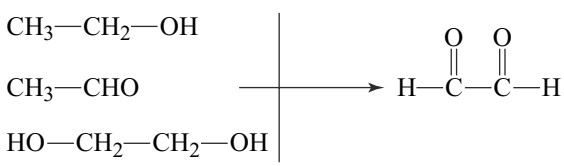
Glyoxal
(Ethandial)



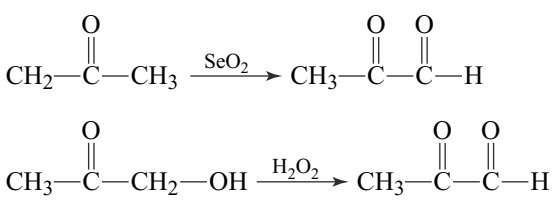
Methyl glyoxal or pyruvaldehyde
(Propandial)

Most of these compounds are yellow in colour. Glyoxal is unusual as it is yellow in liquid but green in vapour state.

Glyoxal may be obtained by the oxidation of ethanol, acetaldehyde or glycol with HNO_3.

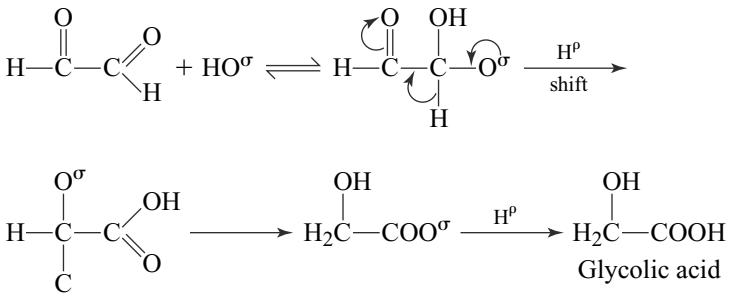


Pyruvaldehyde may be prepared by the oxidation of acetone with SeO_2 or hydroxy acetone with H_2O_2.



Glyoxal (or methyl glyoxal) undergoes usual reactions of a dialdehyde.

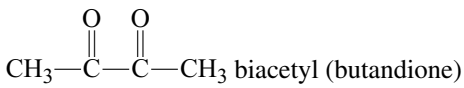
1. It adds HCN, $NaHSO_3$.
2. It condenses with H_2N–OH.
3. It reduces ammoniacal silver nitrate (that is gives silver mirror test).
4. It does not reduce Fehling's solution.
5. As glyoxal has no α-H atom, it undergoes internal Cannizzaro reaction (see Chapter 6, *Name Reactions*) to give glycolic acid.



DIKETONES

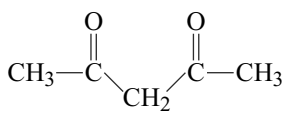
They are classified according to the positions of the two carbonyl groups, such as

1. 1,2-(or α-) diketones



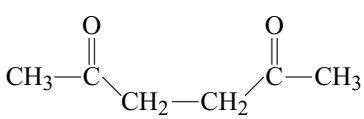
biacetyl (butandione)

2. 1,3-(or β-) diketones



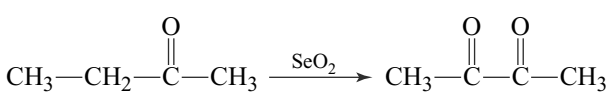
Acetyl acetone (2,4-pentanedione)

3. 1,4– (or γ-) diketones

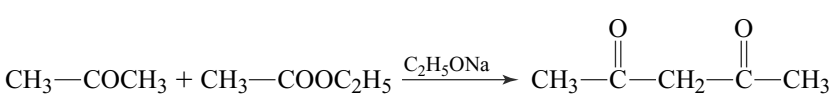


Acetonyl acetone (hexane-2,5-dione)

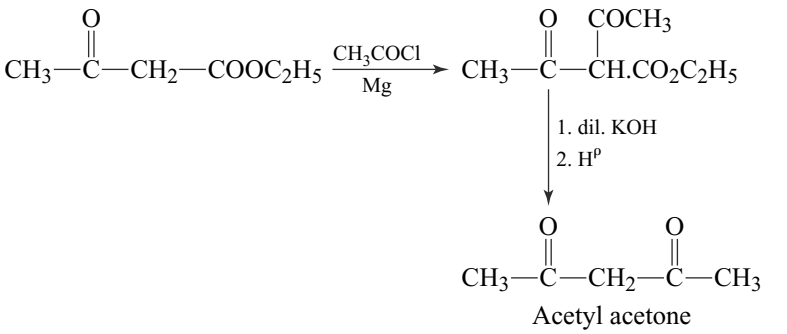
Biacetyl may be obtained by oxidation of 2-butanone by SeO_2.

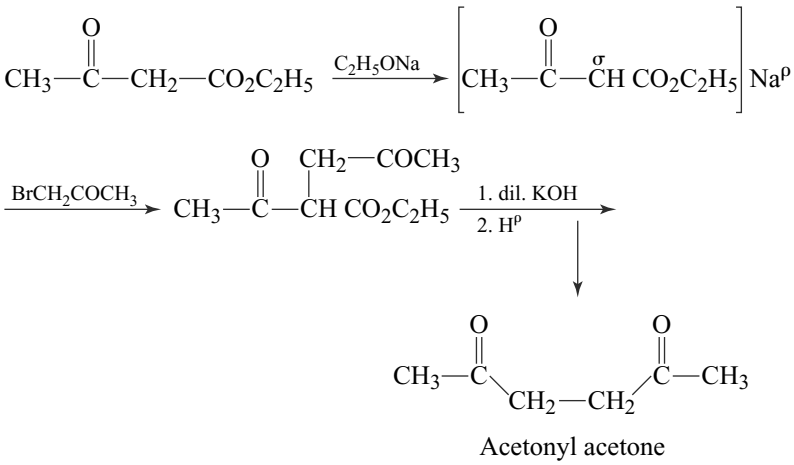


Acetylacetone is prepared by Claisen condensation between acetone and ethyl acetate.

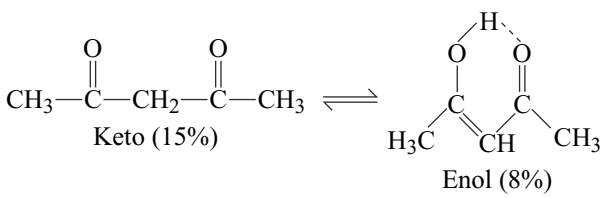


Both acetylacetone and acetonylacetone can be prepared by acetoacetic ester synthesis.



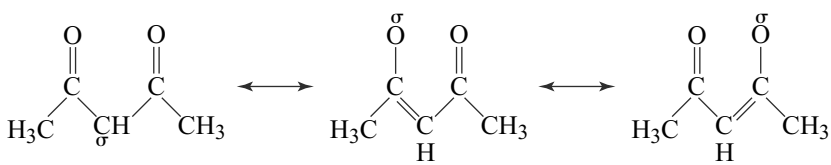


Acetylacetone is unusual (among diketones), as it exists mostly in enol form (see keto–enol tautomerism, Chapter 2 for details) due to intramolecular H-bonding.



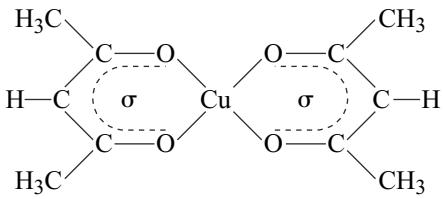
Acetylacetone is moderately acidic ($K_a \sim 10^{-9}$).

The charge delocalization in the anion is responsible for its acidic nature.



The alkali metal salts of acetyl acetone can be alkylated using alkyl halides (R–X) of good SN^2 reactivity. Generally, C-alkylation takes place. This type of alkylation is very important in synthetic reactions of ethyl acetoacetate.

Many polyvalent metal ions (Be^{2+}, Cu^{2+}, Cr^{3+} and Fe^{3+}.) form chelates with enol of acetylacetone, example



Dark blue
[Diacetyl acetonato copper (II)]

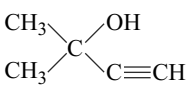
PROBLEMS

Objective-Type Questions

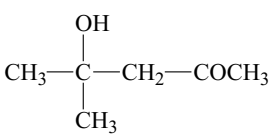
1. Suggest what compound the letter A stands for in the following reaction?

$$MeCOMe + CH{\equiv}CH \xrightarrow[(ii)\ H_2O]{(i)\ NaNH_2} A$$

(a) $HC{\equiv}C{-}C{\equiv}C{-}H$

(b) 

(c) $HC{\equiv}C{-}CH_3$

(d) 

2. What is A in the following reaction?

$$C_6H_5{-}COCH_3 \xrightarrow{A} C_6H_5{-}\overset{\overset{O}{\|}}{C}{-}CHO$$

(a) H_2SO_4 (b) Zn–Hg/HCl
(c) SeO_2 (d) S/KOH

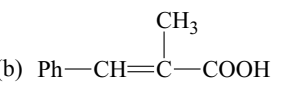
3. Tollen's reagents is reduced by

(a) HCOOH (b) $CH_2ClCOOH$
(c) CH_3COOH (d) CCl_3COOH

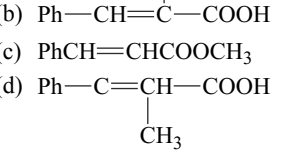
4. The product A of the reaction

$$PhCHO \xrightarrow[(CH_3CO)_2O]{CH_3COONa} A \text{ is}$$

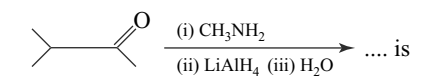
(a) $PhCH{=}CHCOOH$

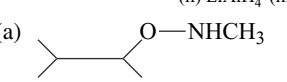
(b) 

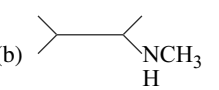
(c) $PhCH{=}CHCOOCH_3$

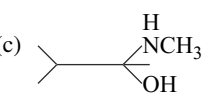
(d) 

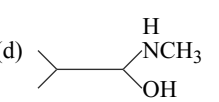
5. The major organic product formed from the following reaction



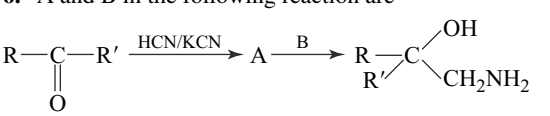
(a) 

(b) 

(c) 

(d) 

6. A and B in the following reaction are



(a) A = $RR'C(OH)COOH$, B = NH_3

(b) A = RR′C(CN)(OH), B = $H_3O^{\oplus}$

(c) A = RR′CH_2CN, B = NaOH

(d) A = RR′C(CN)(OH), B = $LiAlH_4$

7. Nucleophilic addition reaction will be most favoured in

(a) $(CH_3)_2C{=}O$

(b) CH_3CH_2CHO

(c) CH_3CHO

(d) $CH_3{-}CH_2{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}CH_3$

8. The best reagent to convert pent-3-en-2-ol into pent-3-en-2-one is

(a) acidic permanganate

(b) acidic dichromate

(c) chromic anhydride in glacial acetic acid

(d) pyridinium chloro-chromate

9. Reaction of cyclohexanone with dimethylamine in the presence of catalytic amount of an acid forms a compound if water during the reaction is continuously removed. The compound formed is generally known as

(a) a Schiff's base (b) an enamine

(c) an imine (d) an amine

10. The pair of compounds in which both the compounds give positive test with Tollen's reagent is

(a) glucose and sucrose

(b) fructose and sucrose

(c) acetophenone and hexanal

(d) glucose and fructose

11. Which one of the following can be oxidized to the corresponding carbonyl compound?

(a) Propan–2-ol (b) *Ortho*-nitrophenol

(c) Phenol (d) 2-Methyl-propan-2-ol

12. When acetaldehyde is heated with Fehling's solution, it gives a precipitate of

(a) Cu (b) CuO

(c) Cu_2O (d) Cu + Cu_2O + CuO

13. The reaction $CH_3COCH_3 \xrightarrow[Zn(Hg),\ conc.\ HCl]{[H]} CH_3CH_2CH_3$ is known as

(a) Wolff–Kishner reduction

(b) Clemmensen reduction

(c) Cannizzaro reaction

(d) Rosenmund reduction

14. The reduction reaction:

$$R{-}\overset{\overset{O}{\|}}{C}{-}O{-}R' \xrightarrow[KOH]{Hydrazine} RCH_2R'$$

is known as

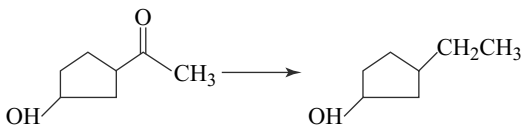
(a) Clemmensen reduction

(b) Wolff–Kishner reduction

(c) Rosenmund reduction

(d) Catalytic reduction

15. The appropriate reagent for the following transformation



is

(a) Zn(Hg), HCl (b) $NH_2{-}NH_2$, OH^-

(c) H_2/Ni (d) $NaBH_4$

16. In which of the following reactions, the oxidized and the reduced forms of the same compound are obtained?

(a) Aldol condensation

(b) Reimer–Tiemann reaction

(c) Perkin reaction

(d) Cannizzaro reaction

17. $CH_3{-}CH_2{-}CN \xrightarrow{X} CH_3{-}CH_2{-}CHO.$

The reagent combination X is

(a) $LiAlH_4$/ether (b) $SnCl_2/HCl/H_3O^+$/

(c) $H_2/Pd/BaSO_4$ (d) $NaBH_4$/ether/H_3O^+

18. $R{-}CH{=}CH{-}CH_2{-}CN \xrightarrow{M} R{-}CH{=}CH{-}CH_2{-}CHO.$

The reagent combination M is

(a) Pd/H_2, $BaSO_4$ (b) $C_5H_5N.CrO_3.HCl$

(c) $AlH(iso\text{-}Bu)_2/H_3O^+$ (d) $LiAlH_4/H_3O^+$

19. Which of the following can distinguish benzaldehyde from ethanol?

(a) $AgNO_3.NH_4OH$

(b) $NaHSO_3$

(c) 2,4-DNP

(d) $CuSO_4$ + Na.K tartarate + NaOH

20. Aldol condensation followed by dehydration on a mixture of carbonyl compound gives methyl vinyl ketone. The mixture of compound is

(a) HCHO + CH_3–CHO

(b) CH_3–COCH3 + CH_3COCH_3

(c) HCHO + CH_3COCH_3

(d) CH_3–CHO + CH_3–CHO

21. Crotonaldehyde ($CH_3{-}CH{=}CH{-}CHO$) can be oxidized easily to crotonic acid by

(a) acidic $K_2Cr_2O_7$ (b) alkaline $KMnO_4$

(c) dil. HNO_3 (d) $AgNO_3/NH_4OH$

22. An organic compound C_3H_6O does not give a precipitate with 2,4-DNP reagent and also does not react with metallic sodium. It could be

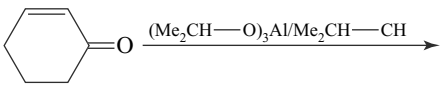
(a) $CH_2{=}CH{-}CH_2{-}OH$

(b) CH_3COCH_3

(c) $CH_2{=}CH{-}O{-}CH_3$
(d) $CH_3{-}CH_2{-}CHO$

23. $CH_3{-}COOH \xrightarrow{CaCO_3} A \xrightarrow{\Delta} B \xrightarrow{H_2N{-}OH} C.$
The end product C is
(a) formaldehyde oxime
(b) methyl nitrate
(c) acetoxime
(d) acetaldehyde oxime

24. Iodoform test is not given by
(a) ethanal (b) ethanol
(c) 3-pentanone (d) 2-pentanone

25.  $\xrightarrow{(Me_2CH{-}O)_3Al/Me_2CH{-}CH}$ X.
The product X is
(a) cyclohexanol (b) cyclohex-2-enol
(c) cyclohexanone (d) cyclohexene

26. The enol form of acetone, after treatment with D_2O gives:
(a) $CH_3{-}\overset{\overset{OD}{|}}{C}{=}CH_2$ (b) $CH_3{=}\overset{\overset{OH}{|}}{C}{-}CH_2D$
(c) $CD_2{=}\overset{\overset{OD}{|}}{C}{-}CD_3$ (d) $CD_3{-}\overset{\overset{O}{\|}}{C}{-}CD_3$

27. During reduction of an aldehyde with hydrazine and KOH, the first is the formation of
(a) R–CO–NH_2 (b) R–CN
(c) R–CH=N–NH_2 (d) R–CH=NH

28. The reagent that can be used for the separation of acetaldehyde and acetophenone is
(a) C_6H_5–$NHNH_2$ (b) $NaOH/I_2$
(c) $NaHSO_3$ (d) H_2N–OH

29. $\begin{matrix}R\\R'\end{\!\!\diagup}C{=}O + H_2N{-}OH \longrightarrow A \xrightarrow{PCl_5} B$
(a) $\begin{matrix}R\\R'\end{\!\!\diagup}C{=}N{-}OH,\ RNH_2$
(b) $R{-}NHCOR',\ \begin{matrix}R\\R'\end{\!\!\diagup}C{=}N{-}OH$
(c) $\begin{matrix}R\\R'\end{\!\!\diagup}C{=}N{-}OH,\ RNHCOR'$
(d) $\begin{matrix}R\\R'\end{\!\!\diagup}C{=}N{-}OH,\ \begin{matrix}R\\R'\end{\!\!\diagup}C{=}NH$

30. Acetone on distillation with conc. H_2SO_4 gives
(a) acrolein (b) phorone
(c) mesityl oxide (d) mesitylene

31. $CH_3{-}CH_2{-}COOH \xrightarrow{RedP/Br_2} X \xrightarrow{NH_3\,(alc.)} Y.$
Y in the above reaction is
(a) ethylamine (b) lactic acid
(c) alanine (d) propylamine

32. When a mixture of calcium acetate and calcium benzoate is dry distilled, the product thus obtained is
(a) benzaldehyde (b) benzophenone
(c) acetophenone (d) acetaldehyde

33. $C_6H_5{-}CO.CH_3 \xrightarrow{X} C_6H_5{-}CO.CHO.$
The reagent X in the above reaction is
(a) HNO_3 (b) H_2SO_4
(c) SeO_2 (d) H_2O_2

34. The product A in the following reaction is
$CH_3{-}CH_2{-}CH_2{-}Br \xrightarrow[(ii)\ Bu{-}Li]{(i)\ PPh_3} R \xrightarrow{CH_3{-}CO{-}CH_3} A$
(a) $CH_3{-}\overset{\overset{O}{\|}}{C}{-}CH_2{-}CH_2{-}CH{=}CH_2$
(b) $\begin{matrix}CH_3\\CH_3\end{\!\!\diagup}CH{-}CH{=}CH{-}CH_3$
(c) $\begin{matrix}CH_3\\CH_3\end{\!\!\diagup}C{=}CH{-}CH_2{-}CH_3$
(d) $\begin{matrix}CH_3\\CH_3\end{\!\!\diagup}CH{-}CH_2{-}CH_2{-}CH_3$

[Hint: Wittig reaction]

35. Which of the following is correct?
(a) Reaction of vegetable oil with H_2SO_4 gives glycerine.
(b) Reduction of any aldehyde gives 2° alcohol.
(c) Alcoholic iodine with NaOH gives iodoform.
(d) Sucrose on reaction with NaCl gives invert sugar.

36. Which of the following is expected to give both iodoform test and Fehling's test?
(a) Ethanol (b) Propanone
(c) Propanal (d) Ethanal

37. $R{-}C{\equiv}C{-}R \xrightarrow[(ii)\ Zn/H_2O]{(i)\ X} CH_3{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{O}{\|}}{C}{-}CH_3.$
What is X?
(a) HNO_3 (b) HNO_2
(c) $KMnO_4$ (d) O_3

38. Formaldehyde reacts with NH_3 to form
(a) hexamethylene triamine
(b) tetramethylene tetramine
(c) hexamethylene tetramine
(d) tetramethylene hexamine

39. $CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{X} CH_3-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-H.$

The reagent X is

(a) H_2O_2 (b) HNO_3

(c) $KMnO_4$ (d) SeO_2

40. $CH_3-CHO \xrightarrow{Ba(OH)_2} A \xrightarrow{H_3O^+/\Delta} B.$

The product B is

(a) crotonic acid (b) crotonaldehyde

(c) acrylic acid (d) acrolein

41. $CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[\text{Distill}]{\text{conc. } H_2SO_4}$ M. The product M is

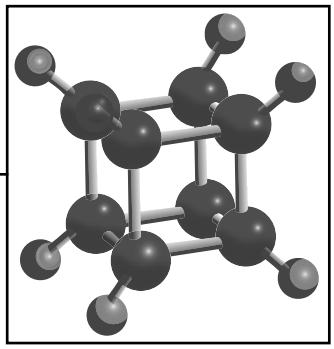
(a) mesityl oxide (b) styrene

(c) mesitylene (d) cumene

Answers

1. (b)	2. (c)	3. (a)	4. (a)	5. (b)
6. (d)	7. (c)	8. (c)	9. (b)	10. (d)
11. (a)	12. (c)	13. (b)	14. (b)	15. (b)
16. (d)	17. (b)	18. (c)	19. (d)	20. (c)
21. (d)	22. (c)	23. (c)	24. (c)	25. (b)
26. (d)	27. (c)	28. (c)	29. (c)	30. (d)
31. (c)	32. (c)	33. (b)	34. (c)	35. (c)
36. (d)	37. (d)	38. (c)	39. (d)	40. (b)
41. (c)				

CHAPTER 15

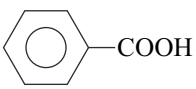


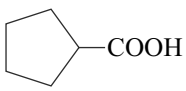
Carboxylic Acids and Derivatives

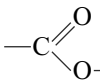
Carboxylic acids contain carboxyl group They may be represented as RCOOH, where R = alkyl, alkenyl, alkynyl, aryl, cycloalkyl, etc. For example,

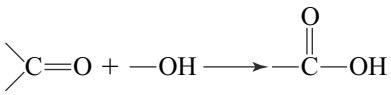
HCOOH Formic Acid (Methanoic acid)	CH_3COOH Acetic Acid (Ethanoic acid)	$CH_2{\equiv}CH{-}COOH$ Acrylic acid (Prop-2-enoic acid)

$HC{\equiv}C{-}COOH$
Propiolic acid
(Propynoic acid)


Benzoic acid

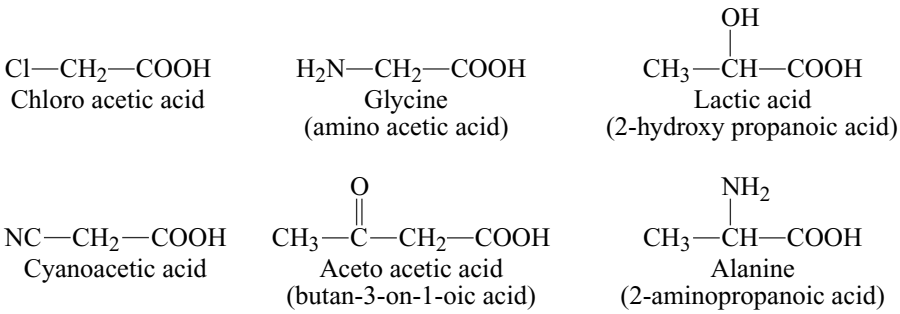

Cyclopentane carboxylic acid

The carboxyl group,  is a combination of carbonyl and hydroxyl groups.

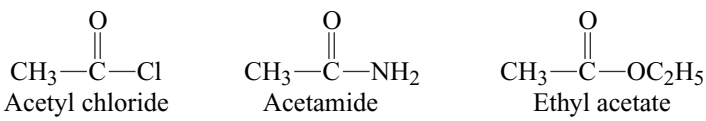


But the combination is so strong that neither group behaves independently. Therefore, the properties of –COOH group are almost the same whether alkyl or alkenyl or aromatic hydrocarbon unit is attached to it.

Acids containing substituents at alkyl group are known as substituted acids. For example,



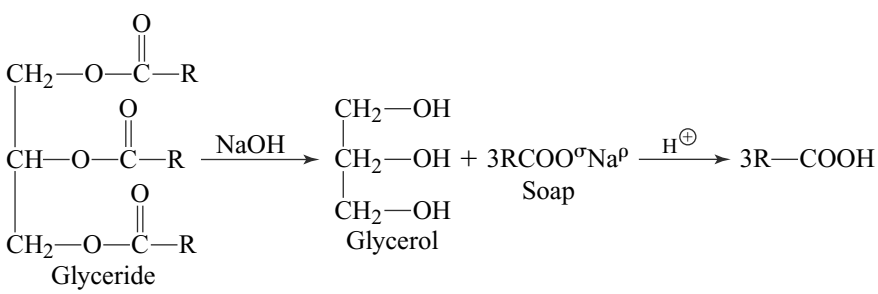
The functional derivatives of carboxylic acids are of the type $R—\overset{O}{\overset{\|}{C}}—X$, where $X{=}Cl, —NH_2, —OR$, etc. They are discussed ahead in this chapter.



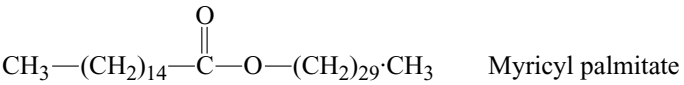
Carboxylic acids (RCOOH) with R (C_{11}–C_{17}) as an alkyl or alkenyl group are also called fatty acids. They are constituents of the fats, waxes and oils of plants and animals. The most abundant fatty acids are palmitic, stearic, oleic and linoleic acids. They occur as ester of the trihydroxy alcohol and glycerol, known as glycerides.

$CH_3(CH_2)_{14}—COOH$	Palmitic acid
$CH_3(CH_2)_{16}—COOH$	Stearic acid
$CH_3(CH_2)_7—CH{=}CH(CH_2)_7COOH$	Oleic acid
$CH_3(CH_2)_4CH{=}CH{\cdot}CH_2{\cdot}CH(CH_2)_7COOH$	Linoleic acid

Alkaline hydrolysis of fats gives salts of fatty acids. The alkali metal salts are used as soaps.



Now, it has been established that much use of saturated fats (butter, ghee, dalda, etc.) in diet may cause coronary thrombosis and paralytic strokes. It is for this reason that oils like sunflower oil and corn oil are now used as cooking media. The honeycomb of the bee is myricyl palmitate.



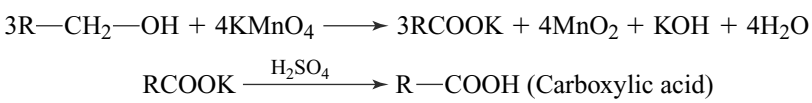
Myricyl palmitate

PREPARATION OF CARBOXYLIC ACIDS

Oxidation of primary alcohols or aldehydes

Primary alcohols are readily oxidized to carboxylic acids. The common oxidizing agents are:

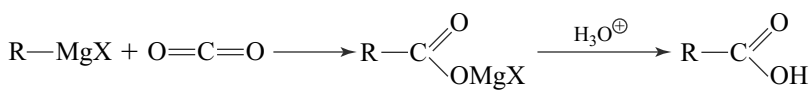
(a) $KMnO_4$ aqueous or alkaline
(b) $K_2Cr_2O_7$ and H_2SO_4
(c) CrO_3 and H_2SO_4



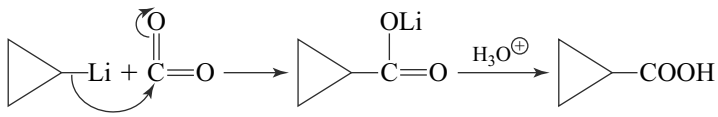
Mild oxidizing agents, such as Tollen's reagent, oxidize an aldehyde to acid.

From Grignard reagents

Carbonation of Grignard reagent (with CO_2) gives salt of carboxylic acid. The free acid is obtained by acidification.

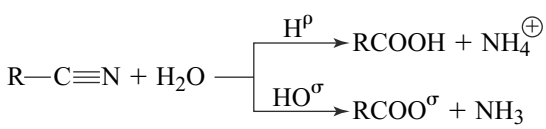


It is a useful method of increasing chain length by one carbon atom.
Organolithium compounds are carbonated in the same way.



Hydrolysis of nitriles (or cyanides)

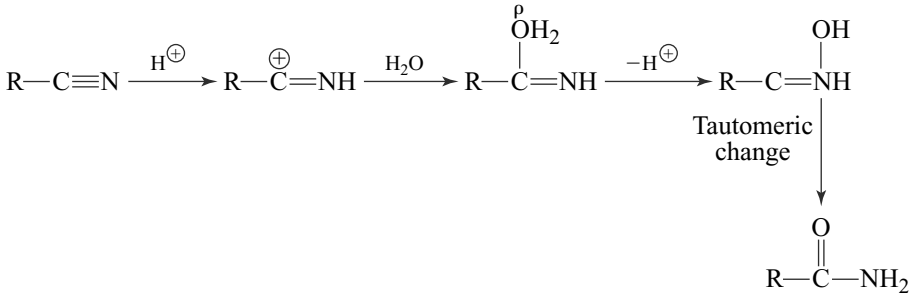
Alkly nitriles (or aryl nitriles) are hydrolyzed to the acid by boiling with aqueous acid or alkali.



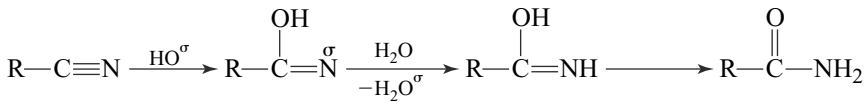
Amides are formed first in both the cases which are further oxidized to the carboxylic acids.

Nitrite to amide

1. Acid hydrolysis

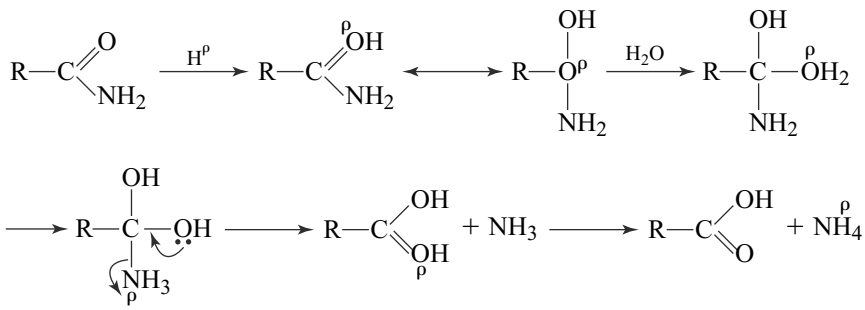


2. Alkaline hydrolysis

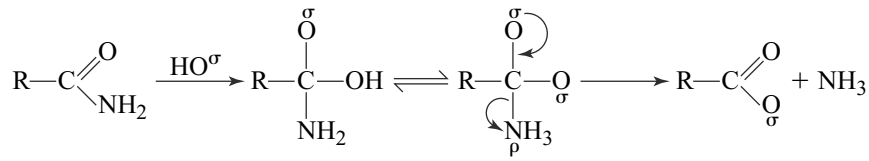


Hydrolysis of amide to acid

1. Acid catalysed

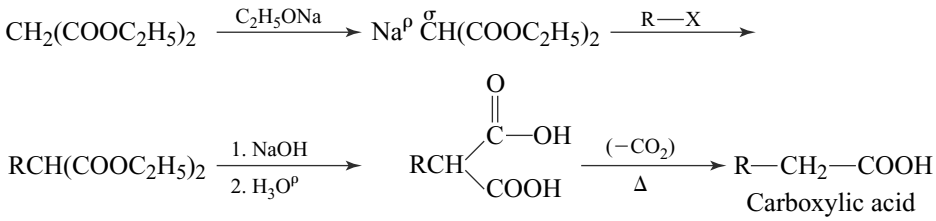


2. Base catalysed



Malonic ester synthesis

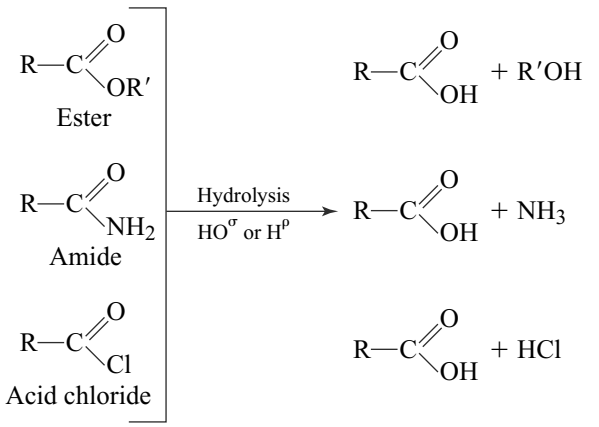
Malonic ester, $CH_2(COOC_2H_5)_2$, has active methylene group ($>CH_2$, active in the sense that H atoms are acidic due to the presence of two strongly electron attracting groups, >C=O). The H atoms of CH_2 group are easily substituted by alkyl groups. The alkyl substituted ester on hydrolysis and heating decarboxylates to give a carboxylic acid. (concept: β-keto acids undergo easy decarboxylation).



This is a useful method of extending a chain by two carbon atoms.

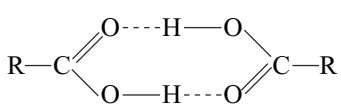
Hydrolysis of ester, amides and acid chlorides to carboxylic acids

Ester, amides and acid chlorides are hydrolyzed to give carboxylic acids but these compounds are generally prepared from carboxylic acids.



PHYSICAL PROPERTIES

The carboxyl group (–COOH) has highly polar ($\overset{\delta+}{O}—\overset{\delta-}{H}$) bond and electron rich oxygen of carbonyl group ($>\overset{\delta+}{O}=\overset{\delta-}{H}$). This bonding situation permits considerable degree of H-bonding. It greatly affects physical properties of carboxylic acids. Indeed, carboxylic acids in the liquid and solid states exist mostly as cyclic dimers due to H-bonding.



These dimeric structures persist in solution in hydrocarbon solvents and to some extent even in the vapour state.

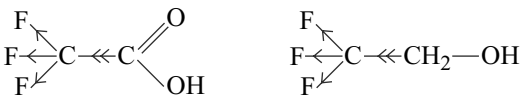
Boiling points and melting points of carboxylic acids

Carboxylic acids have high MP and BP relative to alcohols and alkyl chlorides of comparable weight. It is because of the strength and degree of H-bonding in acids.

Table 15.1

Compounds		Molecular wt.	bp(°C)
Acetic acid	CH_3COOH	60	118
Propanol	$CH_3–CH_2–CH_2–OH$	60	97
Ethyl chloride	$CH_3–CH_2–Cl$	64	13

However, the presence of electron-withdrawing group (especially F or CF_3) near O atom (of –COOH or –OH) shortens oxygen lone pair orbital, thereby decreasing its donor ability. Thus, the degree of self-association through H-bonding decreases that also causes decrease in the BP.



The following order is found.

$$\text{BP}\begin{cases} CH_3COOH > FCH_2COOH > CF_3COOH \\ CH_3—OH > CF_3CH_2—OH > (CF_3)_2CHOH > (CF_3)_3C—OH \end{cases}$$

Water solubility

The high water solubility of lower members (C_1–C_4) is due to H-bonding. Formic, acetic, propanoic and butanoic acids are completely miscible with water in all proportions. As the alkyl chain length increases, the solubility decreases markedly.

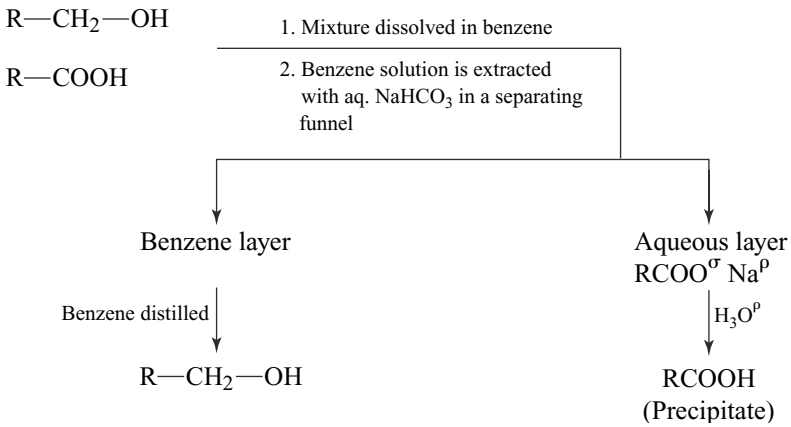
Table 15.2

Acid	Formula	Solubility g/100 g water at 25°C
Formic acid	H–COOH	Miscible in all proportions
Acetic acid	$CH_3–COOH$	
Propanoic acid	$CH_3–CH_2–COOH$	
Butanoic acid	$CH_3(CH_2)_2COOH$	
Pentanoic acid	$CH_3(CH_2)_3COOH$	3.7
Hexanoic acid	$CH_3(CH_2)_4COOH$	1.0
Palmitic acid	$CH_3(CH_2)_{14}COOH$	Insoluble

However, the salts of carboxylic acids (alkali metal salts) are soluble in water, even when the alkyl group becomes large (it may be used for extraction of carboxylic acids by aqueous base). Sodium hydrogen carbonate is good enough to convert any carboxylic acid to its anion.

$$RCOOH + NaHCO_3 \longrightarrow RCOO^{\sigma} + Na^{\rho} + CO_2 + H_2O$$

Separation of an alcohol from an acid may be carried out as



Odour (Smell)

Carboxylic acids have characteristic odours. Formic, acetic and propanoic acids have sharp odours, while those of butanoic to octanoic (C_4–C_8) acids have bad odours. These acids can be detected in minute amounts, especially by dogs (a dog can detect butanoic acid at a concentration of 10^{-17} mole per litre of air). Each person's metabolism produces characteristic blend of compounds (carboxylic acids also). It differs from person to person (even for identical twins). It is used by a sniffer dog to find a culprit by smell. (Sniffer dogs can trace drugs and explosives also.)

DISSOCIATION OF CARBOXYLIC ACIDS

It is discussed in detail in Chapter 4, *Acids and Bases*.

REACTIONS OF CARBOXYLIC ACIDS

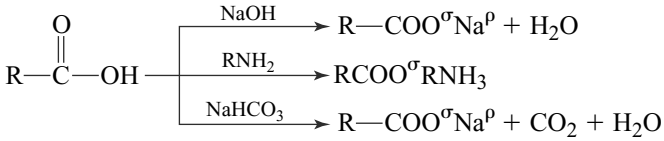
Carboxylic acids undergo several types of reactions:

1. Salt formation
2. Decarboxylation
3. Reduction
4. Reactions at the 2-position (or α-carbon atom).
5. Formation of acid derivatives.

Salt formation

Carboxylic acids are weaker acids (Ka ~10^{-4}) than common mineral acids such as HCl and H_2SO_4. But they are acidic enough to react with inorganic (NaOH) or organic (RNH_2, etc.) bases to form salt. With sodium hydrogen carbonate ($NaHCO_3$), carboxylic acids form sodium salt with the evolution of CO_2. This reaction

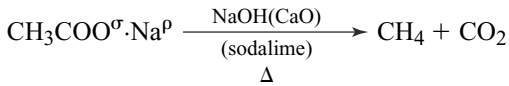
is widely used to test carboxylic acids. (Alcohols and phenols do not evolve CO_2 with $NaHCO_3$, a distinction from carboxylic acids.)



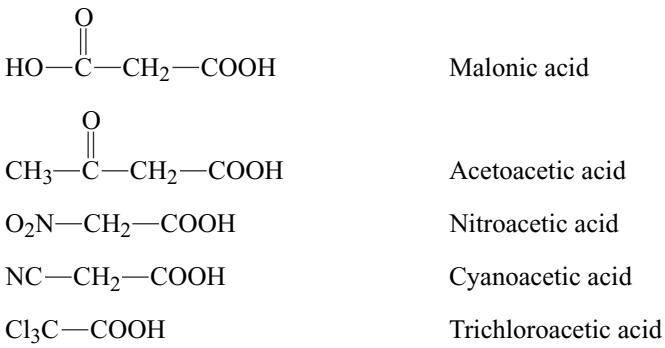
Decarboxylation

Loss of CO_2 from the carboxyl group (or $-COO^{\sigma}$) is termed as decarboxylation ('de' means removal). The ease of reaction varies with the nature of the acid as shown below.

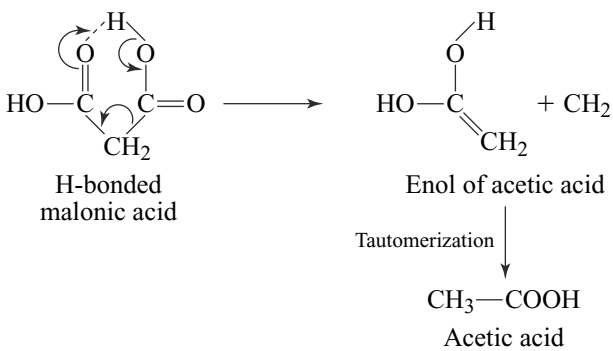
1. The reaction is believed to involve a carbanion intermediate.



2. Many acids lose CO_2 simply by heating (100–150°C). It most readily takes place when the α-carbon (or 2-carbon) carries a strongly electron-attracting group (i.e. –I substituent). For example,

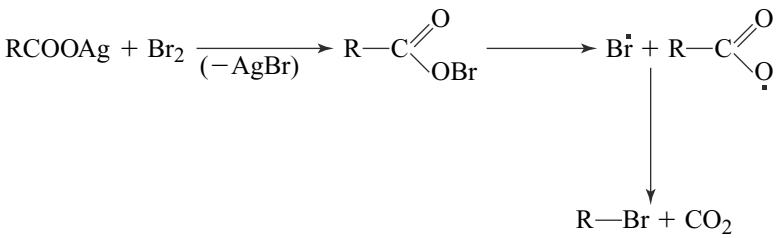


The decarboxylation of β-keto acids is very easy in which H-bonding plays an important role.



3. Kolbe electrolysis
   This reaction gives alkanes. For details, see Chapter 9, *Alkanes*.

4. Hunsdiecker reaction
   An alkyl bromide is formed when the silver salt of a carboxylic acid is treated with Br_2. This reaction is believed to involve free radicals.

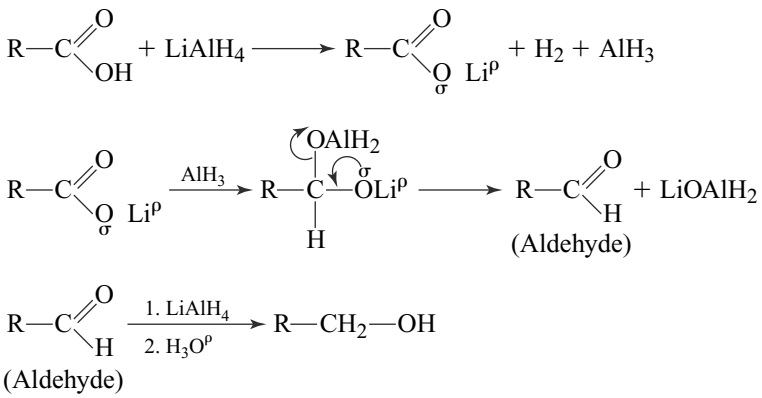


These reactions may be used to remove a carbon from the end of a chain keeping other functional groups intact.

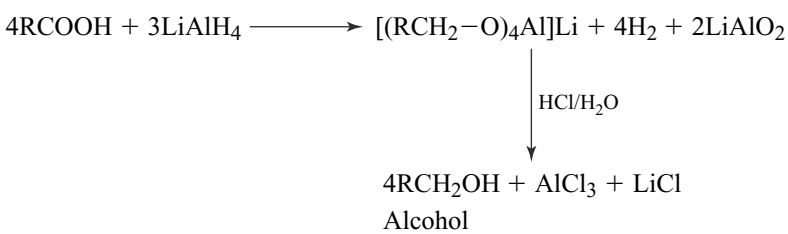
Reduction

It is difficult to reduce carboxylic acids (using catalytic hydrogenation or Na/C_2H_5–OH.

However, $LiAlH_4$ reduces carboxylic acids smoothly to primary alcohols. The reaction proceeds as given below.



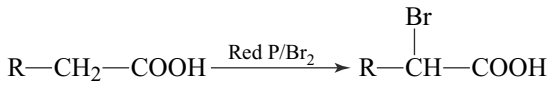
(See Chapter 14 for reduction of aldehyde by $LiAlH_4$.)
The overall reaction can be written as under.



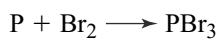
Reactions at the α- (or 2–) position of carboxylic acids

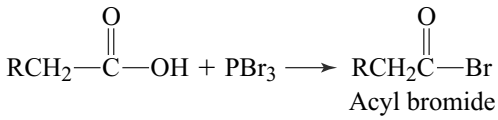
Halogenation

Bromine reacts smoothly with carboxylic acids in the presence of small amount of red phosphorous to form 2-bromo acids. This reaction is known as *Hell–Volhard–Zelinsky reaction (HVZ reaction)*.

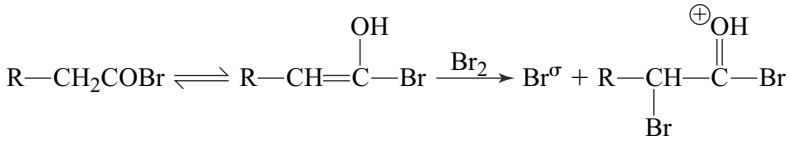


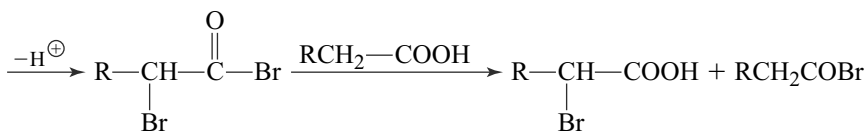
Red P has catalytic effect in this reaction. It is believed that phosphorous first forms PBr_3, which reacts with acid, to give the acid halide —C(=O)Br. This acid halide undergoes substitution at the 2-position.





Acyl bromide

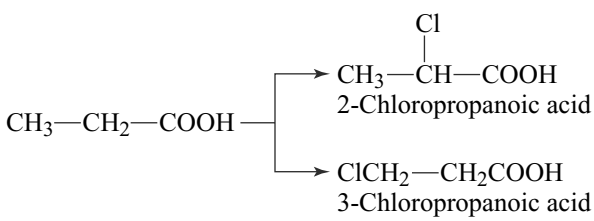




Substitution occurs exclusively at the α-position. Therefore, this reaction is limited to carboxylic acids having α-H atoms.

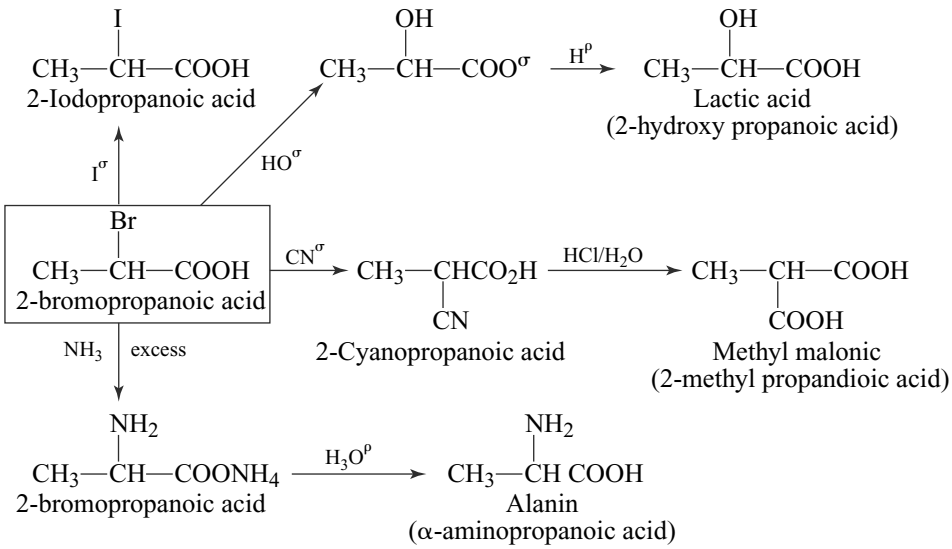
Important points

1. The reaction with Br_2 is specific and α-bromo acid is only obtained.
2. The reaction with Cl_2/P is not overall specific. With chlorine, other position may also be substituted (a radical chlorination).



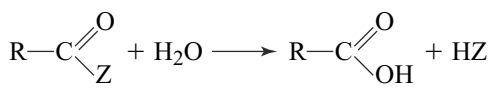
Substitution reaction of 2-halo acids

HVZ reaction is of great synthetic use. It is because of the halogen of a 2-halo acid that is activated by the electron-attracting $-\overset{\overset{O}{\|}}{C}-OH$ group at its adjacent and is readily replaced by nucleophiles like HO^{ρ}, NH_3, CN^{σ} and I^{σ}. The reaction is S_N2 type. It gives variety of substituted acids.

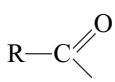


Functional derivatives of carboxylic acid

A functional derivative of a carboxylic acid is a compound, formed by the replacement of –OH of the acid by another group Z (Z = Cl, $-NH_2$, OR, –OOCR). They are hydrolyzed back to the parent acid. Thus, an acid chloride, RCOCl and not a ketone, $RCOCH_3$ is a functional derivative.

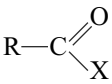
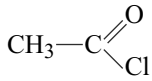
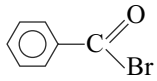
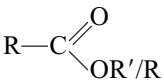
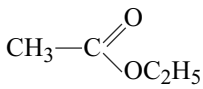
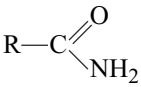
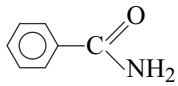
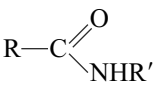
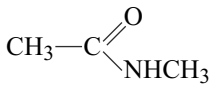
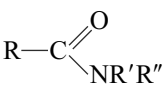
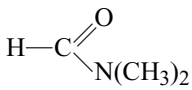
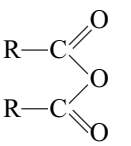
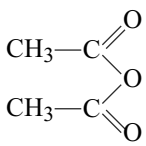
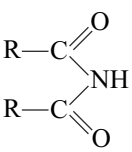
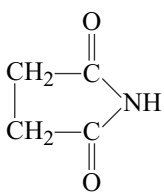
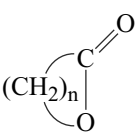
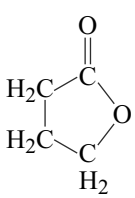


All of the derivatives contain the acyl group.



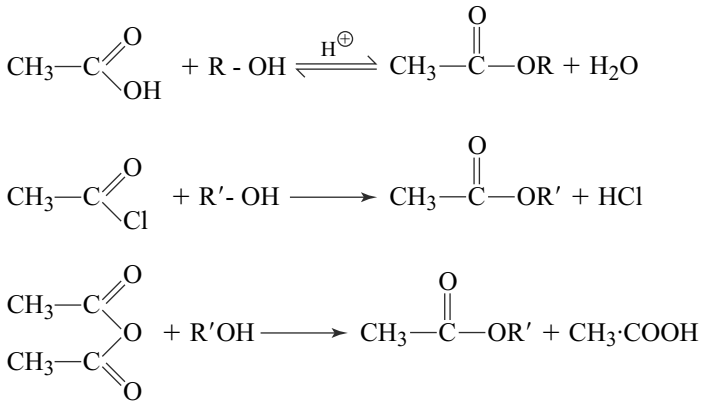
When R is $-CH_3$, the group, $CH_3-\overset{\overset{O}{\|}}{C}$ is called acetyl group.

Table 15.3 Functional derivatives of carboxylic acids

Derivatives	Structure	Examples	
		Structure	Name
Acid halides (acyl halides)	 X = F, Cl, Br, I		Acetyl chloride
			Benzoyl bromide
Ester			Ethyl acetate
Amides (primary)			Benzamide
Amides (secondary)			N-methyl acetamide
Amides (tertiary)			N,N-dimethylformamide
Acid anhydrides			Acetic anhydride
Imides			Succinimide
Lactones (cyclic esters)	 Most stable with $n = 3, 4$		γ-Bbutyro lactone

Formation of acid derivatives

1. **Esters**
   Esters are formed by the reaction of alcohols with carboxylic acids or acid chlorides or acid anhydride.



(For details and mechanism see Chapter 5, *Reaction Mechanism*.)

2. Isomers

Esters show isomerism which result from differences in the alkyl groups. In addition to that, every ester is isomeric with at least one acid. For example, isomers of $C_3H_6O_2$ include the following:

a.	$CH_3—COOCH_3$	methyl acetate	} esters
b.	$H—COOC_2H_5$	ethyl formate	} esters
c.	$CH_3—CH_2—COOH$	propanoic acid	

The isomers are easily tested.

(i) The isomer (c) will liberate CO_2 from $NaHCO_3$

$$CH_3.CH_2.COOH + NaHCO_3 \longrightarrow CH_3.CH_2.COONa + CO_2 + H_2O$$

(ii) The isomers (a) and (b) are distinguished by testing their hydrolysis products.

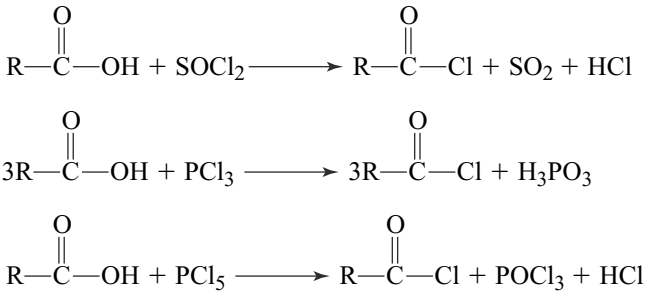
$$\text{a}\quad CH_3—COOCH_3 \xrightarrow[\text{Hydrolysis}]{\text{NaOH}} CH_3—COONa + CH_3{\cdot}OH$$

$$\text{b}\quad H—COOC_2H_5 \xrightarrow[\text{Hydrolysis}]{\text{NaOH}} H—COONa + C_2H_5OH$$

Ethanol forms yellow ppt. of CHI_3 (with $NaOH + I_2$) and HCOONa has reducing properties (forms silver mirror).

3. Acid chlorides

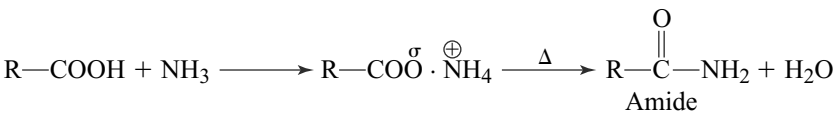
An acid chloride is prepared by replacement of –OH by –Cl. Reagents generally used are $SOCl_2$, PCl_3 and PCl_5.



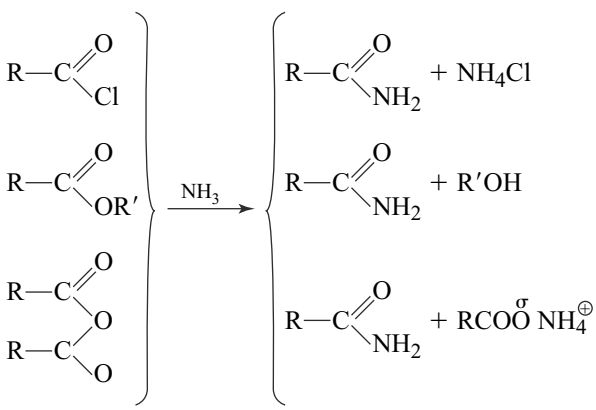
Thionyl chloride ($SOCl_2$) is a better reagent as other products are gaseous (SO_2 and HCl) and leaves no problem of separation of the product.

4. Amides

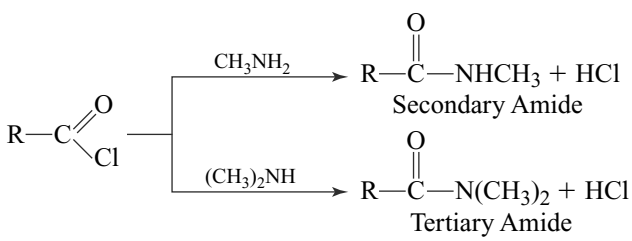
(a) Ammonium salt of carboxylic acid on heating gives amide.



(b) Acid chlorides, esters and anhydrides also react with NH_3 to form amide.

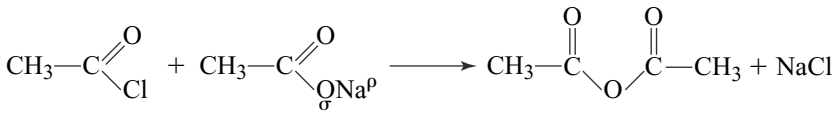


Secondary and tertiary amides are conveniently prepared by *Schotten–Baumann reaction*. In this method, acid chloride reacts with amines to form amides.

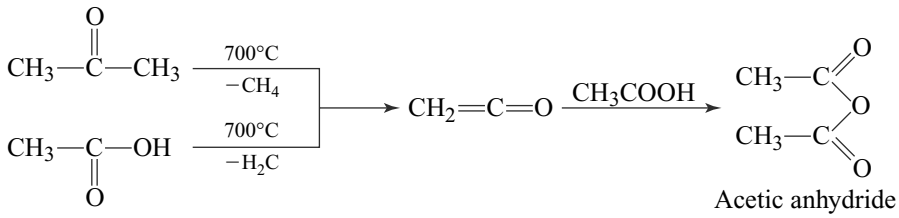


5. Acid anhydride

(a) Acid chloride and sodium salt of carboxylic acid react to form acid anhydride. It is a good method for lower acid anhydride.

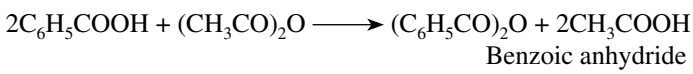


1. Acetic anhydride is most common and is conveniently prepared by the reaction of acetic acid with ketene $CH_2=C=O$. Ketene can be obtained by pyrolysis of acetone or acetic acid.



Acetic anhydride

(b) Higher molecular weight anhydrides are prepared by anhydride exchange that uses acetic anhydride (available and its reaction product is low boiling).



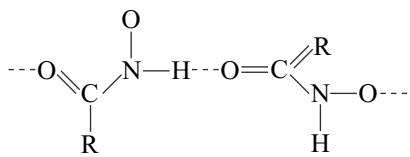
Benzoic anhydride

PHYSICAL PROPERTIES

1. Acid derivatives are polar compounds due to the presence of the C=O group ($\overset{\delta\oplus}{>C}=\overset{\delta-}{O}$).

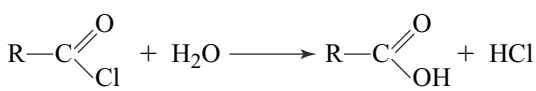
2. Esters, acid chlorides and acid anhydrides have comparable boiling points to those of aldehydes and ketones (polar molecules) of comparable molecular weight.

3. Amides have high boiling points. It is because they are associated molecules through intermolecular H-bonding.



4. Esters have pleasant odour (used in perfumes and flavourings).

5. Acid derivatives are soluble in organic solvents. Lower esters and amides are water-soluble. Acid chlorides are readily hydrolyzed by water.

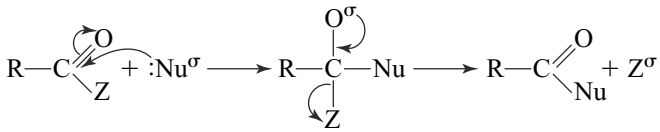


They have sharp irritating odour due to the above reaction.

Chemical Reaction

The carbonyl group (>C=O) plays an important role in the reactions of acid derivatives (as it does for the acids). The main reactions are given below.

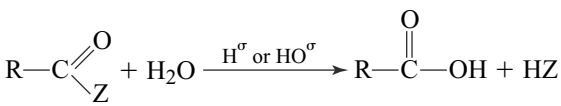
1. Replacement of Z by attack of a nucleophile (Nu–) at the carbonyl carbon.



2. Substitution at 2-carbon which is made possible by the electron-attracting property of >C=O group. Reaction of the second type is Claisen condensation (see Chapter 6, *Name Reactions*) and substitution at active methylene group of ethyl acetoacetate, malonic ester and the like.

Displacement reactions of acid derivatives

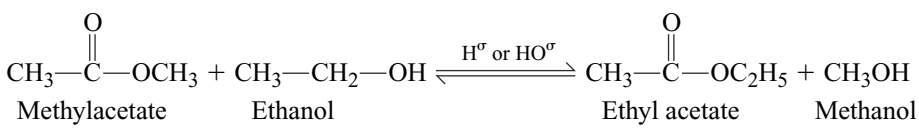
1. Acid derivatives are hydrolyzed to parent acid. (It is discussed in Chapter 5, *Reaction Mechanism*, under the heading, Reactions of >C=O group).



Z = OR, –Cl, $–NH_2$, –OOCR (Anhydride)

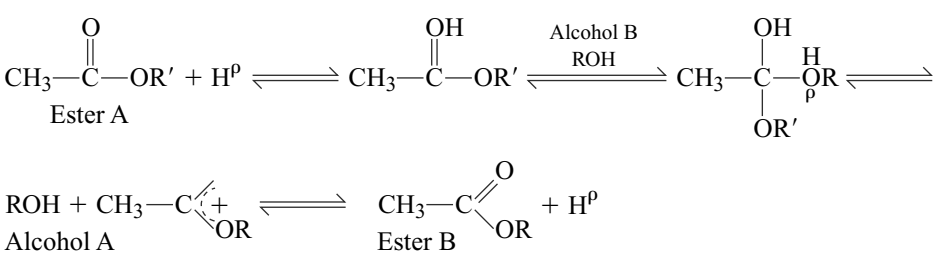
2. Transesterification or ester interchange

   One alcohol may displace another alcohol from an ester. This alcoholysis of an ester is known as ester interchange or transesterification. This reaction is catalyzed by acid (dry HCl or H_2SO_4) or base (RO^{σ}, alkoxide).



Acid catalysed

This reaction is like acid catalyzed esterification.

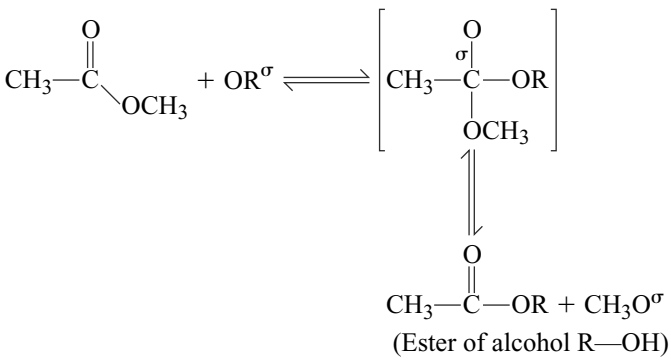


Base Catalysed

Base catalyzed ester interchange is similar to the saponification reaction (i.e., base catalysed hydrolysis of ester). Either methoxide (CH_3O^{σ}) or ethoxide ($C_2H_5O^{\sigma}$) can be used as the catalyst since the following equilibrium is readily established.

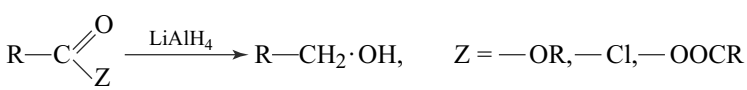
$$ROH + CH_3O^{\sigma} \rightleftharpoons RO^{\sigma} + CH_3OH$$

The mechanism of the reaction may be outlined as below.

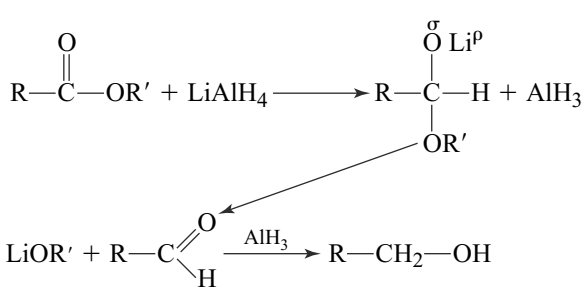


Reduction

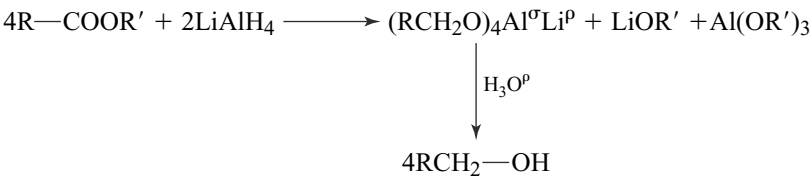
Esters, acid chlorides and anhydrides are reduced by $LiAlH_4$ to primary alcohols. The reaction is like reduction of carboxylic acid and the difference is that no H_2 is evolved.

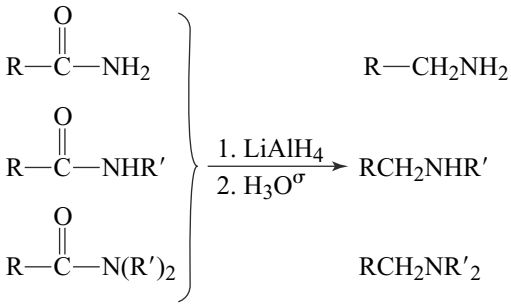


Ester



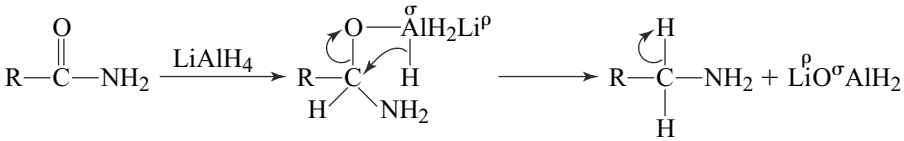
The stoichiometric equation is





Amides are reduced by $LiAlH_4$ to primary amines and N-substituted amides (sec and tert) to secondary and tertiary amines.

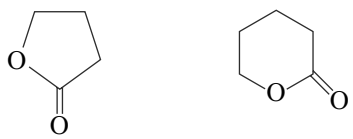
The mechanism of reduction is as under.



The stoichiometric equation is

Lactones

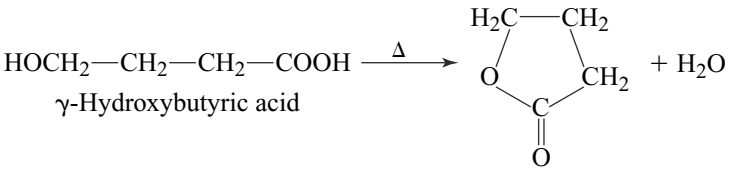
Lactones are cyclic esters formed by intramolecular esterification. In the IUPAC system, lactones are named as 'Olides'.



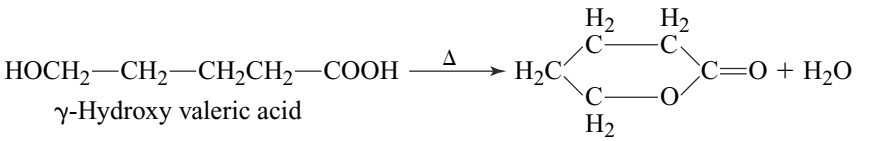
1,4-Butanolide (γ-butyrolactone)

1,5-Pentanolide (δ-valerolactone)

Five- and six-membered rings are strain free and hence γ- and δ-lactones are found. They are formed by heating γ- and δ-hydroxy acids.

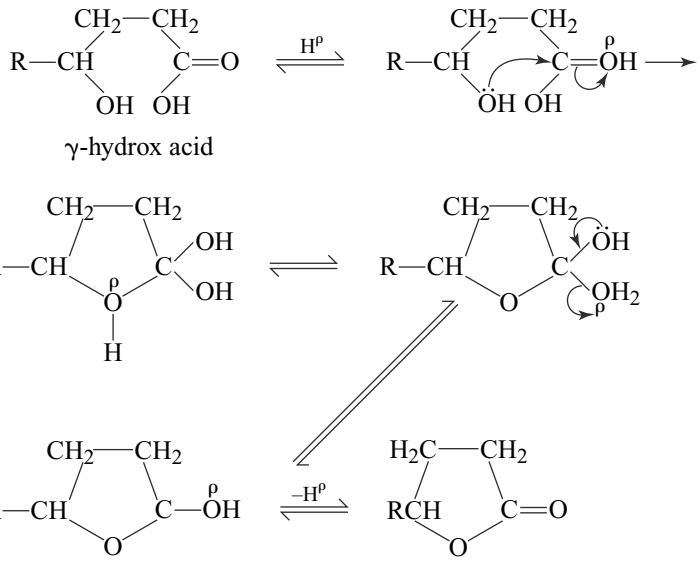


γ-Butyrolactone



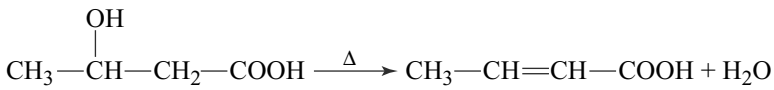
δ-Valerolactone

Lactone formation may be outlined as below.

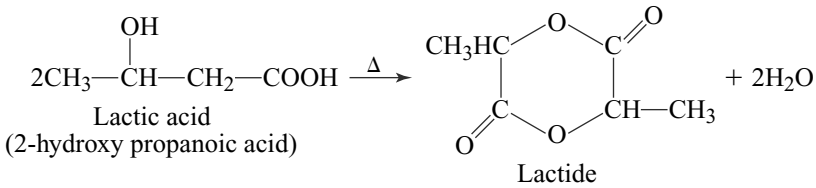


Under similar conditions, the following results:

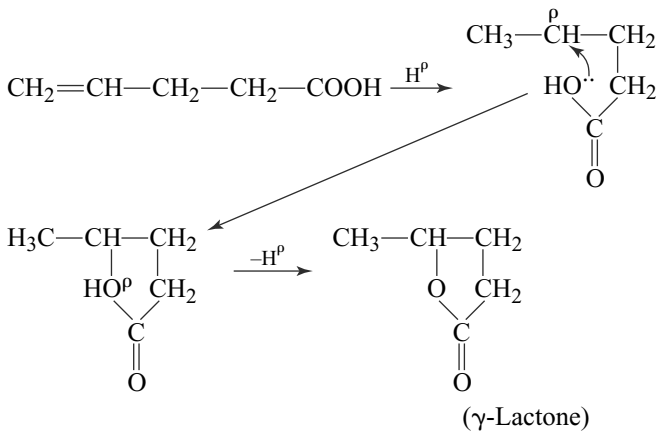
1. 3-Hydroxy acids are dehydrated to α,β-unsaturated acids.



2. 2-Hydroxy acids undergo bimolecular esterification. The products are six-membered dilactone rings called lactides.



Unsaturated acids other than α,β-acids readily cyclize to form lactone in the presence of acid catalyst. The reaction is initiated by the protonation of double bond to give carbocation intermediate, which is attacked by the nucleophile (–COOH group), to form a cyclic ester.



Lactone formation by this mechanism takes place only when five- or six-membered ring can be formed.

Dicarboxylic acids

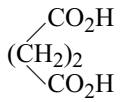
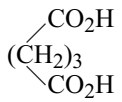
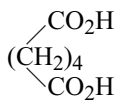
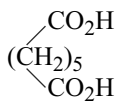
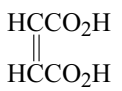
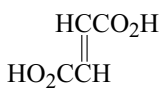
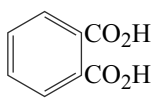
Dicarboxylic acids contain two carboxyl (–COOH) groups. Some common ones are given in the table below.

Table 15.4

Acid	Formula	MP (°C)	$K_1 \times 10^5$ at 25°C	$K_2 \times 10^5$ at 25°C
Oxalic (ethanedioic)	CO_2H | CO_2H	189	3500	5.3
Malonic (propanedioic)	CO_2H / CH_2 \ CO_2H	136 dec.	171	0.22

(Continued)

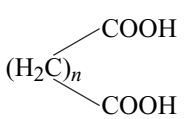
Table 15.4 *(Continued)*

Acid	Formula	MP (°C)	$K_1 \times 10^5$ at 25°C	$K_2 \times 10^5$ at 25°C
Succinic (butanedioic)		185	6.6	0.25
Glutaric (pentanedioic)		98	4.7	0.29
Adipic (heanedioic)		152	3.7	0.24
Pimelic (heptanedioic		105	3.4	0.26
Maleic (*cis*-butenedioic)		130	1170	0.026
Fumaric (*trans*-butenedioic)		sub. 200	93	2.9
Phthalic (benzene-1,2-dicarboxylic)		231	130	0.39[18]

Note:

1. Acids with even number of carbon atoms have higher melting points than acids with odd number of carbon atoms.
2. Oxalic, maleic and malonic acids are stronger in first isonisatin. It is because of their greater stabilization in the mono anions through intramolecular H-bonding (see Chapter 4, *Acids and Bases*).
3. Some of the acids are industrially important, example adipic acid (monomer for nylon), phthalic acid (dye synthesis) and terephthalic acid (monomer for terelyne).
4. Acid strength of dicarboxylic acids is discussed in Chapter 4, *Acids and Bases*.

Dicarboxylic acids may be represented as under.

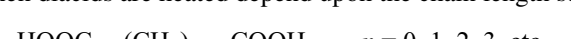


$n = 0, 1, 2, 3,$ etc.

When n > 5, the two carboxyl groups behave independently. But when they are closer, the acids have exceptional properties.

Effect of heat on dicarboxylic acids

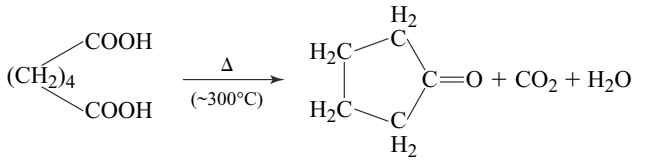
The reactions that occur when diacids are heated depend upon the chain length separating –COOH group.



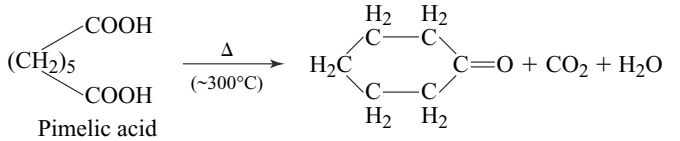
$n = 0, 1, 2, 3,$ etc.

The effect of heat is summerized below.

1. Cyclization takes place when strainless five- or six-membered ring is formed.
Adipic and pimelic acids cyclize with decarboylation to give cyclopentanone (five-membered ring) and cyclohexanone (six-membered ring), respectively.

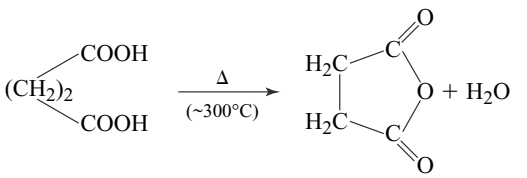


Adipic acid Cyclopentanone

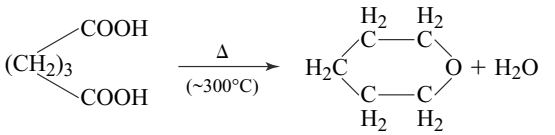


Pimelic acid

2. Succinic and glutaric acids behave differently. They form cyclic anhydrides having five- and six-membered rings.

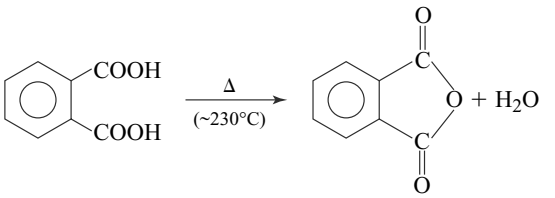


Succinic acid Succinic anhydride

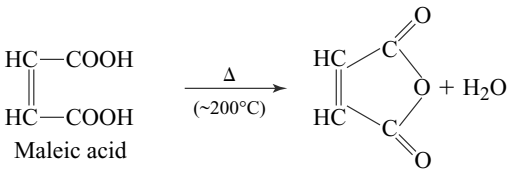


Glutaric acid Glutaric anhydride

3. Phthalic and maleic acids behave similarly. They form five-membered cyclic anhydride.



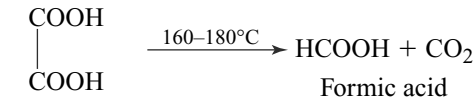
Phthalic acid Phthalic anhydride



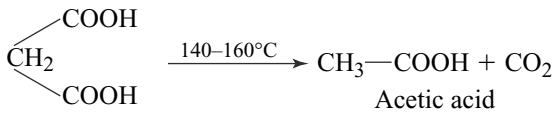
Maleic acid

Maleic anhydride

4. The behaviour of oxalalic and malonic acids is completely different. Each one decarboxylates to give mono carboxylic acid.



Oxalic acid

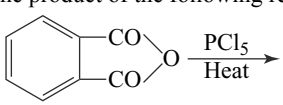


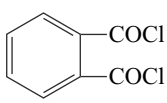
Malonic acid

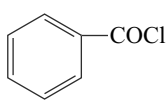
PROBLEMS

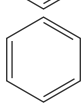
Objective-Type Questions

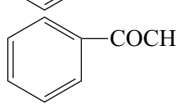
1. What is the product of the following reaction?



(a) 

(b) 

(c) 

(d) 

2. Identify (A) and (B) in the following scheme.

$$CH_3CH_2COOH \xrightarrow{P \text{ and } Br_2} (A) \xrightarrow[(ii)\ H]{(i)\ Alc.\ KOH\ (Excess)} (B)$$

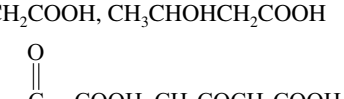
(a) $CH_3CHBrCOOH$; $CH_2 = CH–COOH$
(b) $BrCH_2CH_2COOH$; CH_3CH_2COOH
(c) CH_3CH_2COBr; $CH_2 = CHCOOH$
(d) None of these

3. Identify G and H in the following reaction, where G is $C_4H_8O_3$.

$$\text{Acetate} \xleftarrow[\text{Pyridine}]{Ac_2O} G \xrightarrow{NaHCO_3} CO_2$$

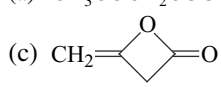
$$G \xrightarrow{CrO_3} H \xrightarrow{\text{Warm}} CH_3COCH_3 + CO_2$$

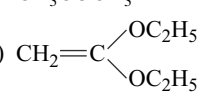
(a) CH_3COCH_2COOH, $CH_3CHOHCH_2COOH$

(b) 

(c) $CH_3CHOHCH_2COOH$, CH_3COCH_2COOH
(d) $CH_3CHOHCH_2COOH$, $CH_3CH_2COCOOH$

4. $CH_3CO_2C_2H_5$ on reaction with sodium ethoxide in ethanol gives A, which on heating in the presence of acid gives compound B. The compound B is
(a) CH_3COCH_2COOH (b) CH_3COCH_3

(c) 

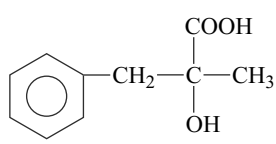
(d) 

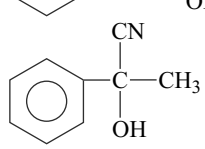
5. The best method for the separation of naphthalene and benzoic acid from their mixture is
(a) distillation (b) sublimation
(c) chromatography (d) crystallization

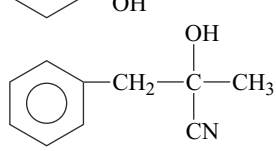
6. In a set of reaction, acetic acid yielded a product D.

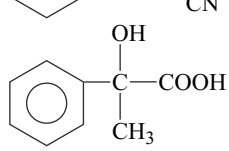
$$CH_3COOH \xrightarrow{SOCl_2} A \xrightarrow[Anhr.AlCl_3]{Benzene} B \xrightarrow{HCN} C \xrightarrow{H.OH} D$$

The structure of D would be:

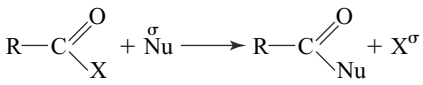
(a) 

(b) 

(c) 

(d) 

7. The reaction



is fastest when X is

(a) Cl (b) NH_2

(c) OC_2H_5 (d) OCOR

8. The OH group of an alcohol or the –COOH group of a carboxylic acid can be replaced by –Cl using

(a) phosphorus pentachloride

(b) hypochlorous acid

(c) chlorine

(d) hydrochloric acid

9. Which of the following carboxylic acid undergoes decarboxylation easily?

(a) $C_6H_5—CO—CH_2—COOH$

(b) $C_6H_5—CO—COOH$

(c) $C_6H_5—\underset{\displaystyle OH}{\underset{|}{CH}}—COOH$

(d) $C_6H_5—\underset{\displaystyle NH_2}{\underset{|}{CH}}—COOH$

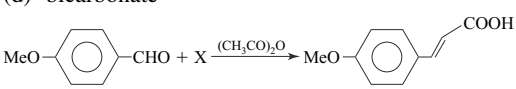
10. When propionic acid is treated with aqueous sodium bicarbonate, CO_2 is liberated. The 'C' of CO_2 comes from

(a) methyl group

(b) carboxylic acid group

(c) methylene group

(d) bicarbonate

11. 

What is X?

(a) CH_3–COOOH (b) CHO–COOH

(c) CH_3COONa (d) $BrCH_2$–COOH

12. When 2-hydroxy benzoic acid is distilled with Zn-dust, it gives

(a) benzaldehyde (b) benzoic acid

(c) phenol (d) 2-hydroxy toluene

13. $C_3H_5N \xrightarrow{\text{Hydrolysis}} C_3H_6O_2 \xrightarrow{Cl_2/P} C_3H_5O_2Cl \xrightarrow{NH_3} C.$

The compound C is

(a) 2-nitropropane (b) 1-nitropropane

(c) 2-aminopropanoic acid (d) 2-hydroxyl propanamide

14. $CH_3CH_2—COOH \xrightarrow{Cl_2/P} A \xrightarrow{\text{alc. KOH}} B.$

The product B is

(a) $CH_3CH_2—CHO$

(b) CH_3CH_2COCl

(c) $ClCH_2—CH_2—COOH$

(d) $CH_2=CH—COOH$

15. When propenoic acid is reduced with $LiAlH_4$, the compound obtained is

(a) $CH_3—CH_2—COOH$

(b) $CH_3=CH_2—CHO$

(c) $CH_2=CH—CH_2—OH$

(d) $CH_3—CH_2—CH_3$

16. What is the correct order of increasing acid strength of the following?

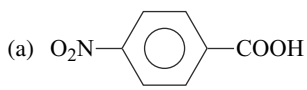
$CH_3–CO_2H$ [A] $MeOCH_2–CO_2H$ [B]

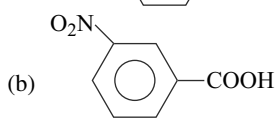
F_3CCO_2H [C] $Me_2CH–CO_2H$ [D]

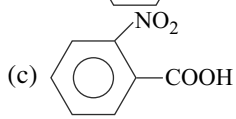
(a) B < D < A < C (b) D < A < C < B

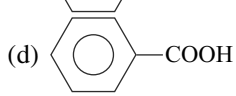
(c) D < A < B < C (d) A < D < C < B

17. Which has the highest p^{Ka} value?

(a) 

(b) 

(c) 

(d) 

18. Which of the following acids has the smallest dissociation constant?

(a) $CH_3CHFCOOH$ (b) $FCH_2–CH_2–COOH$

(c) $BrCH_2–CH_2COOH$ (d) $CH_3–CHBrCOOH$

19. Which of the following is obtained by heating 3-keto-butanoic acid?

(a) 3-Keto butanal (b) Acetone

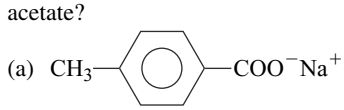
(c) Keto propanal (d) Propanoic acid

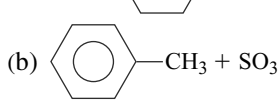
20. The acid that is strongest is

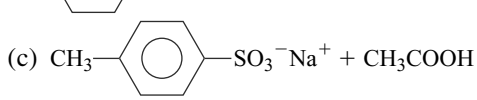
(a) C_6H_5COOH (b) m-$CH_3OC_6H_4COOH$

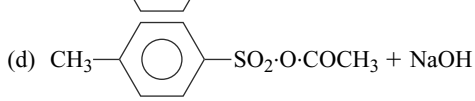
(c) CH_3COOH (d) p-$CH_3.C_6H_4COOH$

21. Which of the following is obtained when 4-methyl-benzene sulphonic acid reacts with excess of sodium acetate?

(a) 

(b) 

(c) 

(d) 

22. 4-Hydroxybutanoic acid on heating gives
(a) propanol-1 (b) but-3-enoic acid
(c) 1,3-butanolide (d) 1,4-butanolide

23. $CH_3{=}CH{-}CH_2{-}CH_2{-}COOH \xrightarrow[(2)\ \Delta]{(1)\ H_3O^+}$ A.
The product A is
(a) a cyclic ether (b) a cyclic ketone
(c) a cyclic ester (d) a cyclic aldehyde

24. The p^{Ka} of aspirin (acetyl salicylic acid) is 3.5, the pH of gastric juice in human stomach is about 2–3 and pH in the small intestine is about 8. Aspirin will be
(a) unionized in the small intestine and in the stomach.
(b) completely ionized in the stomach and almost unionized in the small intestine.
(c) ionized in the stomach and almost unionized in the stomach intestine.
(d) ionized in the small intestine and almost unionized in the stomach.

25. Adipic acid (hexanedioic acid) on heating gives
(a) an ether (b) an ester
(c) a ketone (d) a cyclic ketone

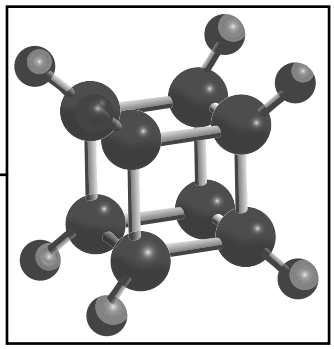
26. Glutaric acid (pentanedioic acid)when heated gives
(a) an ester (b) a ketone
(c) an anhydride (d) an aldehyde

27. Consider
[1] C_6H_5COCl [2] p-$O_2NC_6H_4COCl$
[3] p-$CH_3OC_6H_4COCl$
Mark the decreasing order of reactivity to hydrolysis.
(a) 1 > 2 > 3 (b) 3 > 2 > 1
(c) 1 > 3 > 2 (d) 2 > 1 > 3

Answers

1. (a)	2. (a)	3. (c)	4. (b)	5. (d)
6. (d)	7. (a)	8. (a)	9. (a)	10. (d)
11. (c)	12. (b)	13. (c)	14. (d)	15. (c)
16. (c)	17. (c)	18. (c)	19. (b)	20. (b)
21. (c)	22. (d)	23. (c)	24. (d)	25. (d)
26. (c)	27. (d)			

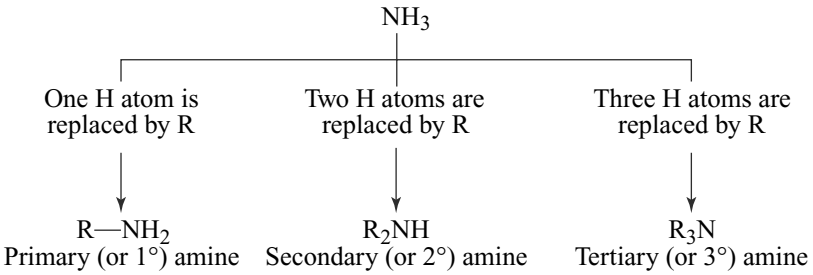
CHAPTER 16



Organic Compounds of Nitrogen

AMINES

Alkyl (or aryl) derivatives of NH_3 are known as amines. They are formed by the replacement of one, two or all three H-atoms of NH_3 (by R or Ar).



Classification

Three classes of amines exist depending upon the number of alkyl groups attached to N.

Table 16.1

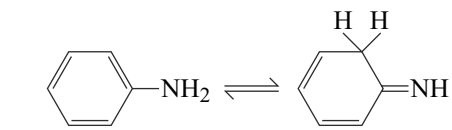
Amine	Functional group	Example	
Primary amine (or 1° amine)	—NH_2	Methyl amine	CH_3—NH_2
Secondary amine (or 2° amine)	>N—H	Dimethyl amine	CH_3, CH_3 >N—H
Tertiary amine (or 3° amine)	>N	Trimethyl amine	CH_3, CH_3—, CH_3 >N—H

In addition to the above, ionic, solids quaternary ammonium salts and hydroxides are also formed. They may be salts of inorganic or organic acids. For example,

CH_3NH_3Cl	Methylammonium chloride (or methylamine hydrochloride)
$(C_2H_5)_4N\ HO$	Tetraethyl ammonium hydroxide
$CH_2 = CH - CH_2 - NH - CH_3\ \ O_2CCH_3$	Allyl dimethyl ammonium acetate

(Aryl amines are discussed in Chapter 7, *Benzene.*)

Vinyl amines (or enamines, R–CH=CH–NH_2) are usually not stable and rearranged to imines R–CH_2–CH=NH, (the C=N bond energy is somewhat greater than C=C). But, aniline is stable and the imine structure is less favourable (aromatic stability in benzene ring).



(Aromatic ring) (Imine)

Isomerism

Various types of structural isomers are possible.

1. **Chain isomers**
   Alkyl groups present in the amine may have different carbon skeleton. It gives chain isomers. For example, C_3H_9N may represent the following reaction.

   $CH_3—CH_2—CH_2—NH_2$ *n*-Propyl amine (1°)

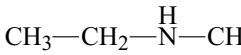
2. **Functional group isomers**
   The same molecular formula may represent all three types of amines. Thus, isomers of C_3H_9N are the following:

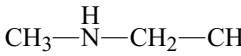
   (a) $CH_3—CH_2—CH_2—NH_2$ *n*-Propyl amine (1°)

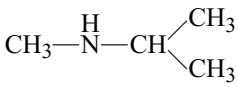
   (b) $CH_3—\overset{H}{N}—CH_2—CH_3$ Ethylmethyl amine (2°)

   (c) $(CH_3)_3N$ Trimethyl amine (3°)

3. **Metamers**
   Amines also show metamerism. For example, the metamers of $C_4H_{11}N$ are given as under.


Diethyl amine (2°)


Methyl *n*-propylamine (2°)


iso-propyl methyl amine (2°)

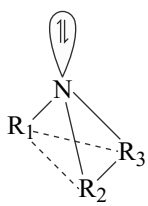
Problem

Write the number of structures of the possible amines of $C_4H_{11}N$.

Ans: Eight amines

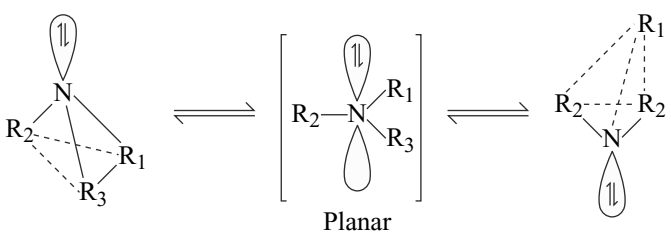
Stereochemistry of amines

The nitrogen atom in amines, like NH_3 is sp^3 hybridized. Three of the sp^3 hybrids form bonds and the fourth sp^3 hybrid keeps non-bonded pair (or lone pair) of electrons. It makes amines tetrahedral in structure but their shapes are trigonal pyramidal.



Pyramidal molecules $NR_1R_2R_3$ have no centre or plane of symmetry (that is, chiral) and are dissymmetric.

But optical isomers have not been isolated. It is because such molecules rapidly interconvert that is known as inversion. It involves a planar transition state, as shown below.



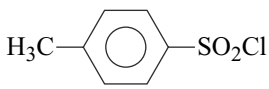
The above situation is very much like an umbrella turning inside out. With NH_3, inversion frequency is about 2.4×10^{10} times per second but with aliphatic tertiary amines, the rate is of the order of 10^3–10^5 times per second. This very large inversion rate does not permit separation of amines into stable optical isomers at room temperature.

Separation of amines (1°, 2° and 3°)

Many preparative methods produce a mixture of primary (1°), secondary (2°) and tertiary (3°) amines. It requires separation of the products.

Hinsberg's method

Reagent: The chemical equation of benzene sulphonyl chloride is $C_6H_5SO_2Cl$. But now, the more reactive compound, *p*-toluenesulphonyl chloride and *p*-$CH_3C_6H_4SO_2Cl$, (tosyl chloride and TsCl) is used.



The reagent behaves differently with the amines given below.

1. Primary amines form the N-alkyl sulphonamide that are soluble in alkali (NaOH or KOH). It is due to acidic H in sulphonamide.

$$C_2H_5{-}NH_2 + p{-}CH_3{-}C_6H_4{-}SO_2Cl \longrightarrow \underset{\text{(Insoluble)}}{p\text{-}CH_3C_6H_4SO_2\overset{\overset{H\ (acidic)}{|}}{N}{-}C_2H_5} + HCl$$

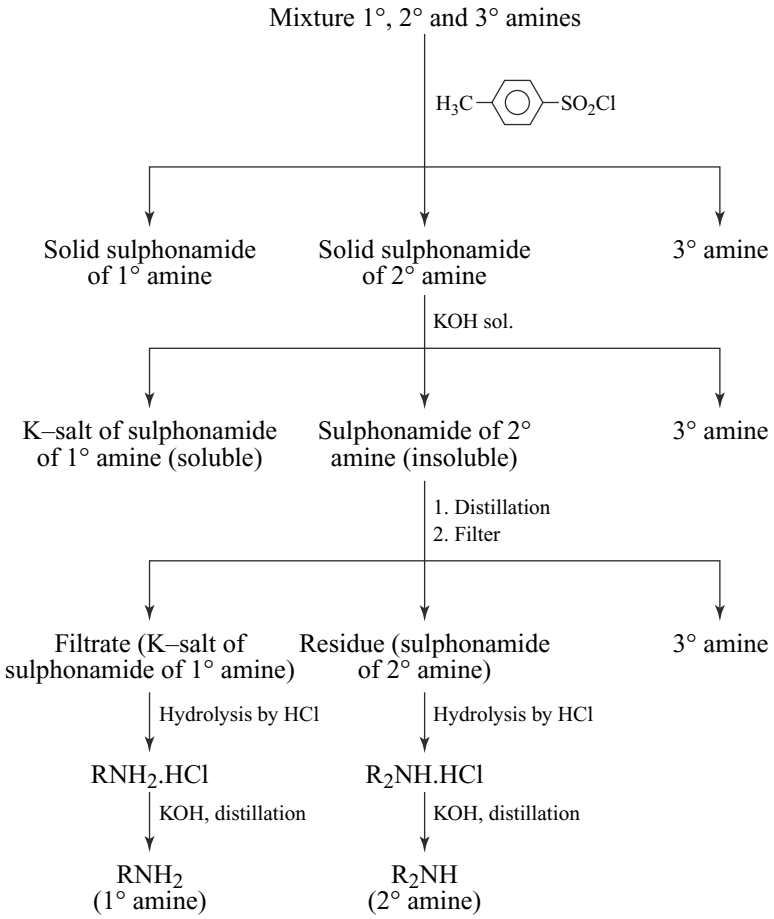
$$p\text{-}CH_3C_6H_4SO_2\overset{\sigma}{N}.C_2H_5K^{\rho}$$
(Soluble)

2. Secondary amines form N,N-dialkyl sulphonamides. They are insoluble in KOH as the sulphonamide has no acidic H atom.

$$(C_2H_5)_2NH + p\text{-}CH_3{-}C_6H_4SO_2Cl \longrightarrow \underset{\text{(Insoluble)}}{p\text{-}CH_3{-}C_6H_4SO_2N(C_2H_5)_2} + HCl$$

3. Tertiary amines do not react with the reagent. It is because 3° amine has no H atom at N.

$$(C_2H_5)_3N + p\text{-}CH_3C_6H_4SO_2Cl \longrightarrow \text{No reaction}$$



Preparation of amines

Reactions that give a mixture of 1°, 2° and 3° amines

1. **Ammonolysis of alkyl halides (Hoffmann's method)**
   When an alkyl halide is heated with an alcoholic solution of NH_3 in a sealed tube at 100°C, all three classes of amines with some quaternary ammonium salt are formed.

$$R{-}X + \ddot{N}H_3 \longrightarrow R\,{}^{\rho}NH_3.X^{\sigma}$$

$$R\,{}^{\rho}NH_3.X^{\sigma} + NH_3 \longrightarrow \underset{1^\circ \text{ amine}}{R{-}NH_2} + NH_4X$$

The primary amine produced initially reacts further with alkyl halide giving secondary and tertiary amines.

$$RNH_2 + RX \longrightarrow R_2\overset{\rho}{N}H_2.X^{\sigma}$$

$$R_2\overset{\rho}{N}H_2X^{\sigma} + NH_3 \longrightarrow \underset{2^\circ \text{ Amine}}{R_2NH} + NH_4.X$$

$$R_2NH + R{-}X \longrightarrow R_3\overset{\rho}{N}H.X^{\sigma}$$

$$R_3\overset{\rho}{N}HX^{\sigma} + NH_3 \longrightarrow \underset{3^\circ \text{ Amine}}{R_3N} + NH_4.X$$

$$R_2N + R{-}X \longrightarrow \underset{\text{(Quaternary ammonium salt)}}{R_4\overset{\rho}{N}.X^{\sigma}}$$

This reaction is S_N2 type. Thus, primary alkyl halides give good yield. The order of reactivity of alkyl halides found is R–I > R–Br > R–Cl

2. Ammonolysis of alcohols

When an alcohol and NH_3 are heated in a sealed tube in presence of aluminium or copper chromite catalyst, a mixture of 1°, 2° and 3° amines is formed.

$$R{-}OH + NH_3 \longrightarrow \underset{1^\circ \text{ Amine}}{R{-}NH_2} + H_2O$$

$$R{-}OH + R{-}NH_2 \longrightarrow \underset{2^\circ \text{ Amine}}{R_2NH} + H_2O$$

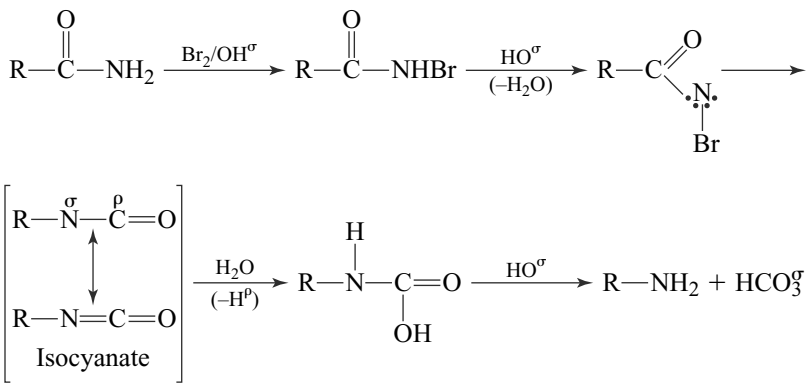
$$R{-}OH + R_2NH \longrightarrow \underset{3^\circ \text{ Amine}}{R_3N} + H_2O$$

The individual amines are separated from the mixture using Hinsberg reagent, as described above.

Preparation of primary amines

1. Hoffmann's bromamide reaction

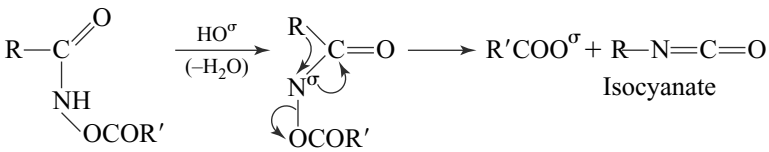
Amides are converted into primary amines by the action of Br_2 and KOH (or NaOH). The reaction proceeds as follows (mechanism is discussed in Chapter 6, *Name Reactions*).



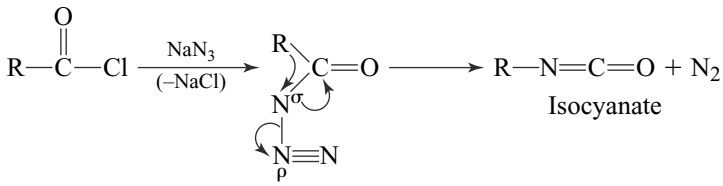
Amine formed contains one carbon atom less than the amide. It is, thus, a degradation reaction.

Lossen, Curtius and Schnidt rearrangements may produce primary amines. These reactions are basically similar to Hoffmann's rearrangement in that all first form isocyanate, which then hydrolyze to primary amine. The reactions are summarized below.

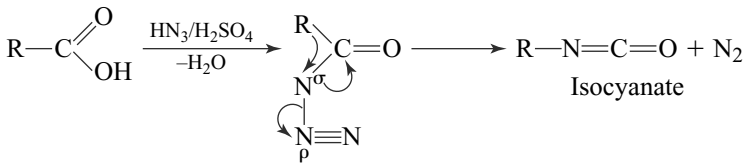
(a) *Lossen rearrangement*
This reaction involves the action of a base on *o*-acyl derivative of hydroxamic acid (RCONHOH). The $RCOO^{\sigma}$ (carboxylate) is the leaving group in the rearrangement. The rearrangement and loss of $R'COO^{\sigma}$ are simultaneous.



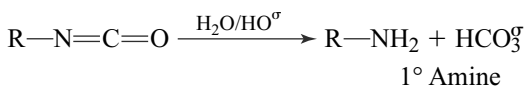
(b) *Curtius rearrangement*
This reaction involves acyl azide. It is obtained by reaction of acyl halide with sodium azide NaN_3. N_2 is a leaving group. The loss of N_2 and rearrangement (migration of R) are concerted process.



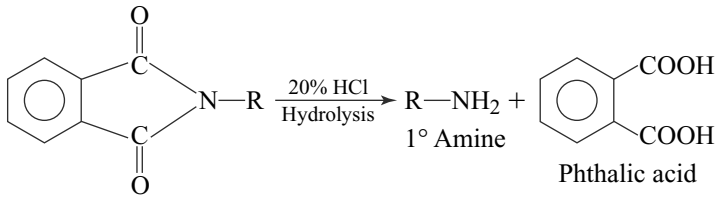
(c) *Schmidt rearrangement*
This reaction also involves acyl azide, which is obtained by the reaction of RCOOH with hydrazoic acid (HN_3) in the presence of conc. H_2SO_4. The leaving group in this reaction is N_2. The rearrangement and loss of N_2 are simultaneous.



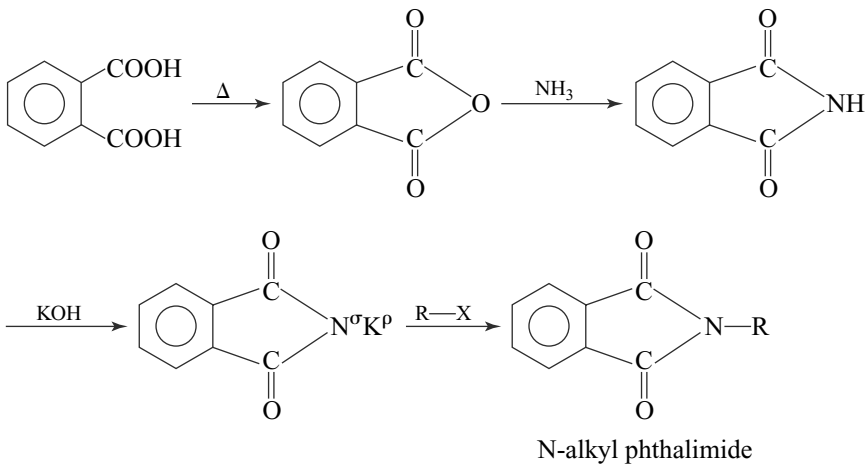
Isocyanate is finally hydrolyzed to the amine.



2. Gabriel phthalimide synthesis
N-alkyl phthalimide on boiling with acid hydrolyze to primary amine.

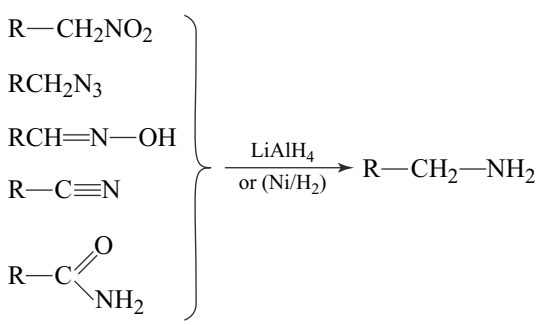


The N-alkyl phthalimide used in the above reaction may be prepared from phthalic acid as shown below.



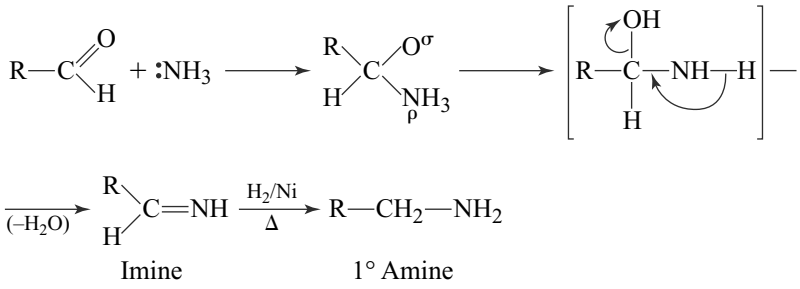
3. Amines by reduction

Variety of N-compounds on reduction can give amines. Primary amines can be obtained by catalytic hydrogenation or lithium aluminium hydride reduction of nitro compounds, azides, oximes, nitriles and 1° amides.



4. Reductive amination

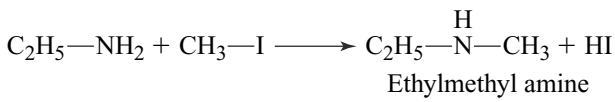
Carbonyl compounds (aldehydes or ketones) can be converted into primary amines by chemical or catalytic reduction. The reaction involves imine as an intermediate, which is reduced to amine.



Imine 1° Amine

Preparation of secondary amines

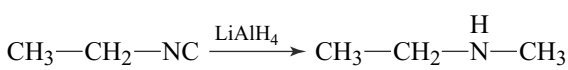
1. **Alkylation of primary amines**
   Primary amines on heating with calculated quantity of alkyl halide (1:1) give secondary amines.



Ethylmethyl amine

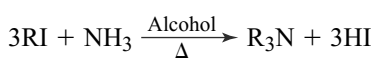
2. **Reduction of N-alkylamides (2° amide)**
   Secondary amines are formed when amides of the type RCONHR′ is reduced by $LiAlH_4$.

3. **Reduction of alkyl isocyanides**
   Alkyl isocyanides may be reduced by $LiAlH_4$ to give secondary amines. This reaction, however, has one limitation that it can produce secondary amines in which one alkyl group is always methyl (due to reduction of the C atom of –NC group).

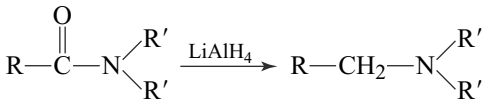


Preparation of tertiary amines

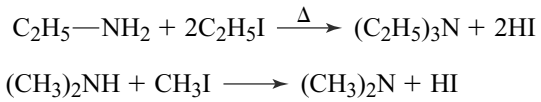
1. **Ammonolysis of alkyl halides**
   When slight excess of alkyl halide is heated with alcoholic ammonia, tertiary amine is formed.



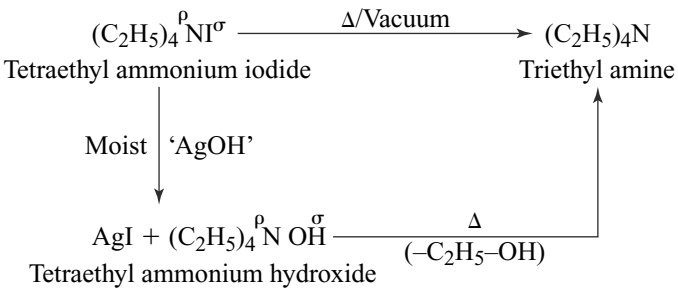
2. **Reduction of N,N-dialkyl amide (3° amide)**
   Amides of the type R–$CONR'_2$ may be reduced by $LiAlH_4$ to a tertiary amine.



3. **Alkylation of 1° and 2° amines**
   Reaction of primary and secondary amines with calculated amounts of alkyl halides gives tertiary amine.



4. **From quaternary salts**
   Quaternary ammonium hydroxides on heating decompose to tertiary amines. Alternatively, when heated in vacuum, quaternary salts itself form tertiary amines. For example,



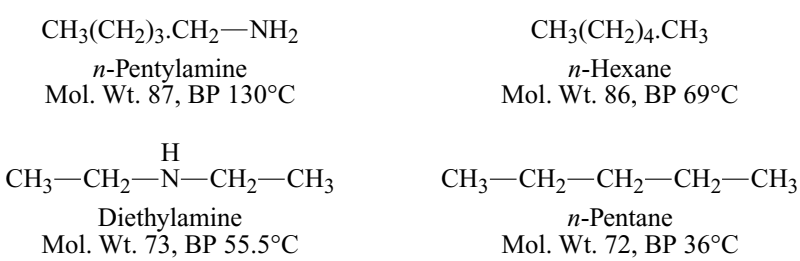
Physical properties of amines

1. **Physical state**
   Methylamine is a gas where its higher members are liquids, while the amines having still larger molecular weight are solids. Lower members have fish-like smell and solid amines have no fish-like smell.
2. **Boiling points**
   Primary and secondary amines can form intermolecular H-bonds of the type N–H - - - - N.

   Tertiary amines have no N–H bonds and are, thus, unable to form H-bonds of the above type.

   Also, N–H - - - N bonds are weaker than O–H - - - O and F–H - - F as N is less electronegative than O and F. Therefore, primary and secondary amines are associated molecules (through H-bonding) but not tertiary amines. It has effect on boiling points as shown below.

   (a) Primary (1°) and secondary (2°) amines have higher boiling points (that is less volatile) than hydrocarbons of similar size, shape and weight.



(b) Isomeric primary and secondary amines generally have higher boiling points than tertiary amines (reason H-bonding effect). It is illustrated by three isomeric hexyl amines, $C_6H_{15}N$.

Table 16.2

Amine	Isomers	BP (°C)
1° Amine	$CH_3(CH_2)_4.CH_2—NH_2$	130
2° Amine	$C_3H_7—\overset{H}{N}—C_3H_7$	111
3° Amine	$(C_2H_5)_3N$	90

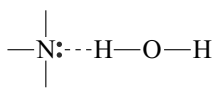
(c) Amines have lower boiling points than alcohols of similar size, shape and weight (H-bond in alcohols is stronger).

Table 16.3

Alcohol	BP (°C)	Amine	BP (°C)
$CH_3CH_2–OH$	78	$CH_3CH_2–NH_2$	17
$CH_3CH_2–CH_2–OH$	97	$CH_3–CH_2–CH_2–NH_2$	49

3. Water solubility

Lower molecular weight amines are soluble in water. It is because of H-bonding between the amine and water of the type.



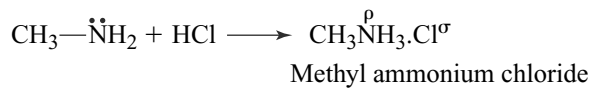
Chemical reactions

1. Basic nature and strength (explained in Chapter 4, *Acids and Bases*).

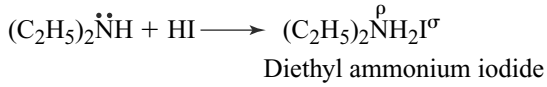
2. Reaction with acids (salt formation).

Amine N has unshared electrons (that is lone pair). This lone pair plays an important role in the reactions of amines.

Amines form salts with mineral acids.



Methyl ammonium chloride



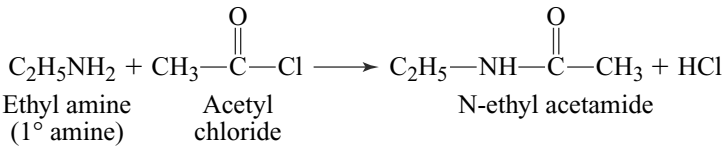
Diethyl ammonium iodide

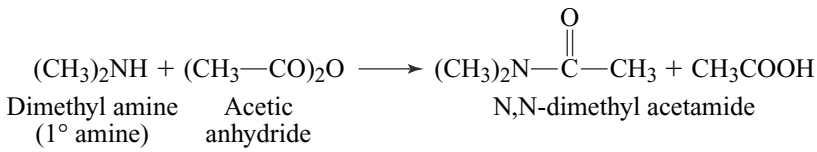
The salts are also represented in the following way.

$CH_3—NH_2.HCl$	$(C_2H_5)_2NH.HI$
Methylamine hydrochloride	Diethylamine hydroiodide

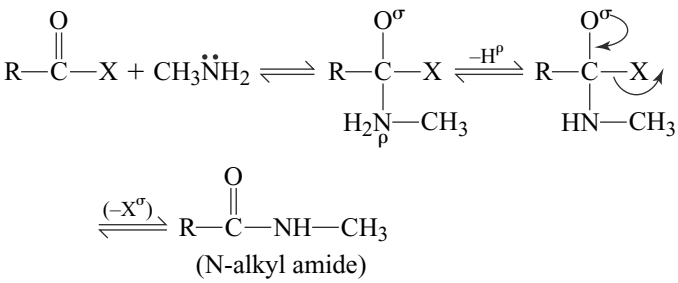
Acylation of amines

Primary and secondary amines react with an acid chloride or an anhydride or an ester to form an amide (2° or 3° amide). This reaction is known as *acylation*.



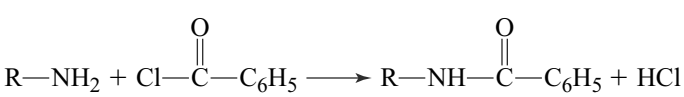


The acylation reaction proceeds in the following way.

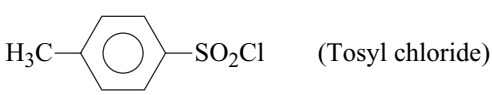


Important points

1. Tertiary amines do not give acylation reaction as they do not have N–H bond.
2. The introduction of the acetyle group ($CH_3—\overset{O}{\overset{\|}{C}}—$) is called *acetylation*.
3. When benzoyl chloride is used for acylation, the reaction is known by the name *Schotten–Baumann reaction or benzoylation*.

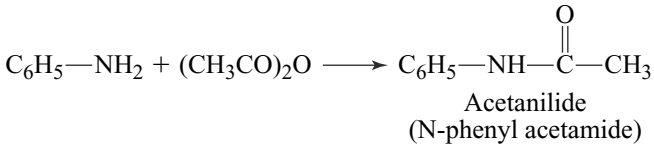


4. Other acylating agents are benzene sulphonyl chloride, $C_6H_5SO_2Cl$ (Hinsberg reagent), and *p*-toluene sulphonyl chloride.



The reactions (3) and (4) are used in laboratory for the characterization of amines (and hydroxy compounds).

5. N-substituted acetamides are generally prepared by shaking amines with acetic anhydride.



Acetanilide
(N-phenyl acetamide)

6. Acetylation is used in organic synthesis to tame reactivity of NH_2 group (see Chapter 7, *Benzene*).

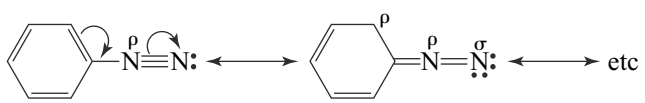
Reaction of amines with nitrous acid

Nitrous acid reacts with all amines (that is 1°, 2° and 3° amines) but the products depend on the class of amine. Nitrous acid is unstable and it is produced in situ by the action of dil. HCl on solid sodium nitrite ($NaNO_2$) at low temperature (0–5°C).

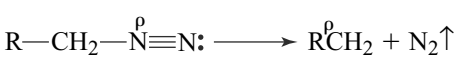
1. Primary amine + [HNO_2]
Primary amines react with nitrous acid at low temperature to form diazonium salt.

[R=alkyl or aryl (C_6H_5)]

Aryl diazonium salts are stable, due to delocalization of positive charge in the ring (see diazonium slats, Chapter 7, *Benzene*).

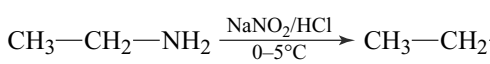


In contrast, alkyl diazonium salts are unstable (no resonance stabilization) and liberate N_2 quantitatively generating carbocation.

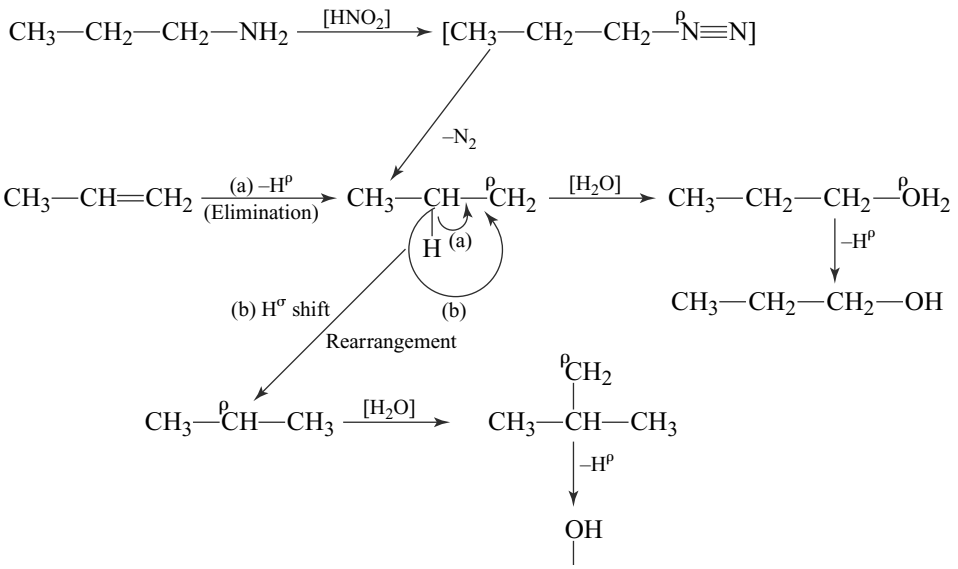


The carbocation undergoes a number of reactions, such as (i) reaction with nucleophile, (ii) elimination of β-proton and (iii) rearrangement. Thus, a wide variety of products may be formed. The overall reaction may be written as under.

Methylamine does not form methyl alcohol. Ethylamine gives satisfactory yield of ethyl alcohol.



n-Propyl amine gives a small amount of *n*-propyl alcohol with many other products. The reaction is summarized as under.



This reaction is the basis of Demjanov rearrangement (see Chapter 6, *Name Reactions*).
This reaction may be used for quantitative estimation and also for distinguishing 1° amines from 2° and 3° amines.

2. Secondary amine + [HNO_2]

With nitrous acid, secondary amines form an yellow oily liquid (or solid) N-nitroso compound $R_2N–N = O$. For example,

$$(C_2H_5)_3NH + [HNO_2] \longrightarrow \underset{\text{N-nitrosodiethyl amine}}{(C_2H_5)_2N—NO} + H_2O$$

Nitrogen is not evolved in the above reaction.
The N-nitrosoamines when treated with phenol and conc. H_2SO_4 give green solution, which changes to deep blue on treatment with aqueous NaOH. The blue colour changes to red on adding large volume of water. The whole reaction is known as Libermann's nitroso reaction. It is used for the test of secondary amines.

3. Tertiary amines + [HNO_2]

Tertiary amines dissolve in nitrous acid in cold forming unstable salts known as nitrites. They decompose to give complex products.

$$R_3N + HNO_2 \longrightarrow \underset{\text{Nitrite}}{R_3N.HNO_2} \text{ or } R_3{}^{\rho}NH.NO_2^{\sigma}$$

Carbylamine reaction

Alcoholic solution of primary amines (aliphatic R–NH_2 or aromatic C_6H_5–NH_2) on warming with aqueous solution of KOH (or NaOH) and chloroform give carbylamine (or isocyanide) that have unpleasant odour (nauseating odour). This reaction is known as carbylamine reaction.

$$R{-}NH_2 + CHCl_3 + 3KOH \longrightarrow \underset{\text{Alkyl isocyanide}}{R.\,NC} + 3H_2O + 3KCl$$

$$C_6H_5NH_2 + CHCl_3 + 2NaOH \longrightarrow \underset{\text{Phenyl isocyanide}}{C_6H_5NC} + 3H_2O + 3NaCl$$

Secondary and tertiary amines do not give this reaction. It is, therefore, used to test primary amines.

Reaction with carbon disulphide (CS_2)

1. **Primary amines**
   On warming with CS_2 primary amines form dithiocarbamic acids. They may be decomposed by $HgCl_2$ to give alkyl isothiocyanates.

$$R{-}NH_2 + S{=}C{=}S \longrightarrow \underset{\text{Dithiocarbamic acid}}{S{=}C\begin{matrix}\diagup SH\\ \diagdown NHR\end{matrix}} \xrightarrow{HgCl_2} \underset{\text{Alkyl isothiocyanate}}{RNCS} + HgS + 2HCl$$

   This is called Hoffmann's mustard oil reaction. It may be used to identify primary amines.

2. **Secondary amines**
   Secondary amines also form dithiocarbamic acids with CS_2 but they are not decomposed by $HgCl_2$, and is different from primary amines.

$$R_2NH + S{=}C{=}S \longrightarrow \underset{\text{Dithiocarbamic acid}}{S{=}C\begin{matrix}\diagup SH\\ \diagdown NR_2\end{matrix}}$$

3. **Tertiary amines**
   Tertiary amines do not react with CS_2 (due to steric factor and lack of N–H bond in 3° amine).
   It is seen that the three classes of amines (1°, 2° and 3°) differ in their reaction with CS_2 followed with $HgCl_2$. This reaction, therefore, may be used to distinguish among the three classes of amines.

Distinction among 1°, 2° and 3° amines

The following chemical reactions can be used to distinguish among 1°, 2° and 3° amines.

Table 16.4

Reactions	Primary amines	Secondary amines	Tertiary amines
1. Reaction with HNO_2	Give clear solution N_2 is evolved quantitatively. Alcohol and other products are formed. $RNH_2 + HNO_2 \longrightarrow R\text{–}OH + N_2$	Yellow oily nitrosamines separate. $R_2NH + HNO_2 \longrightarrow H_2O + R_2NNO$ Nitrosamines may be tested by Libermann's reaction.	Do not react
2. Reaction with benzene sulphonyl chloride	Form sulphonamides soluble in alkali (KOH)	Form sulphonamides insoluble in alkali	Do not react
	← (See separation of amines.) →		
3. Reaction with CS_2 followed by $HgCl_2$	Give dithiocarbamic acids which are decomposed by $HgCl_2$ to alkyl isothiocyanate (Hoffmann's mustard oil reaction)	Give dithiocarbamic acids that are not decomposed by $HgCl_2$.	Do not react
	← (See reaction 6.) →		
4. Reaction with KOH + $CHCl_3$	Form alkyl isocyanides, which have very bad odour. $RNH_2 + CHC_{l3} + 3KOH \longrightarrow RNC + 3H_2O + 3KCl$	Do not react	Do not react

PROBLEMS

Objective-Type Questions

1. In the following sequence of reaction the end product Z is

$$CH_3CH_2OH \xrightarrow{KMnO_4} (X) \xrightarrow[(ii)\ NH_3]{(i)\ SOCl_2} (Y) \xrightarrow{Br_2/NaOH} (Z)$$

(a) acetic acid (b) acetone
(c) methyl amine (d) ethyl amine

2. A compound C_3H_9N reacts with benzene sulphonyl chloride to give a solid insoluble in alkali. The compound is

(a) $CH_3CH_2CH_2NH_2$ (b) $(CH_3)(C_2H_5)NH$
(c) $(CH_3)_3N$ (d) $(CH_3)_2CH\text{—}NH_2$

3. Which one of the following methods is meant neither for the synthesis nor for the separation of amines?
(a) Hinsberg method (b) Hoffmann method
(c) Wurtz reaction (d) Curtius reaction

4. An organic compound having molecular mass 60 is found to contain C = 20%, H = 6.67% and N = 46.67%, while rest is oxygen. On heating, it gives NH_3 along with a solid residue. The solid residue gives violet colour with alkaline copper sulphate solution. The compound is
(a) CH_3NCO (b) CH_3CONH_2
(c) $(NH_2)_2CO$ (d) $CH_3CH_2CONH_2$

5. Acetamide is treated separately with the reagents given below. Which one of these would give methylamine?
(a) PCl_5 (b) Sodalime
(c) $NaOH + Br_2$ (d) Hot conc. H_2SO_4

6. Carbylamine test is performed in alcoholic KOH by heating a mixture of
(a) chloroform and silver powder
(b) trihalogenated methane and a primary amine
(c) an alkyl halide and a primary amine
(d) an alkyl cyanide and a primary amine

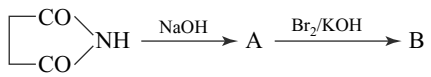
7. Hinsberg's reagents is
(a) phenyl isocyanide
(b) benzenesulphonyl chloride
(c) *p*-toluenesulphonic acid
(d) *o*-dichlorobenzene

8. A positive carbylamine test is given by
(a) N,N-dimethyl aniline
(b) 2,4-dimethyl aniline
(c) N-methyl-*o*-methyl aniline
(d) *p*-methyl benzylamine

9. Gabriel phthalimide reaction is used for the preparation of
(a) primary aromatic amines
(b) secondary amine
(c) aliphatic primary amines
(d) tertiary amines

10. $R—CH_2—NH_2 \xrightarrow[X]{CHCl_3/KOH}$ X. The product X is
(a) an amide
(b) a nitro compound
(c) an alkyl isocyanide
(d) an alkyl cyanide

11. In the given reaction, B is

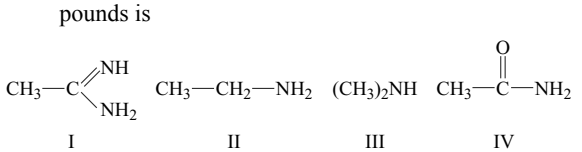


(a) α-alanine (b) β-alanine
(c) ethylenediamine (d) γ-aninobutyric acid

12. The amine that cannot liberate nitrogen on reaction with nitrous acid is
(a) ethylamine (b) *t*-butylamine
(c) trimethylamine (d) isopropylamine

13. Which is expected to have the highest p^{Kb} value?
(a) NH_3 (b) $R_3C–NH_2$
(c) R_2NH (d) $R–NH_2$

14. The correct order of basicities of the following compounds is



I II III IV

(a) 2 > 1 > 3 > 4 (b) 1 > 3 > 2 > 4
(c) 3 > 1 > 2 > 4 (d) 1 > 2 > 3 > 4

15. Which of the following reagents can be used for separation as well as distinction of 1°, 2° and 3° amines?
(a) HNO_2 (b) $CHCl_3$ + KOH
(c) $C_6H_5OSO_2Cl$ (d) $CS_2/HgCl_2$

16. $R_2NH + [HNO_2] \longrightarrow$ X.. The product X is
(a) $R_2NH_3NO_2^-$ (b) $R_2N–NO_2$
(c) $R_2N–NO$ (d) RNH–NO

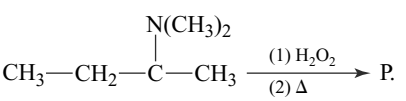
17. Total number of isomers expected from C_3H_9N are
(a) 2 (b) 3
(c) 5 (d) 4

18. $PhCOCl + CH_3—NH_2 \xrightarrow{C_2H_5N}$ A. The product A is
(a) $PhCOC_5H_5N$ (b) $PhCON(CH_3)_2$
(c) $PhCONHCH_3$ (d) PhCONHPh

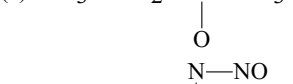
19.

The dominant product M is
(a) $CH_2=CH–CH_2–CH_3$
(b) $CH_3–CH=CH–CH_3$
(c) $CH_3–CH_2–CH_2–NHCH_3$
(d) $CH_3–CH_2–CH_2–CH_2–NH–CH_3$

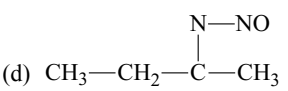
20.



The main product P is
(a) $CH_3–H_2–CH=CH_2$
(b) $CH_3–CH=CH–CH_3$
(c)



(d)



21. $R—Cl + NaN_3 \longrightarrow A \xrightarrow{LiAlH_4}$ B. The product B is
(a) R–NHNH2 (b) R–NH2
(c) RNH–NH–NH_2 (d) R_2NH

22. Which of the following can form 2° amines on reduction?
(a) R–NC (b) R–CN
(c) $R–NO_2$ (d) $R–CONH_2$

23. The boiling point order for (1) CH_3NH_2, (2) $(CH_3)_2NH$ and (3) $(CH_3)_3N$ is
(a) 1 < 2 < 3 (b) 3 < 1 < 2
(c) 1 < 3 < 2 (d) 2 < 3 < 1

24. Which of the following are isolable intermediates in Hoffmann's degradation of amides?

(a) R–CONHBr (b) $RCONBr_2$

(c) $RCON^{\sigma}Br$ (d) RNCO

25. Which of the following statements is true for Hoffmann's rearrangement with migrating group having chiral centre?

(a) It proceeds with complete inversion of configuration.

(b) It proceeds with complete retention of configuration.

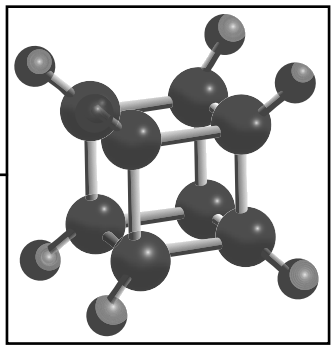
(c) It proceeds with complete racemization of configuration.

(d) It proceeds with both retention and inversion.

Answers

1. (c)	2. (b)	3. (c)	4. (c)	5. (c)
6. (b)	7. (b)	8. (b,d)	9. (c)	10. (c)
11. (b)	12. (c)	13. (a)	14. (b)	15. (c)
16. (c)	17. (d)	18. (c)	19. (b)	20. (a)
21. (b)	22. (a)	23. (c)	24. (a,c,d)	25. (a)

CHAPTER 17



Carbohydrates

Carbohydrates are naturally occurring polyhydroxy aldehydes or polyhydroxy ketones or substances, which are hydrolyzed to form them. They are optically active. They have the general formula $C_x(H_2O)_y$, that is the hydrate of carbon, and so the name carbohydrate. They are also called saccharides.

Carbohydrates are the various sugars, the starches and cellulose and glycogen. They are important for the maintenance of life in both plants and animals.

Carbohydrates are formed in green plants by photosynthesis. It is a complex chemical combination of CO_2 and H_2O in the presence of sunlight (visible light) and chlorophyll (a green plant pigment). The overall reaction is

$$6CO_2 + 6H_2O \xrightarrow[\text{Chlorophyll}]{h\nu} \underset{\text{Glucose}}{C_6H_{12}O_6} + 6O_2$$

Polymeric substances such as starches and cellulose, $(C_6H_{10}O_5)n$, with $n > 1000$ are also formed by a series of enzyme-catalysed reactions.

Carbohydrates are important in many ways. Our food such as starch-containing grains, fruits and honey contains carbohydrates. They are actually the ultimate source of energy.

Carbohydrates are broken down to the starting materials by animal metabolic reaction. It is reversal of photosynthesis, which produces energy that is used by animals for sustenance of life.

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O + \text{Energy}$$

We clothe ourselves with cotton, linen and rayon, which are cellulose. Furnitures, house doors and windows are made of wood, which is cellulose. Paper, the indispensable material for present civilization, is made of cellulose.

CLASSIFICATION AND NOMENCLATURE

Carbohydrates are generally known by their common names that end in 'ose', those with an aldehyde group as aldoses and those with a keto group as ketoses.

Carbohydrates have been classified into three main groups:

Monosaccharides

They are polyhydroxy aldehydes or ketones, which cannot be hydrolyzed to smaller units. They are further classified according to the number of carbon atoms. Those having three, four, five and six carbon atoms are known as trioses, tetroses, pentoses and hexoses, respectively.

Oligosaccharides (in Greek, oligos means few)

Carbohydrates that are hydrolyzed to two to nine monosaccharides are known as oligosaccharides. In oligosaccharides smaller units are joined together by acetal-type linkages. They are further subdivided into the following groups:

Disaccharides

They hydrolyze to two monosaccharide units. For example, lactose, maltose and sucrose.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} \xrightarrow[\text{Hydrolysis}]{H_2O} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

Trisaccharides

They hydrolyze to three molecules of monosaccharides, example raffinose.

$$C_{18}H_{32}O_{16} + 2H_2O \longrightarrow \underset{\text{Galactose}}{C_6H_{12}O_6} + \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

Polysaccharides

They hydrolyze to several (>10) monosaccharide units, example starch and cellulose having the general formula $(C_6H_{10}O_5)_n$.

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} + nH_2O \longrightarrow \underset{\text{Glucose}}{nC_6H_{12}O_6}$$

Some important naturally occurring carbohydrates are given below:

Table 17.1 Naturally occurring carbohydrates

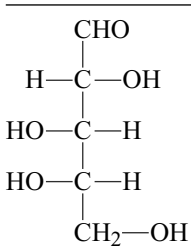
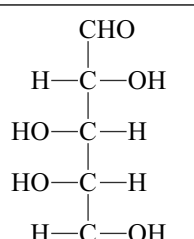
Monosaccharides	
Pentoses ($C_6H_{10}O_5$)	**Hexoses ($C_6H_{12}O_6$)**
L-arabinose	D-glucose
D-ribose	D-galactose
D-xylose	D-mannose
	D-fructose
Oligosaccharides	
Disaccharides ($C_{12}H_{22}O_{11}$)	**Trisaccharides ($C_{18}H_{32}O_{16}$)**
Sucrose (D-glucose + D-fructose)	Raffinose (D-glucose + D-fructose + D-galactose)
Maltose (D-glucose + D-glucose)	
Lactose (D-galactose + D-glucose)	
Polysaccharides	
Plants	**Animals**
Starch	Glycogen
Cellulose	

Most naturally occurring monosaccharides are pentoses or hexoses. The most abundant aldopentoses (five carbon sugars containing an aldehyde group) are L-arabinose, D-ribose, D-xylose and 2-deoxy-D-ribose (deoxy means without oxygen, thus, 2-deoxy-D-ribose is D-ribose in which the 2-hydroxyl group is replaced by hydrogen). D-ribose is a component of ribonucleic acid (RNA) and Vitamin B_{12}. 2-deoxy-D-ribose is part of the deoxyribonucleic acid (DNA) chain.

There are three important aldohexoses, D-glucose, D-mannose and D-galactose. Among these, D-glucose is the most abundant in nature.

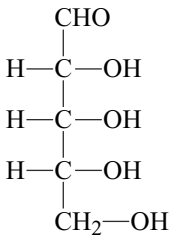
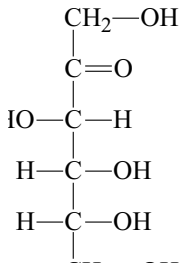
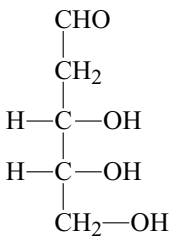
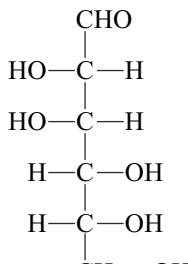
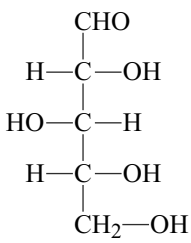
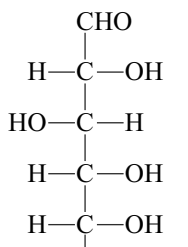
There is another important monosaccharide, D-fructose (a ketohexose) that is found in fruit juices and in honey. Linked to glucose it forms the disaccharide sucrose, which is common table sugar. The structures and configurations of aldeopentoses, aldohexoses and fructose are given below. They exist largely in the cyclic form involving combination of the carbonyl group and a hydroxyl group further down the chain. (We shall see it later.)

Table 17.2 Structure and configuration of pentoses and hexoses

Pentoses	**Hexoses**
 L-arabinose	 D-galactose

(*continued*)

Table 17.2 (*continued*)

Pentoses	Hexoses
 D-ribose	 D-fructose
 2-Deoxy-D-ribose	 D-mannose
 D-xylose	 D-glucose

SUGARS AND NON-SUGARS

Sugars are carbohydrates, which are soluble in water and sweet in taste. Monosaccharides and disaccharides are sugars. The polysaccharides are tasteless and insoluble in water and are known as non-sugars.

REDUCING AND NON-REDUCING SUGARS

Carbohydrates that reduce Tollen's reagent (ammoniacal $AgNO_3$ solution) or Fehling's solution (Cu^{2+} stabilized by tartarate ion in alkaline medium) or Benedicts solution are known as reducing sugars. All monosaccharides (aldoses or ketoses) are reducing sugars. Most disaccharides are also reducing sugars but sucrose is non-reducing sugar (reason we shall see later in this chapter).

Monosaccharides

Monosaccharides are colourless, sweet, water-soluble compounds. Sugars, D(+) glucose; (an aldohexose) and D(–) fructose (a ketohexose) are the most abundant naturally occurring monosaccharides. Glucose occurs in honey (a mixture of glucose and fructose) and sweet fruits like grapes and mangoes. Glucose is a crystalline compound (MP 146°C). It is dextrorotatory; the optical rotation of a fresh solution of glucose is +112°C (which decreases to +52°C on keeping the solution for some time). Glucose is also known as dextrose because of its dextrorotatory nature. It can be obtained by hydrolysis of sucrose.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^{\oplus}} \underset{D(+)\text{ glucose}}{C_6H_{12}O_6} + \underset{D(-)\text{ glucose}}{C_6H_{12}O_6}$$

On commercial scale, glucose is obtained by hydrolysis of starchy substances, example maize, rice and potatoes.

Fructose is the most important ketohexose. It is found in many fruits (so called fruit sugar). It is a crystalline substance, MP 120°C. Fructose is laevorotatory (–92°C) and is also known as laevulose. It is the sweetest sugar.

Commercially, fructose is obtained by hydrolysis of inulin (a polysaccharide found in dahlia tubers).

$$(C_6H_{10}O_5)_n + nH_2O \xrightarrow{H^{\oplus}} \underset{\text{Fructose}}{nC_6H_{12}O_6}$$

Glucose and fructose are constituents of sucrose (a disaccharide, cane sugar). When sucrose, which is dextrorotatory, is hydrolyzed, an equimolar mixture of glucose and fructose with a net negative rotation is obtained. This is known as inversion of cane sugar.

Reaction of D(+) glucose

D(+) glucose is an aldohexose. It has the molecular formula $C_6H_{12}O_6$ (which is established by elemental analysis and molecular weight determination). It has a –CHO group, one primary alcoholic group (CH_2–OH) and four secondary alcoholic groups (CH–OH).

It gives the following reactions:

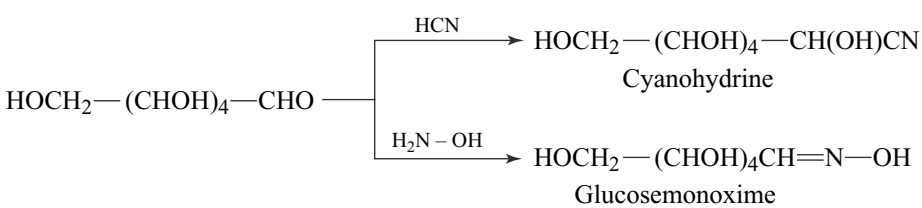
1. Glucose on acetylation with acetic anhydride gives pentaacetate.

$$OHC—(CHOH)_4—CH_2—OH \xrightarrow{(CH_3CO)_2O} OHC—(CHOCOCH_3)_4—CH_2OCOCH_3$$

It also forms pentamethyl derivative when heated with $(CH_3)_2SO_4$ and NaOH.

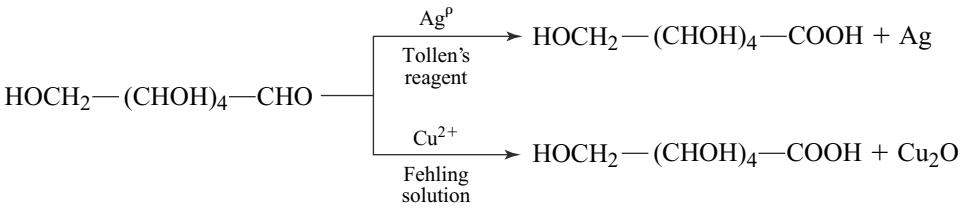
Both the above reactions show that glucose has five –OH groups.

2. Glucose reacts with HCN to form a cyanohydrine, and with hydroxyl amine (H_2N–OH) it gives a monoxime.

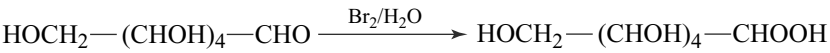


Oxidation

1. Tollen's reagent and Fehling's solution (mild oxidizing agents) oxidize glucose (reducing agent) to gluconic acid. This proves the presence of –CHO group in glucose.

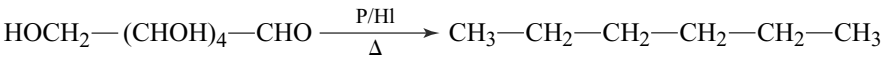


2. Br_2-water (a mild oxidizing agent) oxidizes glucose to gluconic acid. This also proves the presence of –CHO group in glucose.



3. Nitric acid oxidizes glucose to a dicarboxylic acid, saccharic acid. It shows the presence of a primary alcoholic group (CH_2–OH) in glucose.

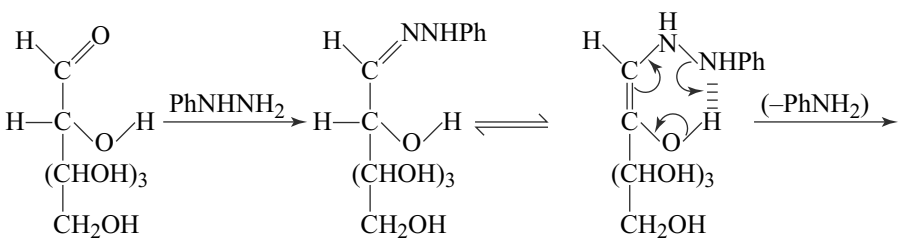
4. Glucose on heating with HI and phosphorus gives *n*–hexane. It suggests that all six carbon atoms in glucose are present in a straight chain.

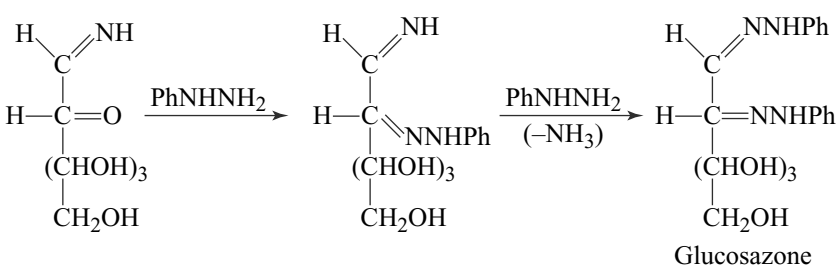


On the basis of the above reactions, Baeyer proposed the open-chain structure of glucose as

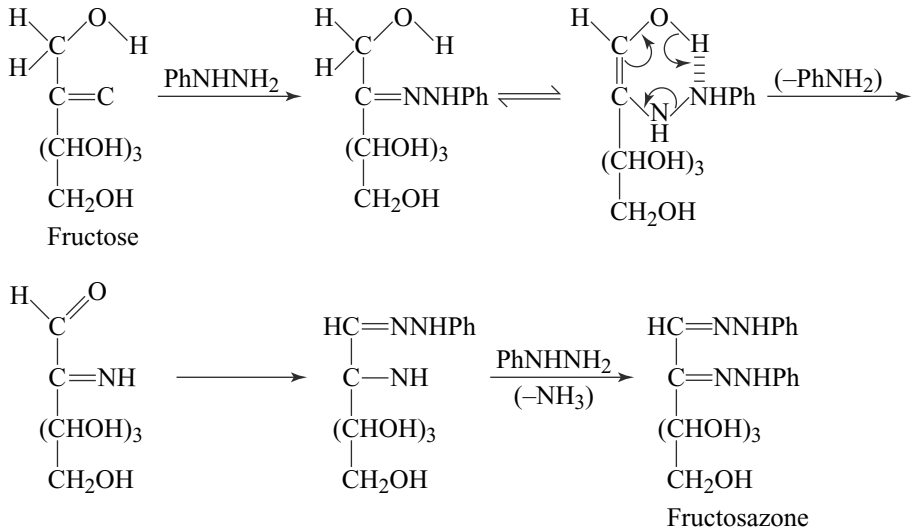
Reactions of D(+) glucose (and fructose) with phenyl hydrazine (osazone formation).

Glucose (or fructose) when treated with phenyl hydrazine (in 1:1 ratio) forms a phenyl hydrazone. However, with excess of phenyl hydrazine a yellow to orange crystalline solid, the osazone, is formed.

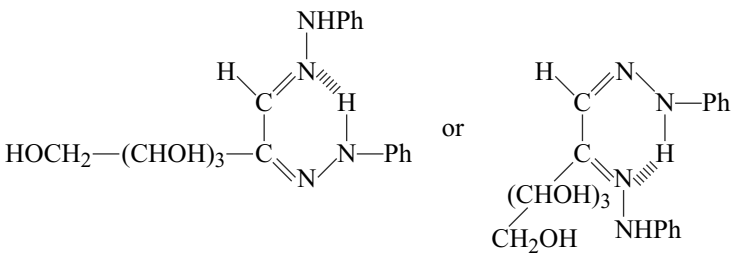




Osazone from Fructose



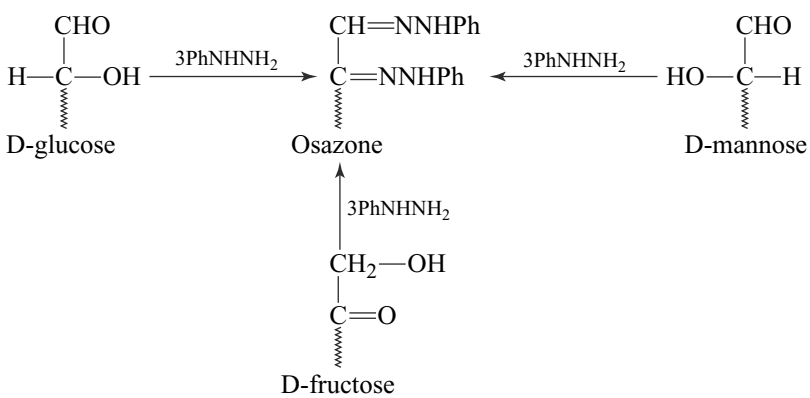
The osazone is stabilized by chelation.



This structure is supported by X-ray studies and nuclear magnetic resonance spectra. Such an intramolecular H-bonding does not allow reaction to proceed beyond the second carbon.

Some important points

1. Formation of osazone requires three moles phenyl hydrazine per mole of sugar.
2. First two carbon atoms of the sugar are involved in osazone formation.
3. Glucose, fructose and mannose (D-forms) form the same osazone.



It shows that configuration at C-3, C-4 and C-5 are the same in all the three sugars.

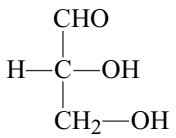
4. Not only sugars, α-hydroxy ketones also form osazone, example benzoin PhCHOHCOPh.
5. Osazones of different sugars differ in crystal shape. This property is used analytically to identify a particular sugar by observing its osazone through microscope.

Configuration of D(+) glucose

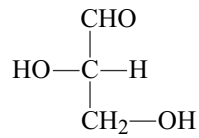
The open-chain structure of D(+) glucose is,

$$HOCH_2—\overset{*}{C}HOH\overset{*}{C}HOH\overset{*}{C}HOH\overset{*}{C}HOHCHO$$

It contains four chiral centres (marked by stars). Therefore, it can form $2^4 = 16$ optical isomers. All are known, but which of them is D(+) glucose? This problem was solved by E. Fisher. Fisher arbitrarily took glyceraldehyde as standard. He assigned the configuration D to glyceraldehyde that bears –OH group towards right in the Fisher projection formula and configuration L(–) to its image, that is

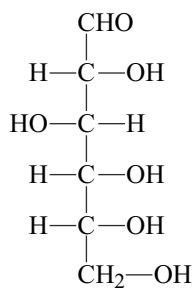


D(+) glyceraldehyde



L(−) glyceraldehyde

The configuration of all sugars has been determined by comparing them with D- or L-glyceraldehydes. On this basis, D(+) glucose has the configuration

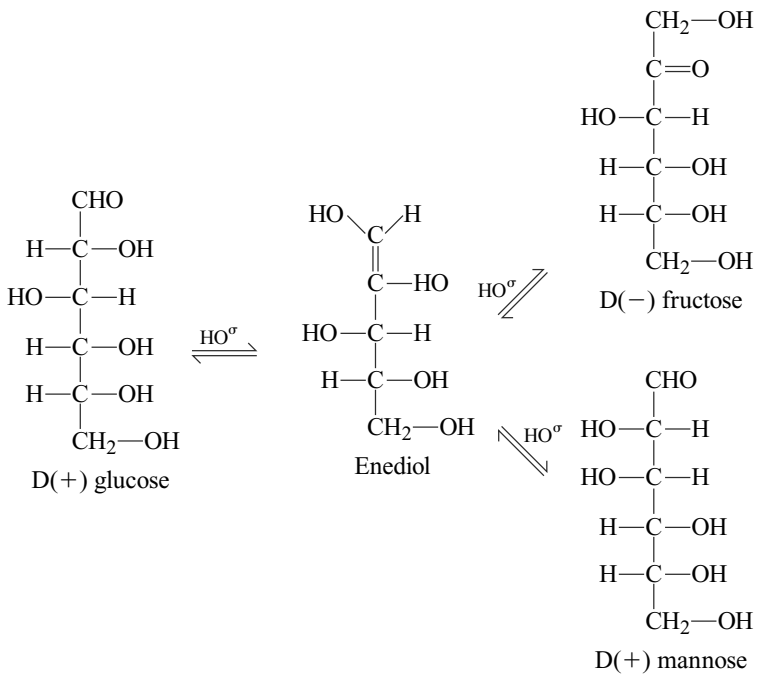


D(+) glucose

Reaction of D-glucose with dilute NaOH (Lobry–de Bruyn–van Ekenstein Rearrangement)

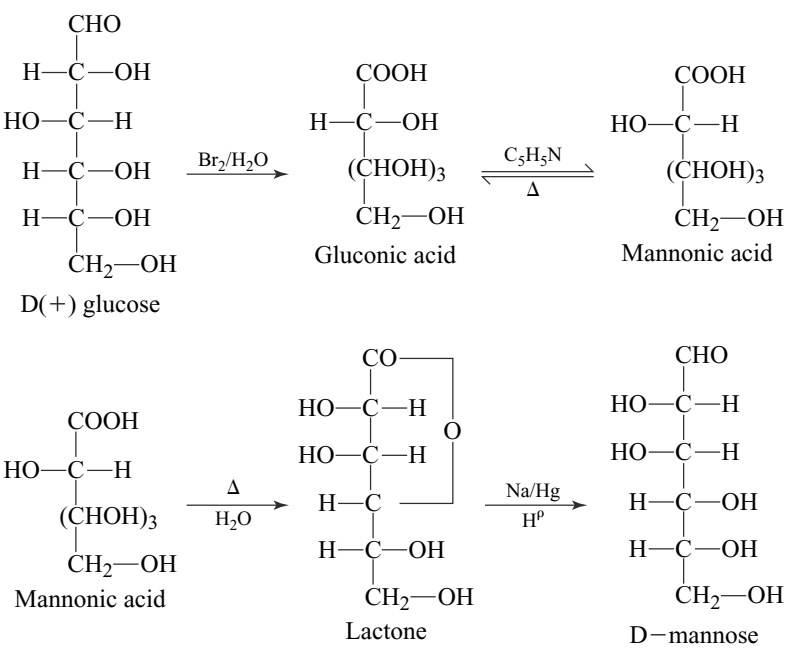
When D-glucose is treated with dilute NaOH, a mixture of D-glucose, D-mannose and D-fructose is obtained. This reaction is known as Lobry–de Bruyn–van Ekenstein rearrangement. It is quite general for monosaccharides.

It has been shown that this isomerization involves the formation of an enediol as transient intermediate. In this stage, stereochemistry at C-2 vanishes due to formation of a C–C double bond.



Epimerization

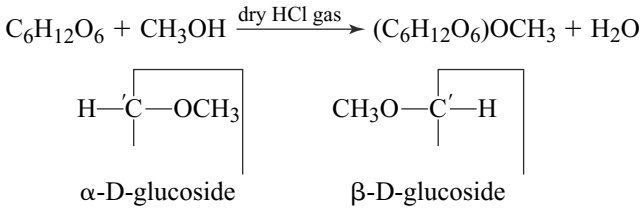
A pair of diastereomeric aldose that differ only in configuration about C-2 are called epimers, example D(+) glucose and D(+) mannose. The interconversion of such diastereomers is called epimerization. It occurs through aldonic acid. The aldonic acid is heated with pyridine when equilibrium is set up between the aldonic acid and its epimer. The two acids are then separated by fractional crystallization. The epimeric acid lactone is reduced by Na(Hg) to the epimeric aldose.



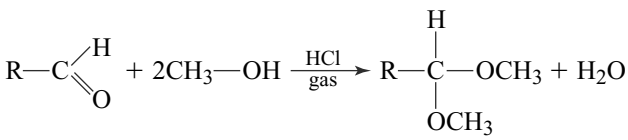
The reaction is proved to be useful for producing relatively unavailable sugar from their more plentiful isomer.

Glucoside formation

Glucose reacts with methyl alcohol (monohydric alcohol) in the presence of dry HCl gas to form acetals, which are called methylglucosides. Glucose forms two methyl glucosides, which are methyl α-D-glucoside and methyl β-D-glucoside.



This is the reaction under which an aldehyde is converted to a dimethyl acetal.

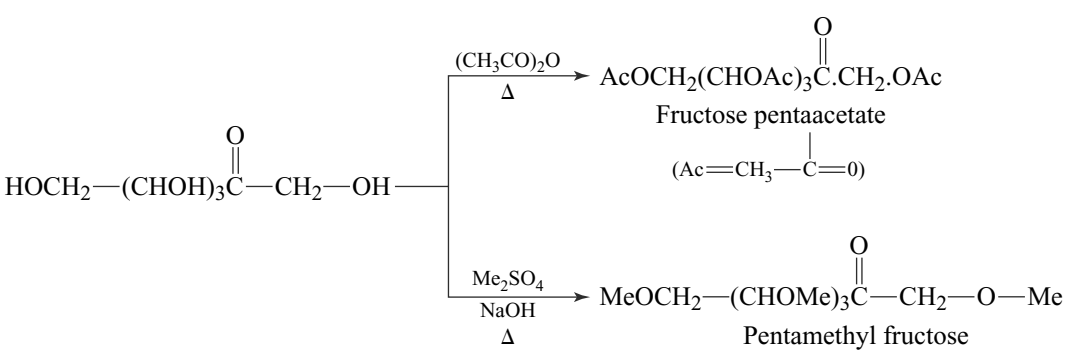


Reactions of D(–) fructose

Fructose is a ketohexose. Its molecular formula is $C_6H_{12}O_6$. It has two primary alcoholic (CH_2–OH) groups, three secondary alcoholic (CH–OH) groups and a ketonic (>C=O) group. It gives the following reactions:

Reaction of –OH groups

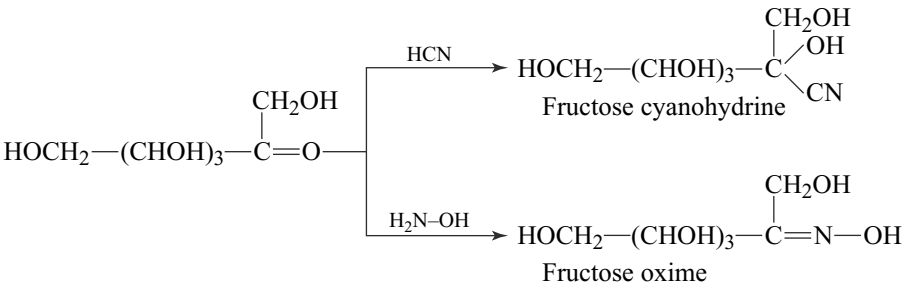
Fructose forms pentaacetyl derivative when heated with acetic anhydride. It also forms pentamethyl derivative when heated with dimethyl sulphate (Me_2SO_4) and NaOH.



These reactions show that fructose has five hydroxyl (–OH) groups.

Reactions of >C=O group

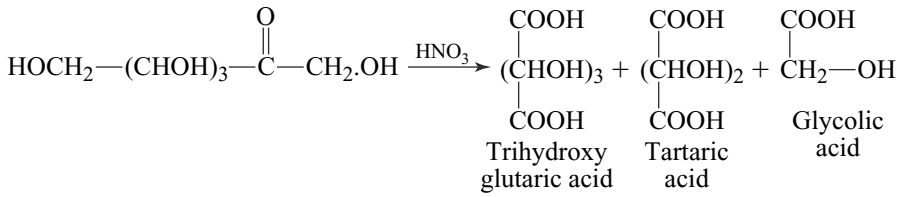
Fructose forms cyanohydrine with HCN and a monoxime with hydroxyl amine (H_2N–OH).



These reactions show presence of carbonyl group (>C=O) in fructose.

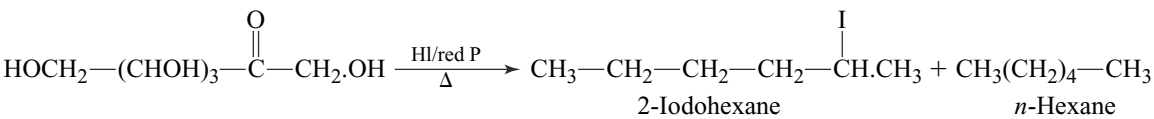
Oxidation of fructose

Fructose is not oxidized by a mild oxidizing agent, such as Br_2–water. However, it is oxidized by nitric acid to a mixture of trihydroxy glutaric acid, tartaric acid and glycolic acid. All these acids contain lesser number of carbon atoms than fructose. It shows that carbonyl group in fructose must be ketonic in nature (ketones are always oxidized with cleavage of C–C bonds).



Reduction

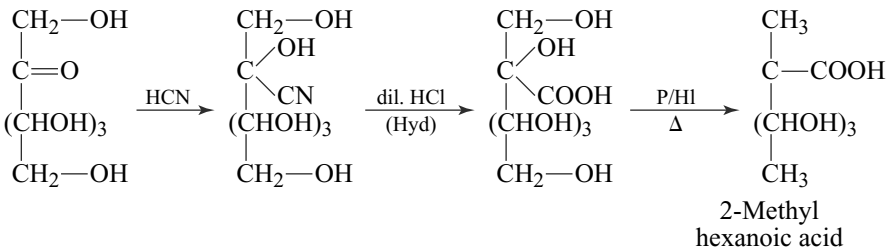
Fructose when reduced with red P and HI, a mixture of 2-iodohexane and n-hexane are produced.



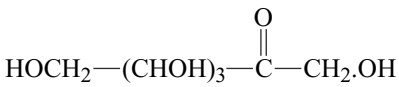
This reaction shows that all the carbon atoms in fructose are present in a straight chain.

Position of keto group in fructose

When the cyanohydrine of fructose is hydrolyzed (by dilute HCl) and the product is reduced with HI and red P, 2-methyl hexanoic acid is obtained. The branching at the second carbon indicates that fructose is a 2-ketohexose.



On the basis of the above reactions, the open-chain structure of fructose was proposed as

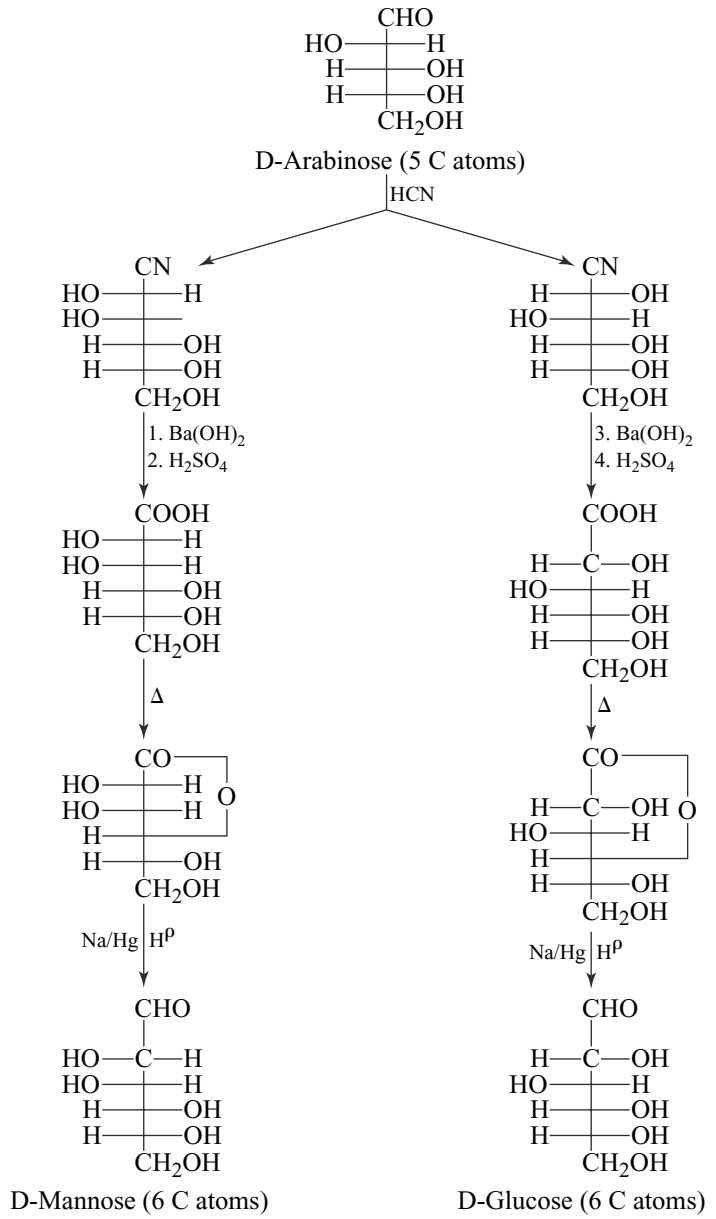


ASCENDING (OR CHAIN LENGTHENING) SUGAR SERIES

There are many methods for this purpose. The most common and classical method is Kiliani reaction. It consists of four steps:

1. Formation of cyanohydrine of the aldose.
2. Hydrolysis of cyanohydrine to carboxylic acid.
3. Conversion of carboxylic acid to lactone.
4. Reduction of lactone with Na-amalgam to an aldose having one more C atom in the chain.

Formation of cyanohydrine converts the aldehydic carbon into a new chiral centre. As such a mixture of two steroisomeric cyano hydrines is obtained, example conversion of D-arabinose to D-glucose (and D-mannose).



Actually one of the epimers predominates in this method.

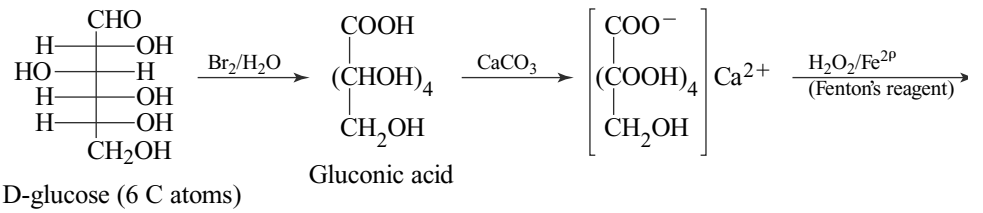
DESCENDING SUGAR SERIES (CHAIN SHORTENING)

Many methods have been used to reduce number of carbon atoms in an aldose. The common ones are (i) Ruff degradation and (ii) Wohl's degradation.

Ruff Degradation

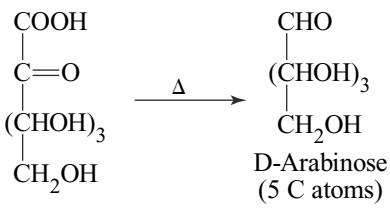
This reaction consists of the following steps:

1. Aldose to aldonic acid by Br_2-water oxidation.
2. Conversion of aldonic acid to its Ca salt.
3. Ca salt to α-keto acid.
4. Heating of a-keto acid to lower aldose.



D-glucose (6 C atoms)

Gluconic acid

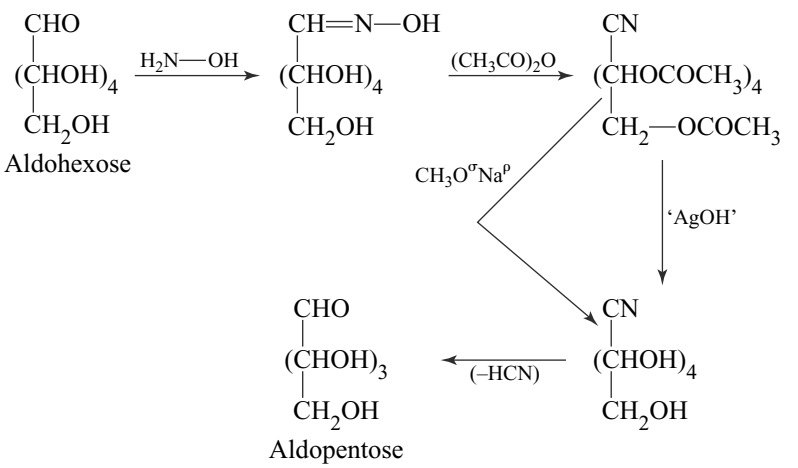


D-Arabinose
(5 C atoms)

Wohl's Degradation

This method consists of the following steps:

1. Aldose to oxime by reaction with hydroxyl amine.
2. Conversion of oxime to cyano compound by heating with acetic anhydride (dehydration).
3. Conversion of cyano compound to lower aldose by heating with ammoniacal silver nitrate.



Aldohexose

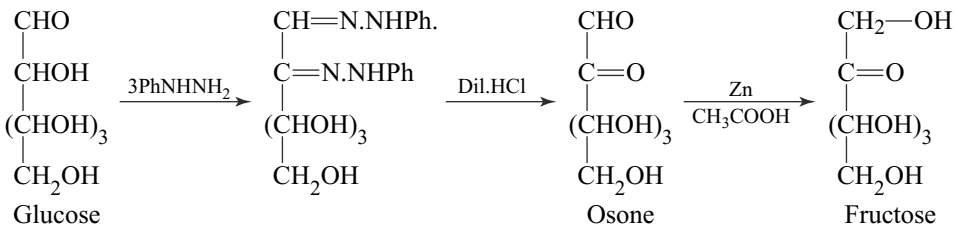
Aldopentose

The use of a solution of $CH_3O^{\sigma}Na^{\rho}$ in chloroform instead of an aqueous solution of ammoniacal silver nitrate gives better yield of the final product. This is Zemplen's modification.

Both the above methods start with an aldose. Therefore, if a ketohexose has to be converted into a ketopentose, it is first transformed into the corresponding aldohexose.

Interconversion of Aldose to ketose

One such example is the conversion of glucose into fructose. Glucose is interacted with excess phenyl hydrazine to form the osazone. The osazone is then hydrolyzed with dilute HCl to the osone. Reduction of this osone with zinc and acetic acid results in the formation of fructose.

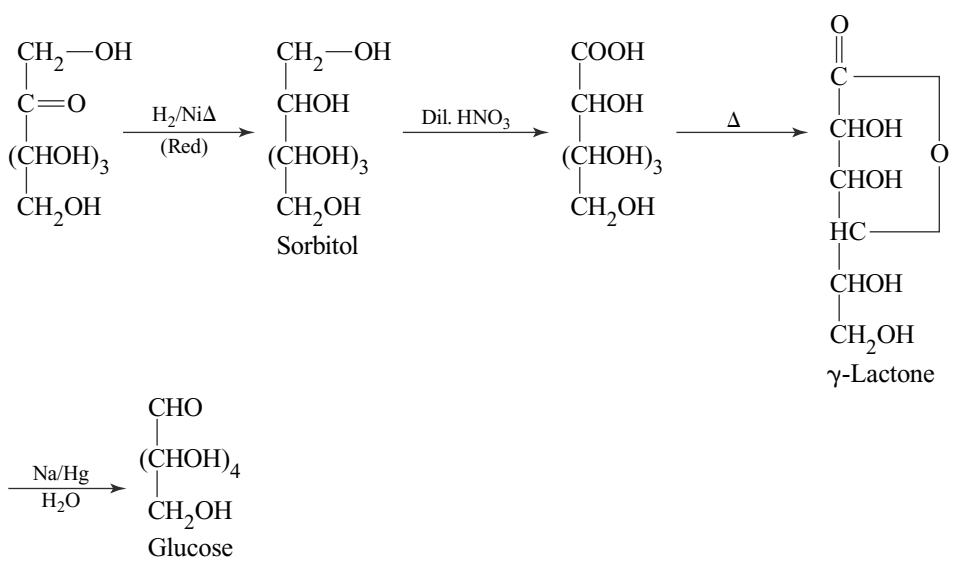


In the reduction step, aldehyde group (–CHO) is reduced over ketonic group (>C=O) preferentially.

Interconversion of Ketose to aldose

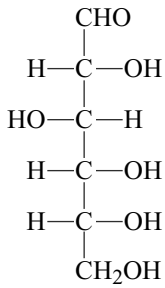
One such example is the conversion of fructose into glucose.

Fructose is first catalytically hydrogenated to a polyhydric alcohol, sorbitol. This alcohol on oxidation with dilute HNO_3 gives a monocarboxylic acid. This on heating forms a *γ*-lactone that on reduction gives glucose (aldose).



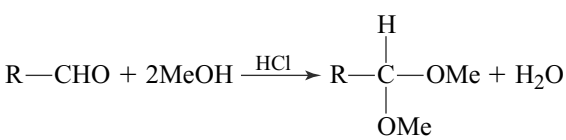
Ring structure of D(+) glucose (cyclic structure)

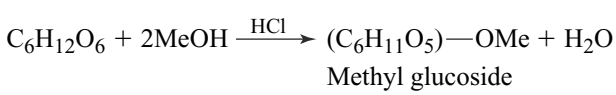
By all physicochemical methods available, the open-chain structure with configuration of D(+) glucose was established as



However, the above structure fails to explain a number of facts such as the following:

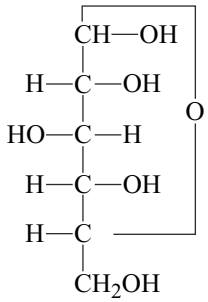
1. Unlike aldehydes, neither does glucose give Schiff test nor does it form an addition compound with $NaHSO_3$.
2. D(+) glucose exists in two isomeric forms known as α- and β-D-glucose. The α-form of D(+) glucose (or ordinary glucose) obtained by crystallization from aqueous ethanol has a m. p. of 146°C and a specific rotation of $[\alpha]_D = +112^\circ C$ in aqueous solution. On the other hand, when D-glucose is crystallized from its saturated solution at 110°C, (or from pyridine) a new form, the β-D-glucose with a m. p of 150°C and a rotation of $[\alpha]_D = +19^\circ C$ is obtained.
3. The open-chain structure does not account for mutarotation. The specific rotation of a freshly prepared solution of α-D-glucose falls from +112°C to +52°C and that of the β-forms increases from +19°C to +52°C, that is the α- and β-forms of D-glucose in solution slowly changes into an equilibrium mixture of both, α-D(+) glucose ≡ Eq mix ≡ β-D(+) glucose.
4. D(+) glucose forms two different monomethyl derivatives (called methyl glucosides) with methanol and anhydrous HCl. This is the condition under which an aldehyde is converted to a dimethyl acetal.





The glucosides do not reduce Fehling's solution or Tollen's reagent and do not undergo mutarotation (as –OH is not at C-1). Methyl glucosides are not hydrolyzed by water, acid hydrolysis is required to convert them into methanol and glucose.

To account for these experimental facts, a cyclic structure was proposed for D-glucose in which the carbonyl group is not free, rather it is tied up in combination with the –OH group situated at C-5 to form a hemiacetal as shown below:

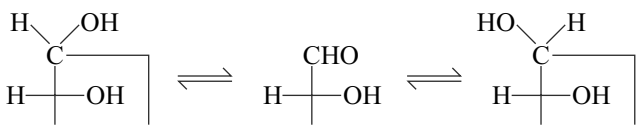


The formation of the cyclic hemiacetal generates a new chiral centre at C-1. Two structures are thus possible differing in configuration about C-1. The isomer having –OH at right side is called α-D-glucose whereas that having –OH on the left side is called β-D-glucose, thus leading to the two isomeric glucosides.

α-D-glucose
II

β-D-glucose
III

Such a pair of diastereomeric sugars, which differ in configuration around C-1 are called anomers. In aqueous solution, these hemiacetals undergo facile hydrolysis to open-chain form I which then again forms hemiacetal ring giving either of the anomers. This facile opening and the closing of the hemiacetal ring accounts for mutarotation.



α-D
II

I

β-D
III

The presence of small amount of the open-chain form explains the reactions like osazone formation, reduction of Fehling's solution ($Cu^{II} \longrightarrow Cu^{I}$) and Tollen's reagent ($Ag^{I} \longrightarrow Ag^{0}$). The reaction with Schiff reagent and bisulphite is reversible and the concentration of open-chain form is too low for a reasonable yield.

Ring size in D(+) glucose

Like a six-membered ring (pyranose form) as is proposed for D(+) glucose, a five-membered ring (furanose form) is also possible by ring closer at C-4. However, ring closer at C-2 and C-3 is ruled out because such small rings are not so stable.

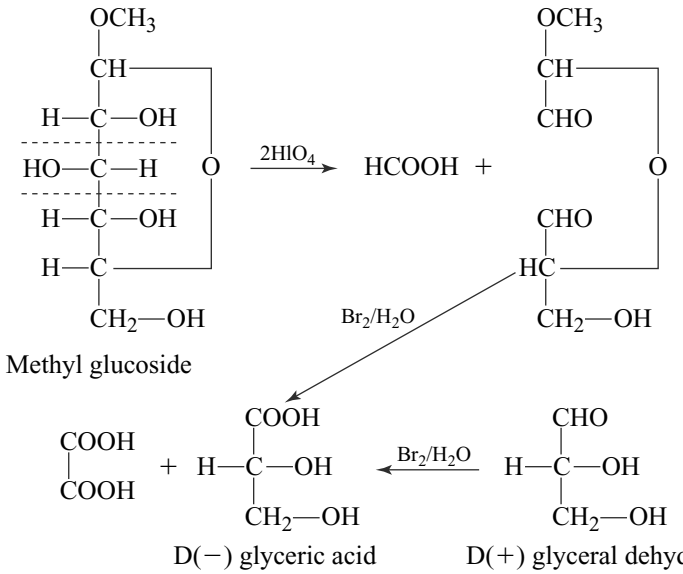
Pyran

Furan

There are various methods to determine ring size such asHaworth method and (ii) periodic acid method.

The second one is an elegant method of determining both the ring size of glucosides and the configuration at position of glycosidic linkage.

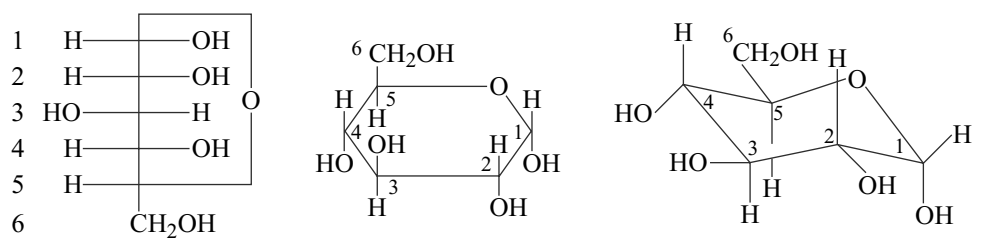
Periodic acid splits 1,2-glycols, and one molecule of acid is used for each pair of adjacent alcoholic groups. The pyranoside consumes 2 moles of HIO_4 and produces one molecule of formic acid and an acetal dialdehyde.



Oxidative hydrolysis of the acetal dialdehyde gives D(–) glyceric acid and oxalic acid. Since D(+) glyceraldehyde is oxidized to D(–) glyceric acid, the configuration at C-5 of D(+) glucose and D(+) glyceraldehyde are the same. The above sequence of reactions exclusively proves ring closer at C-5. X-ray analysis also supports this structure.

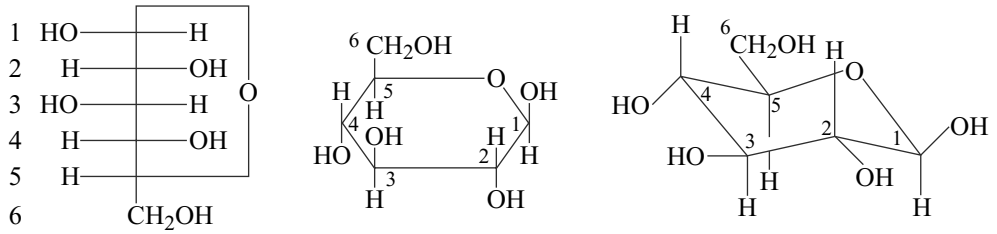
Since glucose has a six-membered ring (like cyclohexane), the predominant conformation is chairform. X-ray analysis of crystalline α-D-glucose supports this. The –OH groups located on C-2, C-3, C-4 and the CH_2–OH group on C-5 occupy equatorial positions in α- and β-forms both. But the –OH group on C-1 is axial in the α-form and equatorial in the β-form. It suggests that the β-form (or β-anomer) should be of slightly lower energy, that is more stable than the α-form. (In the α-form, the –OH group at C-1 will suffer 1,3-diaxial interactions with the H atoms at C-3 and C-5).

Ring structures of α- and β-D(+) glucose



α-D(+) Glucose MP = 146°C. $[\alpha]_D = +112°$

Fig. 17.1



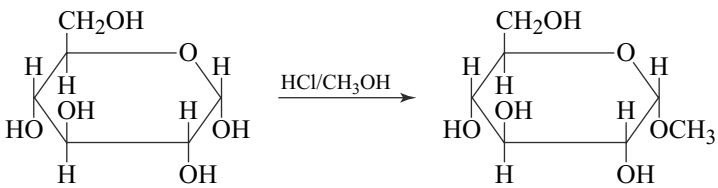
Fisher projection formula | Haworth formula | Conformational formula

β-D(+) Glucose MP = 150°C. $[\alpha]_D = +19°$

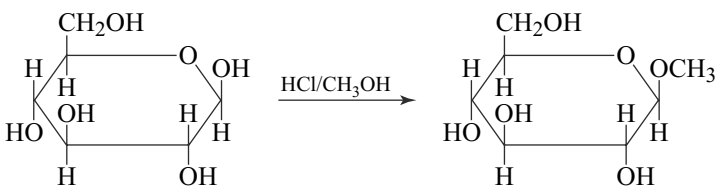
Fig. 17.2

Glycosides, aglycone and N-glycosides

Abundantly glucose and fructose occur in the free state in nature, but they and some other sugars are found combined with hydroxyl compounds. The common name for such compounds is glycoside, actually O–glycoside (it denotes that the linkage to the hydroxyl compounds is through oxygen). For example, the methyl glucosides of glucose formed by the acid-catalysed reaction of methanol with a molecule of glucose.



α-D glucose | Methyl α-D Glucoside
MP = 150°C. $[\alpha] = +158°$

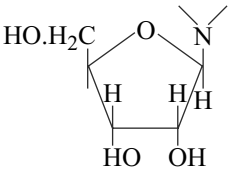


β-D glucose | Methyl β-D Glucoside
MP = 107°C. $[\alpha]_D = -33°$

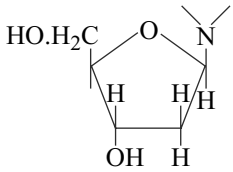
Fig. 17.3

The cyclic sugar is a hemiacetal and the glycoside is an acetal. (The glycosides do not undergo mutarotation because, being acetals, they are fairly stable in aqueous solution.)

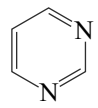
The additional group in the glycoside (methyl in the above reaction) is known as the aglycone group. In a disaccharide, the aglycone is other sugar. Polysaccharides are formed by combination of many sugars by such linkages. Biologically, the N-glycosides are very important. In N-glycosides, the sugar is D-ribose and the aglycone is linked to the sugar by a C–N bond to an N-base (generally a pyrimidine or purine derivative). These glycosides are commonly known as ribonucleosides and deoxy-ribonucleosides.



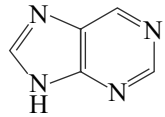
Ribonucleoside
(part structure)



Deoxyribonucleoside
(part structure)

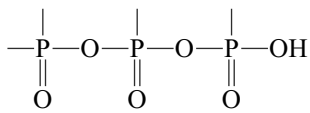


Pyrimidine

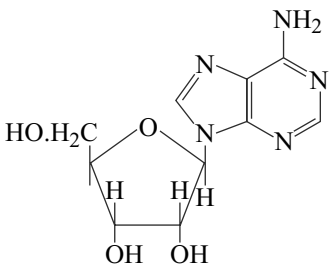


Purine

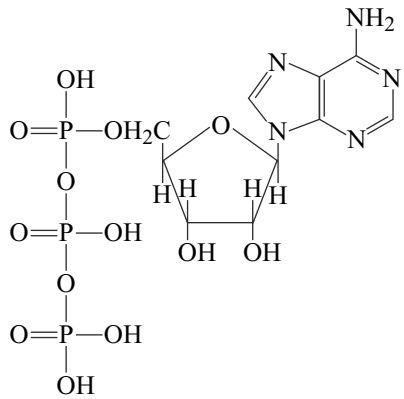
Important purine ribonucleoside is adenosine. When adenosine is esterified at the 5 position with a triphosphoryl group, the product is known as adenosine triphosphate (ATP). It is an energy-rich compound present in muscle tissues.



Triphosphoryl group



Adenosine



Adenosine triphosphate (ATP)

Disaccharides

Disaccharides contain two monosaccharide units. They on acid or enzyme hydrolysis produce the component monosaccharides (generally hexoses).

More important disaccharides are sucrose, lactose, maltose and cellobiose (molecular formula $C_{12}H_{22}O_{11}$). The hydrolysis products of these are as follows:

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+(\text{or enzyme})} C_6H_{12}O_6 + C_6H_{12}O_6$$

Sucrose ⟶ D(+) glucose + D(–) fructose

Lactose ⟶ D(+) glucose + D(+) galactose

Maltose ⟶ D(+) glucose + D(+) glucose

Cellobiose ⟶ D(+) glucose + D(+) glucose

The bond between the hexoses is an O–glycoside linkage. It may proceed in two ways:

1. One monosaccharide may link through its anomeric –OH (that is –OH at C-1) with alcoholic group of the other. This type of linking forms a reducing disaccharide, example, lactose and maltose.
2. Both the monosaccharides may also link through their anomeric –OH (that is, the –OH at C-1). It forms a non-reducing disaccharide, example, sucrose (this disaccharide is acetal type, has no reducing properties and forms no phenylosazone).

Sucrose (Cane sugar, $C_{12}H_{22}O_{11}$)

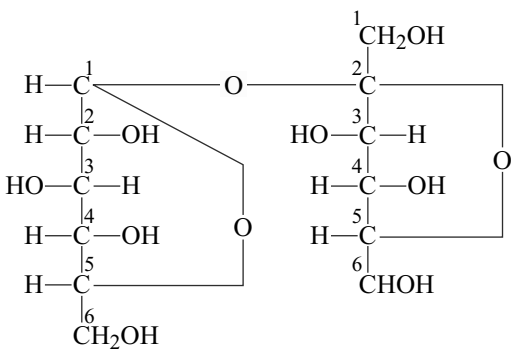
Sucrose is the most common disaccharide. It occurs widely as the free sugar in plants, fruit and honey. The principal source is sugar cane and sugar beet.

1. It is non-reducing non-mutarotating sugar.
2. It does not form osazone (unless partially hydrolyzed)
3. The above observations suggest that the potential carbonyl function of both (that is C-1 of glucose and C-2 of fructose) is tied up in the glycosidic linkage.
4. It is colourless, crystalline and sweet substance soluble in water (high solubility in water, 1.5 g sucrose dissolves in 1 g of water at room temperature).
5. Sucrose is dextrorotatory $[\alpha]_D = 66.5^\circ C$.
6. It is hydrolyzed by acid or the enzyme invertase to give an equimolar mixture of D(+) glucose and D(–) fructose.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+ \text{(or invertage)}} \underset{\text{D-Glucose}}{C_6H_{12}O_6} + \underset{\text{D-Fructose}}{C_6H_{12}O_6}$$

7 Sucrose is dextrorotatory $[\alpha] = 66.5$. D-glucose is dextrorotatory $[\alpha] = +52^\circ C$ but D-fructose has large levorotation, $[\alpha] = -92^\circ C$. The complete hydrolysis of sucrose to glucose and fructose, thus, causes an inversion of the sign of rotation and the product is known as invert sugar. (Honey is chiefly invert sugar as bees contain the enzyme invertase.)

Structure of sucrose



Fisher projection formula

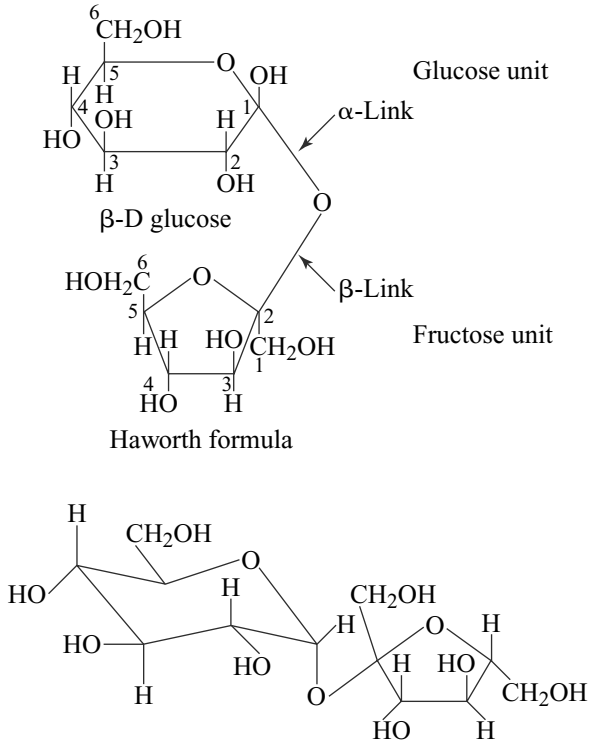


Fig. 17.4

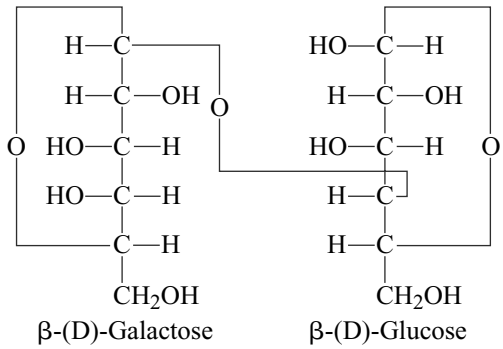
Lactose

Lactose is found in the milk of mammals (~5%). Its molecular formula is $C_{12}H_{22}O_{11}$.

1. It is a reducing sugar (reacts with Fehling's solution).
2. It forms osazone.
3. It exists in α- and β-forms and undergoes mutarotation.
4. Acid hydrolysis or treatment with emulsin (an enzyme, which splits β-linkage only) gives equal amounts of D(+) glucose and D(+) galactose.

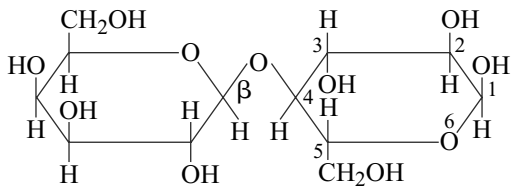
$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+(\text{or emulsin})} \underset{\text{D-glucose}}{C_6H_{12}O_6} + \underset{\text{D-galactose}}{C_6H_{12}O_6}$$

5. Chemical reactions show that (+) lactose is a substituted D-glucose in which a D-galactosyl unit is attached to one of the oxygens, that is, it is a galactoside, not a glucoside. It has the following structure:



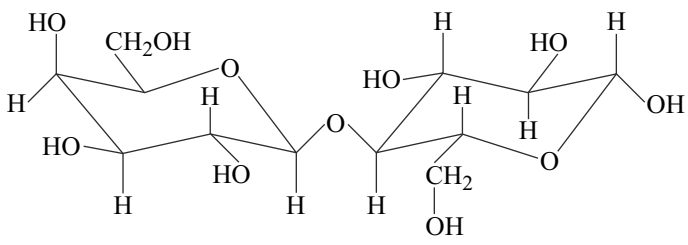
Fisher projection formula

Fig. 17.5



Lactose
Haworth formula

Fig. 17.6



Conformational formula

Fig. 17.7

Maltose

Maltose is the hydrolysis product of starch.

$$(C_6H_{10}O_5)_{11} + H_2O \xrightarrow{\beta\text{-Amylase}} \underset{\text{Maltose}}{C_{12}H_{22}O_{11}}$$

Maltose is hydrolyzed to two molecules of D(+) glucose.

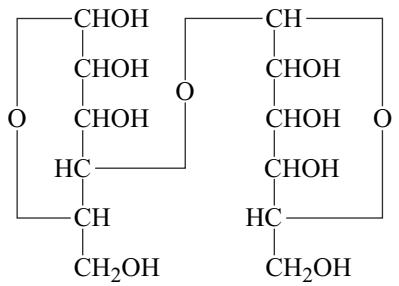
$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

1. It is a reducing sugar (reduces Tollen's reagents and Fehling's solution).
2. It forms osazone.
3. It undergoes mutarotation.

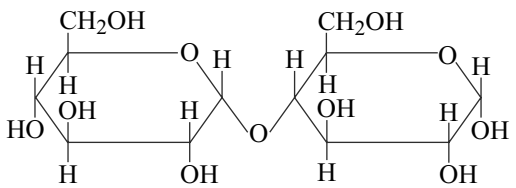
$$\underset{[\alpha] = +162^\circ}{\alpha\text{-Form}} \rightleftharpoons \underset{[\alpha] = +136^\circ}{\text{Equilibrium}} \rightleftharpoons \underset{[\alpha] = +112^\circ}{\beta\text{-Form}}$$

All the above facts show that maltose contains a carbonyl group, which is present in the hemiacetal form.

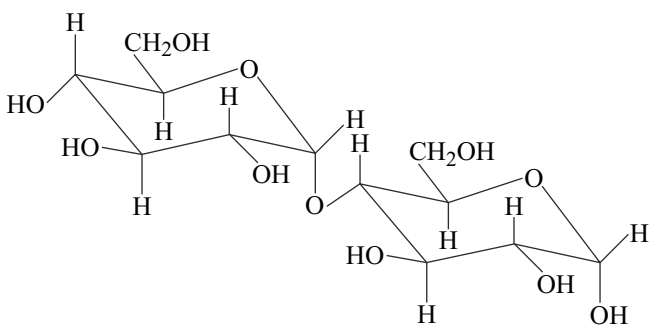
4. Evidences indicate that glucose units are linked through α-glycosidic linkage (C-1 of one glucose and the C-4 of another glucose)



Fisher projection formula



Maltose
Haworth formula



Conformational formula

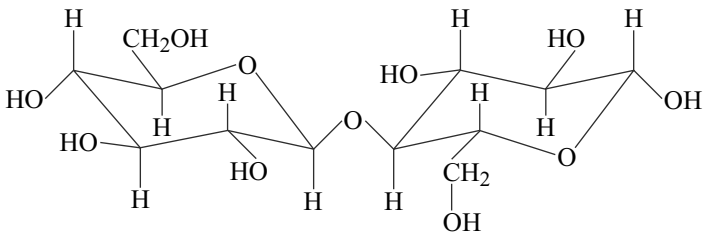
Fig. 17.8

Cellobiose

It is hydrolysis product of cotton fibres.

1. It is a reducing sugar.
2. It forms osazone.

3. It exists in α and β-forms.
4. It undergoes mutarotation.
5. It is hydrolyzed by the enzyme emulsion (which is specific for the hydrolysis of β-glycosidic linkage).
6. The above and many other evidences indicate that cellobiose contains two pyranose rings and a glucoside linkage to an –OH group on C-4.



Conformational formula

Polysaccharides

Polysaccharides are carbohydrates made up of many (hundreds or even thousands) monosaccharides. The monosaccharide units are linked together by O–glycosidic linkage which can be broken by hydrolysis.

Cellulose and starch are most important polysaccharides. Both are produced in plants from CO_2 and H_2O by photosynthesis, and are very large polymers of D(+) glucose. Their general formula is $(C_6H_{10}O_5)n$. It shows that polymerization proceeds with loss of water.

Starch

Starch is the reserve food material of plants and is found chiefly in seeds, roots and tubers. Rice, Wheat, potatoes and corn are familiar edible forms of starch. It is hydrolyzed by amylase (an enzyme) present in saliva. The ultimate product is glucose, which is source of energy. Starch occurs as granules whose shape and size differ and depends upon the plant from which it is obtained. Starch is white amorphous powder, insoluble in cold water. Solution of starch in water gives blue colour with iodine. The colour is thought to develop due to adsorption of I_2 into the channels of starch structure.

On hydrolysis with dilute acids (or enzyme), starch breaks down to molecules of variable complexity, then maltose and ultimately to D-glucose

$$(C_6H_{10}O_5)_n \xrightarrow[\text{or enzyme}]{H^{\oplus}} \underset{(m < n)}{(C_6H_{10}O_5)_m} \longrightarrow \underset{\text{Maltose}}{C_{12}H_{22}O_{11}} \longrightarrow \underset{\text{D-Glucose}}{C_6H_{12}O_6}$$

Starch is non-reducing (that is fails to reduce Tollen's reagent and Fehling's solution) and does not form osazone.

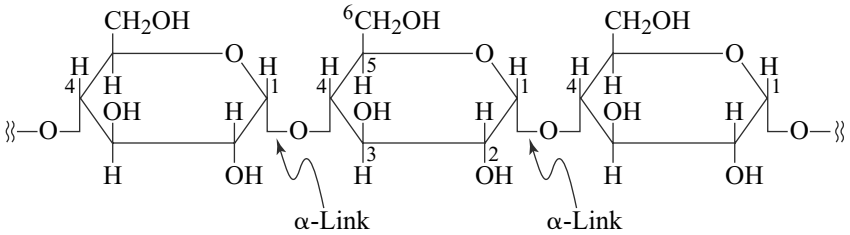
Starch contains the following:

1. A water soluble fraction called amylose (20%).
2. A water insoluble fraction called amylopectin (80%).

Amylose

Amylose on partial hydrolysis (by acid or enzyme), gives (+) maltose as the only disaccharide. Ultimate hydrolysis product is D-glucose. Evidences show that amylose is a straight chain polymer of D-glucose held together by α-glycosidic linkages involving C-1 of one glucose and C-4 of another glucose.

The molecular mass of amylose can range from 10,000–50,0000, i.e. it may have 100–3000 D-glucose units.

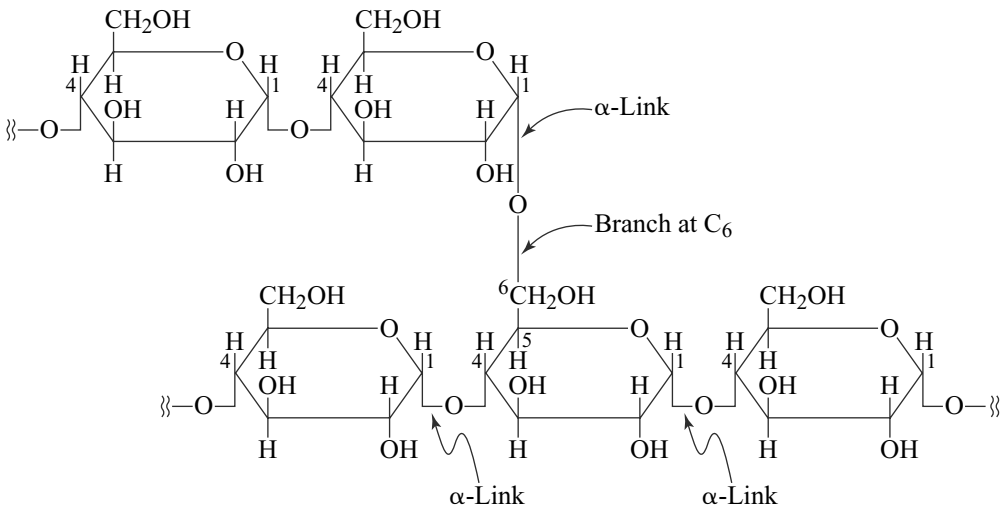


Amylose

Amylopectin

It is insoluble in water. On partial hydrolysis, it also gives (+) maltose. Chemical evidences show that it has highly branched structure. In amylopectin

1. D-glucose units are joined by α-glycosidic linkage involving C-1 of one glucose and C-4 of the other.
2. One end of each chain is joined through C-1 to a C-6 on the other chain.



Amylopectin

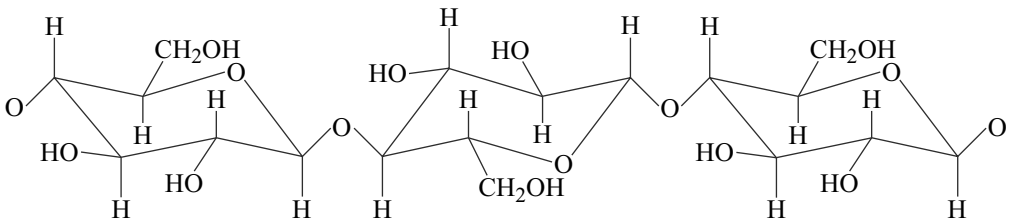
CELLULOSE

Cellulose is the chief component of plants (the fibrous tissue in the cell walls of plants) and cotton. Wood contains 45–50 per cent while cotton contains 90–95 per cent cellulose. It gives plants their texture, rigidity, form and durability.

Cellulose is highly insoluble in water having molecular formula $(C_6H_{10}O_5)n$. Cellulose is a non-reducing sugar (that is does not reduce Fehling's solution or Tollen's reagent). It does not form osazone. On vigorous reaction with dilute H_2SO_4 under pressure, it gives only D-glucose. On partial hydrolysis (by enzyme), it gives cellobiose only.

Hydrolysis products and many other evidences suggest that

1. Cellulose is a straight-chain polymer of glucose units having β-glycosidic linkage.
2. The β-glycosidic linkage is between C-1 of one glucose unit and C-4 of the other.



Cellulose

Structural analyses further show that long chains of cellulose are held together by hydrogen bonds between the –OH groups. This close packing due to H-bonding is responsible for rope-like structure of cellulose, which gives structural rigidity.

Cellulose is the natural fibre obtained from cotton, wood, hemp and jute. Wood is a combination of many substances. Most woods are about 50 per cent cellulose and about 30 per cent lignin; the remainders are other carbohydrates, fats and terpenoid resins. It is used in the manufacture of textile and paper. Many of its derivatives are also used in textile industry, such as the following:

1. *Cellulose acetate*
   It is used for making rayon acetate yarn, photographic film and cellulose acetate plastics.
2. *Cellulose nitrate and cellulose xanthate*
   These are used for making viscous rayon fibre.

Cellulose ether (Sodium carboxymethyl cellulose)

It is also known as cellulose gum. It is used as adhesive, detergent promotor and ceramic glaze binder.

Cellulose as food

Cellulose (in grasses) is food for many animals such as cow, sheep and buffalo (called ruminants, termite is also a ruminant). These creatures have ability to metabolize cellulose with the help of appropriate microorganisms in their intestinal tracts. Man, however, cannot use cellulose as food because he lacks the necessary hydrolytic enzymes.

Table 17.3 Polysaccharides and their function in cells

Polysaccharide	Chemical constitution	Source	Function
Starch	1:4- and 1:6-linked glucan	Plants	Food
Cellulose	1:4-linked glucan	Plants, microbes	Food and cell wall material
Glycogen	1:4- and 1:6-linked glucan	Animals	Food
Pectin	Galactose polymer	Cell wall and plant cytoplasm	Gelating agents
Hyaluronic acid	1:4- and 1:3-linked N – acetyl glucosamine	Ground substance in animal cells	Glue or cement
Heparin	Glucosamine sulphate, glucuronic acid	Liver tissue	Anticoagulant of blood
Chondroitin sulphates	Glucuronic acid 4–6 sulphate esters of N-acetyl glucosamine	Cartilages and tendons	Polyelectrolyte

PROBLEMS

Objective-Type Questions

1. Glycolysis is
(a) oxidation of glucose to glutamate
(b) conversion of pyruvate to citrate
(c) oxidation of glucose to pyruvate
(d) conversion of glucose to haem

2. In Haworth projection, the α-anomer of glucose contains the –OH group
(a) above the plane of ring
(b) below the plane of ring
(c) in the plane of ring pointing outwardly
(d) inside the plane of ring pointing inwardly

3. In Haworth projection, the β-anomer of glucose contains the –OH group
(a) above the plane of ring
(b) below the plane of ring
(c) in the plane of ring pointing outwardly
(d) inside the plane of ring pointing inwardly

4. Maltose is a
(a) 1,4′-α-glycoside (b) 1,4′-β-glycoside
(c) 1,2′-α-glycoside (d) 1,2′-β-glycoside

5. Sucrose is a
(a) 1,4′-β-glycoside (b) 1,4′-α-glycoside
(c) 1,2′-β-glycoside (d) 1,2′-α-glycoside

6. Invert sugar is
(a) cellobiose (b) maltose
(c) sucrose (d) lactose

7. Sucrose is a
(a) reducing sugar
(b) non-reducing sugar
(c) mixture of glucose and fructose
(d) monosaccharide

8. Glycogen
(a) is a linear polymer with no branching.
(b) contains more branching than amylopectin.
(c) contains less branching than amylopectin.
(d) cannot be digested by human beings.

9. Which of the following is a linear polymer?
(a) Amylopectin (b) Glycogen
(c) Starch (d) Amylose

10. Glucose (or fructose) molecule reacts with X number of molecules of phenyl hydrazine to give osazone. The value of X is
(a) one (b) two
(c) three (d) four

11. The complete hydrolysis of cellulose gives:
(a) L-glucose (b) D-fructose
(c) D-ribose (d) D-glucose

12. The number of chiral carbons in β-D (+) glucose is
(a) four (b) three
(c) six (d) five

13. Which carbohydrate is an essential constituent of plant cells?
(a) Starch (b) Cellulose
(c) Sucrose (d) Maltose

14. α-D (+)-glucose and β-D (+)glucose are
(a) enantiomers (b) epimers
(c) anomers (d) geometrical isomers

15. The harmone that helps in the conversion of glucose into glycogen is
(a) bile acids (b) adrinaline
(c) insulin (d) cortisone

16. D (+) glucose and D (+) mannose are
(a) anomers (b) epimers
(c) enantiomers (d) conformers

17. The carbohydrates that are stored in the human body as polysaccharide are
(a) starch (b) glucose
(c) glycogen (d) galactose

18. α- and β-Glucose differ in orientation of –OH group around
(a) C_1 (b) C_2
(c) C_3 (d) C_4

19. Cellulose is a straight-chain polysaccharide composed of only
(a) D-glucose units joined by α-glycosidic linkage
(b) D-glucose units joined by β-glycosidic linkage
(c) D-galactose units joined by α-glycosidic linkage
(d) D-galactose units joined by β-glycosidic linkage

20. D-glucose and D-mannose are
(a) C_3-epimers (b) C_2-epimers
(c) C_4-epimers (d) C_5-epimers

21. Methyl α-D-glucoside and methyl β-D-glucoside are
(a) enantiomers (b) enantiomorphs
(c) epimers (d) anomers

22. Sucrose on complete hydrolysis gives
(a) glucose + glucose (b) glucose + galactose
(c) glucose + fructose (d) glucose

23. Fructose contains
(a) one primary and four secondary –OH groups.
(b) two primary and three secondary –OH groups.
(c) two primary and two secondary –OH groups.
(d) three primary and three secondary –OH groups.

24. Maltose on complete hydrolysis gives
(a) D(+) glucose + D(+) galactose
(b) D(+) glucose + D(–) fructose
(c) D(+) glucose + D(+) mannose
(d) D(+) glucose + D(+) glucose

25. Glucose contains
(a) one primary and four secondary –OH groups.
(b) two primary and three secondary –OH groups.
(c) two primary and two secondary –OH groups.
(d) three primary and three secondary –OH groups.

26. Lactose on complete hydrolysis gives
(a) D(+) glucose + D(–) fructose
(b) D(+) glucose + D(+) galactose
(c) D(+) glucose + D(+) glucose
(d) D(+) glucose + D(+) glucose

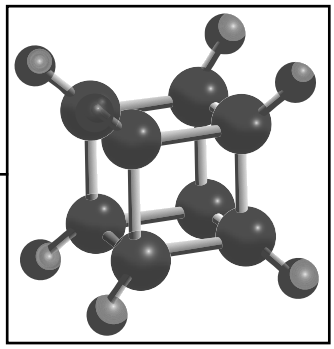
27. Which of the following pairs contain only reducing carbohydrate?
(a) Fructose, lactose (b) Glucose, maltose
(c) Sucrose, starch (d) Galactose, cellulose

28. Which of the following has a branched-chain structure?
(a) Amylose (b) Amylopectin
(c) Cellulose (d) Galactose

Answers

1. (c)	2. (b)	3. (a)	4. (a)	5. (d)
6. (c)	7. (b)	8. (b)	9. (d)	10. (c)
11. (c)	12. (d)	13. (b)	14. (c)	15. (c)
16. (b)	17. (c)	18. (a)	19. (b)	20. (b)
21. (d)	22. (c)	23. (b)	24. (d)	25. (a)
26. (b)	27. (a,b)	28. (b)		

CHAPTER 18



Amino Acids, Proteins and Nucleic Acids

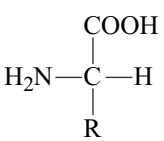
Amino acids are compounds that contain amino ($-NH_2$) and carboxyl (–COOH) groups. The amino group can be present at different carbon atoms in the chain with respect to the carboxyl group. It forms α, β, γ, δ, etc. amino acids, example

$H_2N–CH_2–COOH$	α-amino acid (glycine)
$H_2N–CH_2–CH_2–COOH$	β-amino acid (β-amino propanoic acid)

All the natural amino acids, which form proteins, are α-amino acids, $R.CH(NH_2)COOH$. In two of the amino acids (proline and hydroxy proline), the amino group is secondary (>NH) by virtue of being part of a pyrolidine ring.

CONFIGURATION OF NATURAL AMINO ACIDS

All amino acids (except glycine, R=H) have a chiral centre at the α-position. They are optically active and belong to the L-series (Fisher nomenclature),



L-amino acid

Some amino acids are also found in D-configuration (that is bears $–NH_2$ in the right-hand side in the projection formula).

NOMENCLATURE OF AMINO ACIDS

Generally, amino acids are known by their common names. It depends either on their source or on some special property. For example, the first member is called glycine because of its sweet taste (in Greek, Glykys means sweet). Similarly, *tyrosine* (in Greek, Tyros means cheese) was isolated from caseine, *cystine* (in Greek, Kystis means bladder) was obtained from urinary calculi.

Amino acids are generally represented by three-letter names, example *gly* for glycine and *ala* for alanine. It is very useful in designating the sequences of amino acids in proteins and peptides.

Classification of amino acids

Depending upon the respective number of amino and carboxyl groups, three types of amino acids are found.

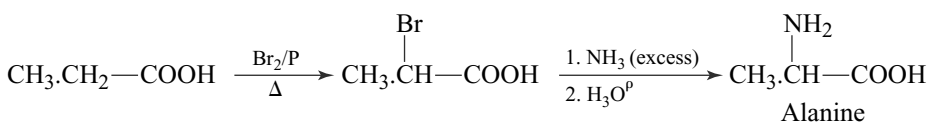
1. **Neutral amino acids**
   Amino acids, which have equal number of amino (or imino) and carboxyl groups, are neutral amino acids. For example, glycine and alanine.
2. **Acidic amino acids**
   Amino acids, which have excess of carboxyl group over amino group, are acidic amino acids, example aspartic and glutamic acids.
3. **Basic amino acids**
   Amino acids, which have excess of amino group over acid group, are basic amino acids, example lysine and arginine.

ESSENTIAL AND NON-ESSENTIAL AMINO ACIDS

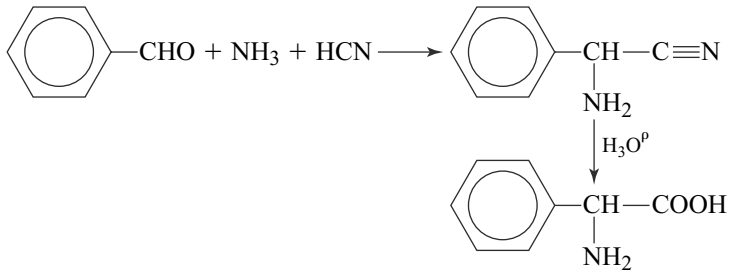
Organisms differ in their ability to synthesize amino acids. The amino acids, which are indispensable for human beings yet the body cannot synthesize them, are known as *essential* amino acids. They are 10 in number. The amino acids, which the body can synthesize, are known as *non-essential* amino acid.

Synthesis of amino acids

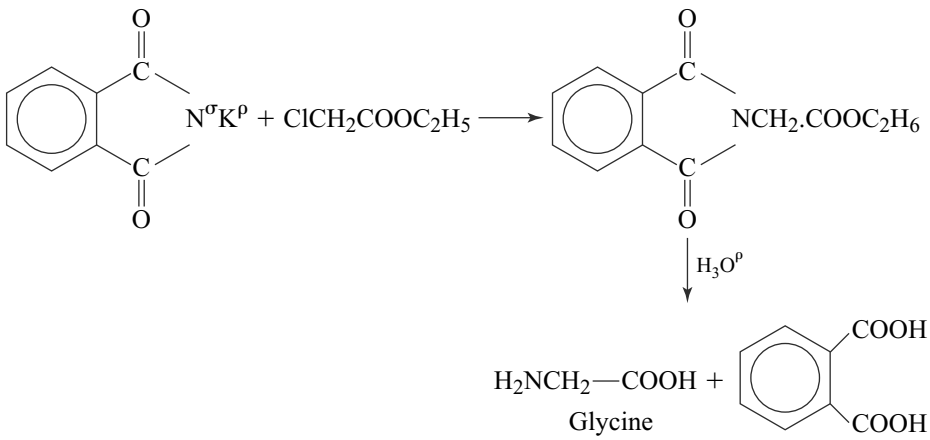
` 1. **By amination of α-haloacids**



2. **Strecker synthesis**
   This reaction is similar to cyanohydrine formation



3. **Gabriel phthalimide synthesis**
   In this method, α-haloesters are used instead of α-haloacids.



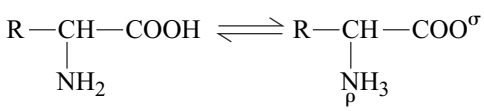
4. From proteins
5. From malonic esters

Properties of amino acids

1. Amino acids are generally colourless crystalline solids of high melting points.
2. They are soluble in water.
3. They behave like salt because of the presence of basic NH_2 group and acidic –COOH group in the same molecule.

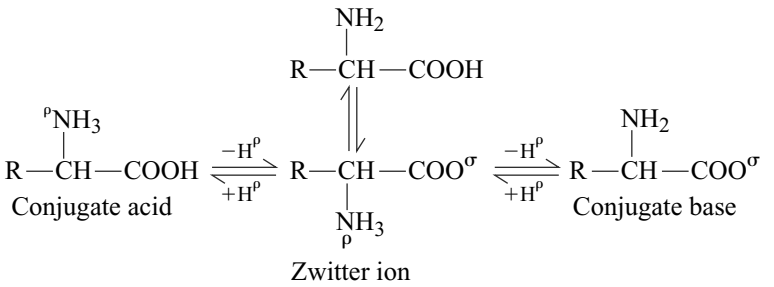
Zwitter ion (or dipolar ion)

Amino acids contain basic $–NH_2$ and acidic –COOH groups in the same molecule. Therefore, proton transfer occurs internally from –COOH group to NH_2 group. It forms a dipolar ion, which is called *Zwitter ion*.



Zwitter ion

Because of dipolar nature amino acids behave amphoteric (that is can accept H^{ρ} from a stronger acid and also donate a proton to a stronger base). In water, amino acids establish the following rapid equilibrium.

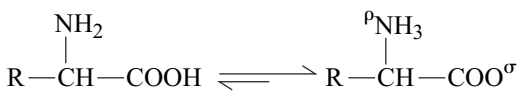


The proportions of these species is pH dependent:

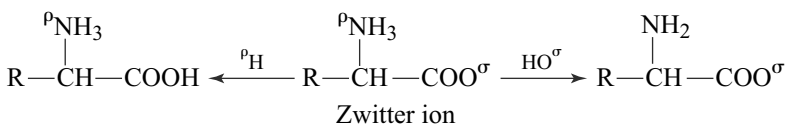
1. At low pH (that is high H^{ρ} concentration), the conjugate acid is the predominant form.
2. At high pH (that is low H^{ρ} concentration), the conjugate base is favoured.
3. As the equilibrium between the neutral molecule and the Zwitter ion involves no net change in H^{ρ} or HO^{σ} concentrations, the ratio of these two ions is independent of pH.

Isoelectric point of an amino acid

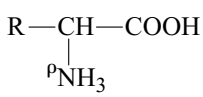
Amino acids are present in aqueous solution mostly as Zwitter ion (bipolar ion).

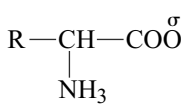


But in acid, the $-COO^{\sigma}$ function accepts a proton to generate –COOH function, while in basic solution the $-\overset{\oplus}{N}H_3$ function changes to $-NH_2$.



Thus, in an electrolytic experiment:





However, at a particular pH, the acid is as Zwitter ion (neutral ion) and there will be no net migration towards any electrode. This particular pH is known as *isoelectric point*. Thus, isoelectric point is the pH at which amino acid exists only as a Zwitter ion (or dipolar ion) with zero net charge. Generally, at isoelectric point, water solubility of the amino acid is least. It is used in the separation of amino acid obtained by the hydrolysis of proteins.

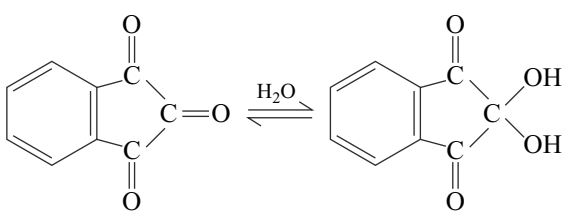
Table 18.1 Isoelectric point of amino acids

Neutral amino acids	$pI = \frac{pK_a\,(COOH) + pK_a^{\rho}(NH_3)}{2}$
For glycine	$pI = \frac{2.34 + 9.6}{2} = 5.97 \approx 6$
Basic amino acids	pI > 7 (because of free NH_2)
Lysine	pI ≈ 9.7
Acidic amino acids	pI < 7 (because of free –COOH)
Glutamic acid	pI ≈ 3.2

Test of amino acids

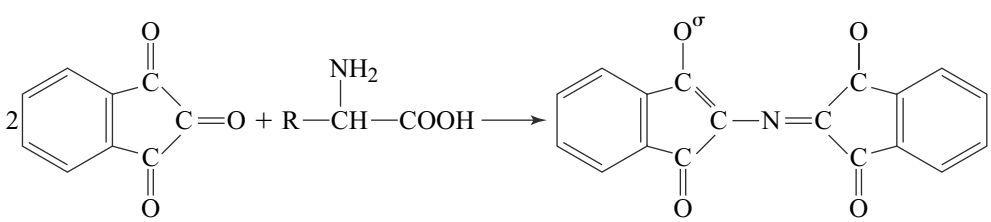
Ninhydrin test

The ninhydrin is hydrate of triketone (indane-1,2,3 trione)



(Ninhydrin)

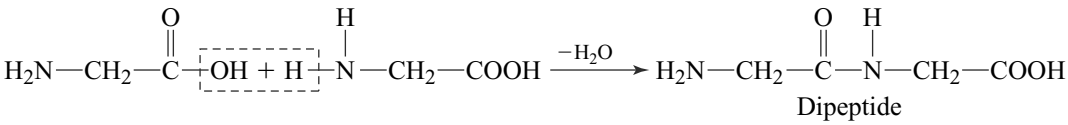
An alcoholic solution of ninhydrin, when heated with a solution of amino acid, produces a blue–violet colour.



It is a highly sensitive test. All amino acids except proline and hydroxyl proline give the same colour (λ_{max} = 5700). Proline and hydroxyl proline give yellow colour (λ_{max} = 4400).

Peptides

Peptides are polyamides. They are formed by reaction (condensation reaction) between amino group and carboxyl group of amino acids.



Peptides are in fact secondary amides having linkage, called peptide linkage.

They are classified according to the number of amino acid residues per molecule of peptide, such as dipeptide and tripeptide and finally, polypeptide.

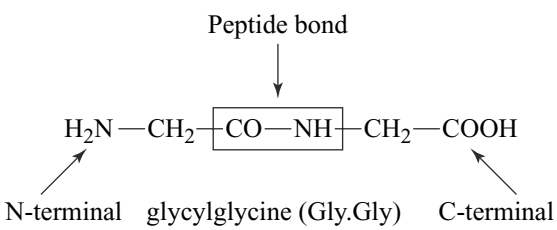
N-terminal and C-terminal

A peptide has free amino group at one end, called the N-terminal and a free carboxyl group on the other end, called the C-terminal. According to convention, N-terminal amino acid unit (free NH_2 group) is written at the left end and the C-terminal amino acid unit (free –COOH group) at the right end.

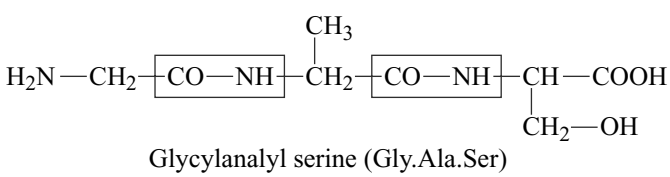
Naming of peptides

Peptides are named from N-terminal to C-terminal through the sequential listing of the names of amino acids. It is done by replacing '*ine'* by 'yl' in the names of all amino acids except the C-terminal. Peptides are abbreviated by using three-letter notations for amino acids. Some examples illustrate the above theory.

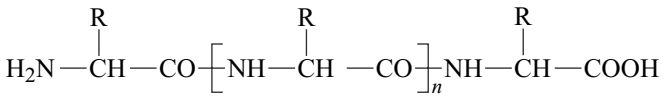
Dipeptide



Tripeptide

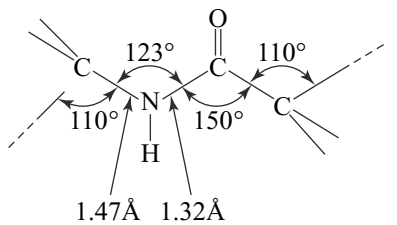


Polypeptide

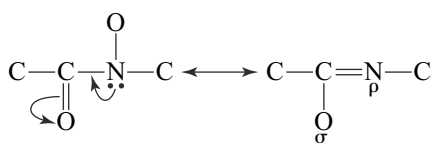


Structure

X-ray examinations indicate that the entire amide group is flat, that is carbonyl carbon, N and the four atoms linked to them all lie in a plane, having H (of NH) and O (of CO) trans to each other. The C–N bond length (of –CO–NH–) is 1.32, shorter than usual C–N single bond length of 1.47.



It shows some double bond nature in C–N bond (due to resonance). It restricts free rotation resulting into predominance of *trans isomer*.



Polypeptides are amphoteric (because of the presence of NH_2 and –COOH functions). They have isoelectric point at which they are least soluble and have large tendency to aggregate.

The study of peptides is important as it gives insight into the structure of proteins. However, some peptides are important biologically.

Table 18.2

Peptide	Structure	Function
Oxytocin	Ile-Tyr-Cys Gln-Asn-Cys-Pro-Leu-Gly	Responsible for contraction of uterus during childbirth, stimulates ejection of milk from mammary glands
Glutathione	Glu-Cyst-Gly	Found in most living cells
Bradykinin	Arg-Pro-Pro-Gly-Phe- Ser-Pro-Phe-Arg	Released in blood plasma during sting bite and causes pain

PROTEINS

Proteins are polyamides of α-amino acids. The distinction between a protein and a peptide is arbitrary. Proteins have very high molecular weights, above 10,000 (a peptide has molecular weight less than 10,000).

Some characteristics of proteins

1. Proteins are *amphoteric* and have *isoelectric point* (like amino acids).
2. All proteins are optically active (α-C is a chiral centre).
3. Many proteins are water soluble, but the solution is colloidal in nature.
4. Proteins undergo irreversible changes under the influence of heat, strong acids or bases. It is called *denaturation* of protein, example coagulation of egg white by heat is denaturation of the protein egg albumen.
5. Colour reaction
   (a) Ninhydrin reaction: Proteins, when interacted with a pyridine solution of ninhydrin, give *deep blue* to *violet pink* colour (in some cases even *red*).
   (b) Proteins, on reaction with nitric acid, give *yellow* to *orange* colour. (That is why our skin turns yellow when it comes in contact with nitric acid.)
   (c) An alkaline solution of protein forms bluish violet colour with aqueous copper sulphate.

Classification of proteins

1. On the basis of shape

   According to this classification, proteins form two groups:

   (a) Fibrous proteins

   They are found as long fibres (or planar sheets) and are generally insoluble in water but soluble in strong acid or alkaline solution. Some examples are:

   Keratin: It is found in hair, skin, nail etc.

   Myosine: It forms muscular fibre.

   Fibroin: It is found in silk.

   (b) Globular proteins

   They are spherical in shape and soluble in water (coloidal solution). All enzymes, as well as many hormones are globular proteins. For example,

   Insulin: Pancreas

   Albumen: Egg white

   Thyroglobulin: Thyroid gland

   Hemoglobin: Oxygen transported from the lungs to the tissues

   Fibrinogen: Converts into fibrous and fibrin (insoluble), causes clotting of blood

2. On the basis of structure

   Following types of proteins are found depending upon their structure:

(a) Simple proteins

They give amino acids only on hydrolysis. For example,

Albumen: Egg albumen

Globulin: Tissue globulin, serum globulin

Glutelins: Gluetin from wheat, oxyzerin from rice

(b) Conjugated proteins

Proteins, which contain some non-protein residues in the protein molecule, are called conjugated proteins. The non-protein part is called *prosthetic group*. It imparts special and specific reactivity to the protein.

Table 18.3

Class of protein	Prosthetic group	Examples
Chromoproteins	Heme (iron porphirin) Zn	Hemoglobin, Mioglobin cytochromes, Alcohol dehydrogenase (enzyme)
Nucleoproteins	Nucleic acids	DNA, RNA
Lipoproteins	Lipids, Cholesterol ester	High density lipoprotein (HDL) in blood
Glycoproteins	Carbohydrates	Mucin (a component of saliva), interferon
Phosphiproeins	Phosphate group	Casein of milk
Flavoproteins	Flavin nucleotides	Succinate dehydrogenase (enzyme)

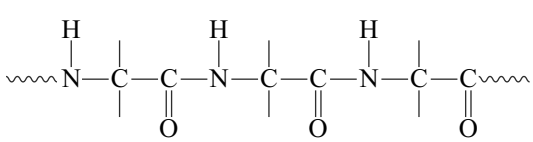
Structure of proteins

Proteins have complex structure. It can be seen at four levels:

1. **Primary structure**
   It represents the specific sequence of amino acids in the polypeptide chain. It is established by hydrolysis of proteins (by acid or base or enzyme).

$$\text{Protein} \longrightarrow \text{Peptides} \longrightarrow \text{Amino acid}$$

The infrared spectrum shows amide group.



The first primary structure that was elucidated was that of insulin (antidiabetic hormone) by F. Sanger (1950) for which he got the Nobel Prize.

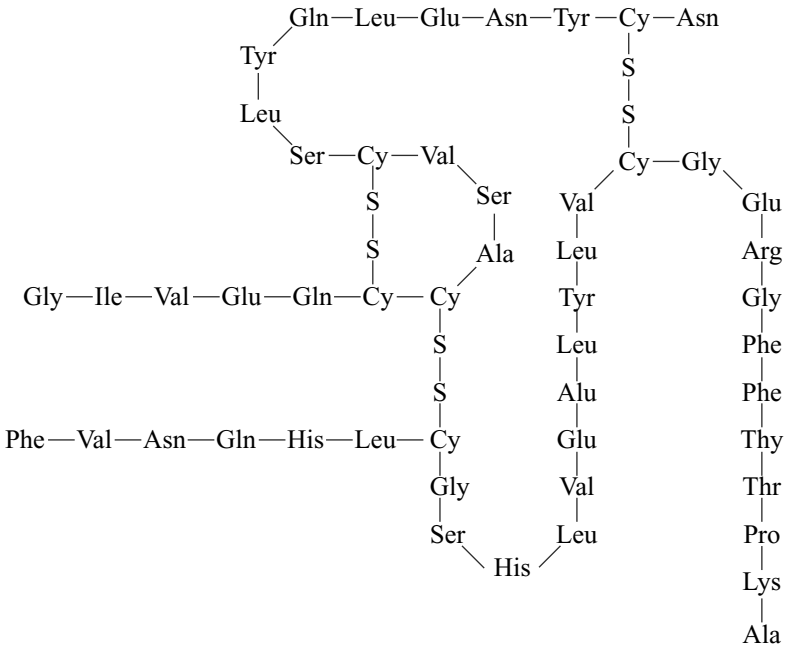


Fig. 18.1

It has 51 amino acids.

2. Secondary structure

The secondary structure represents the different conformations that the protein chain can adopt. The H-bonding between the N–H of one amino acid and C=O of another properly situated amino acid is mainly responsible for secondary structure. Three types of secondary structures are found:

(a) *α-helix (L. Pauling, 1951)*

In α-helix, the coiling of peptide chain is right-handed (spiral like) with R groups outside the spiral. The H-bonds are between N–H and C=O groups that are four peptide bonds apart.

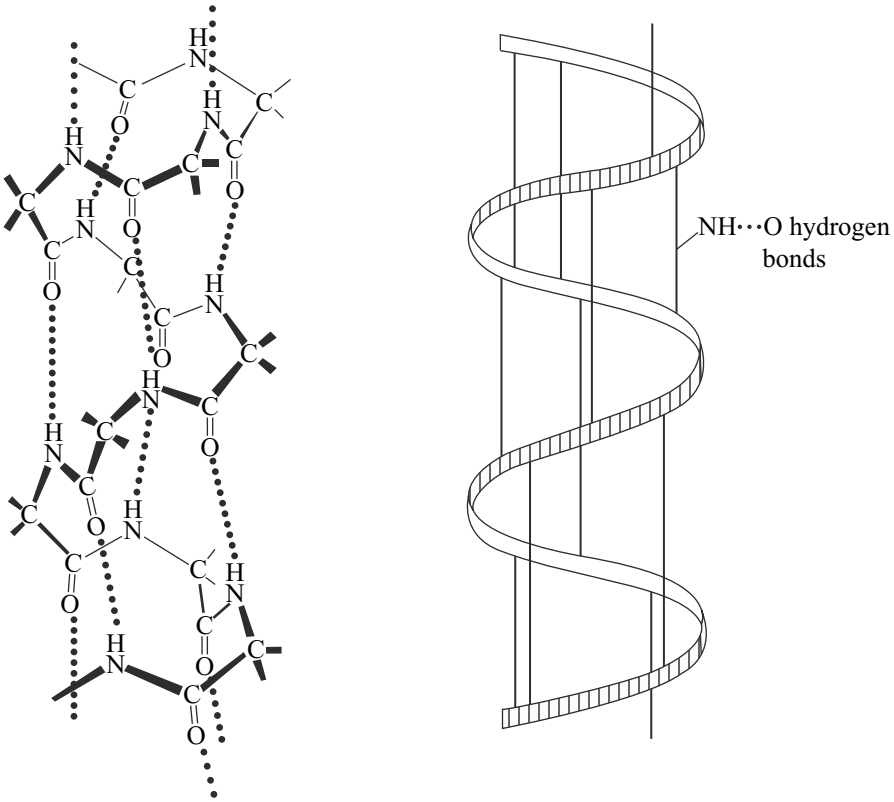


Fig. 18.2

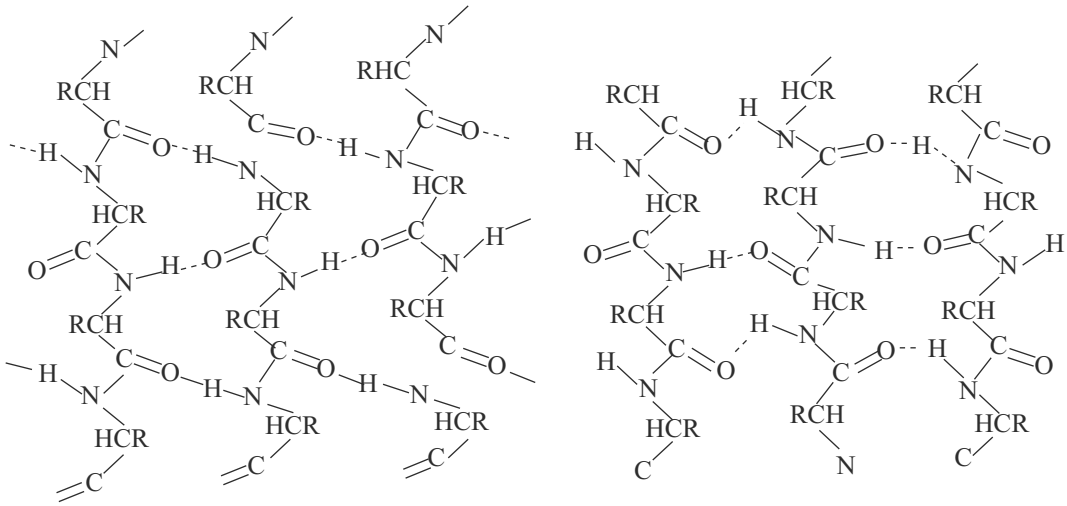
(b) β-*structure (L. Pauling, 1951)*

Proteins are not always perfect α-helix. It is because of (i) *Steric hindrance* among certain amino acid side chains, or (ii) the lack of H-bonding. The above effects are sufficient to reduce the stability of the normal α-helix and allow the chain to fold. It results into what is called the *pleated sheet or* β-*structure*. The inter-chain amide H-bonding holds the chains together.

Two types of pleated sheets are found: (i) parallel pleated sheet and (ii) anti-parallel pleated sheet

In *parallel pleated sheets*, chains run in the same direction with their N-terminals at the same end. In a*nti-parallel pleated sheets*, chains run in opposite directions, that is N-terminal of one chain and C-terminal of another chain, and are on the same side.

The β-sheet is found parallel in *Keratin* (protein in hair) and anti-parallel in *fibroin* (silk protein).



Parallel β-conformation

Anti-parallel β-conformation

Fig. 18.3

3. Tertiary structure

This structure represents the way in which the coiled chain is folded and hydrated in the natural state. The bonding responsible for tertiary structure is:

(a) Van der Waals force: It originates due to interaction among side chains (e.g. in phenylalanine and tryptophan).

(b) Additional H-bonding: For example, among the side chains of serine and histidine.

(c) Ionic bonding: It is between $-COO^{\ominus}$ and $H_3\overset{\oplus}{N}$ at different sites (example aspartic acid and lysine).

(d) Covalent bonding: It is disulphide linkages (example between two cystein units).

Because of tertiary structure, the entire protein molecule develops a particular molecular shape. Two major shapes are found:

(i) Fibrous protein

The fibrous proteins have a rod-like shape because of the rigid helical arrangement. For example, silk collagen and α-keratin, which are insoluble in water.

(ii) Globular protein

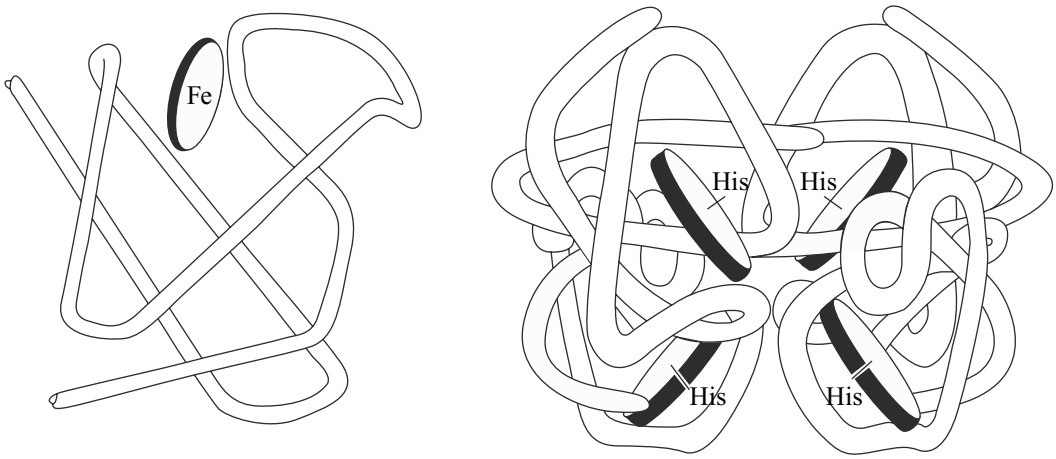
They have polypeptides that are held partly as helices and are partly folded randomly to give the entire molecule a spherical shape. Examples are haemoglobin, and mioglobin that soluble in the body's aqueous medium.

4. Quarternary structure

This structure results due to the grouping together of two or more peptide chains. Such proteins are called *oligomers* (dimers, trimers etc.). Ionic forces, Van der Waals forces, and H-bonds are responsible for quarternary structure (covalent bond is absent in quarternary structure). The individual peptide chains of an oligomeric protein are called *protomers*. They may be the same or different.

Myoglobin (a chromoprotein) contains only one protomer that is coiled in a random way.

Haemoglobin is a tetramer (that is contains four polypeptide chains: α_1, α_2, β_1 and β_2 and insulin is a hexamer.



Mioglobin Haemoglobin

Fig. 18.4

Functions of protein

Protein is a large solid component of cells. It serves the cell in many ways, that is

1. As structural material: Collogen and keratin (protein in hair, nail etc.). Actin and myosin (helical proteins) form part of muscle structure, responsible for contraction and relaxation of muscle.
2. As antibiotics or hormones: For example,

   Insulin: A regulator of glucose in blood.

   Gramicidin: An antibiotic.

   Gama globulin: It is responsible for immunity of cells to foreign matter.
3. As regulator of water content:

   Albumen: A globular protein (serum plasma) regulate water content.
4. As enzymes: It is perhaps the most notable activity of a protein. An enzyme is a protein. It has specific and selective effect on biological reactions. For example, a list of enzymes and their effects are given below.

Table 18.4

Enzymes	Effects
Lactate dehydrogenase	Catalyzes the dehydrogenation of lactic acid to give pyruvic acid.
Ribonuclease	Catalyzes breakdown of RNA.
α-amylase	Helps the hydrolysis of α-amylose.
Chymotrypsin	It catalyzes the hydrolysis of proteins during digestion (specific for hydrolysis of polypeptide linkages that contain aromatic amino acids residues).
Carboxypeptidase (pancreatic enzyme)	Cleaves the carboxyl terminal amino acid from a peptide chain

Nucleic Acids

Nucleic acids are very high molecular weight (10^4 to 4 x 10^9) polymers. They are found in the nucleus (so nucleic acid) and the cytoplasm of cells.

Types of nucleic acids

Two types of nucleic acids are found:

1. **Deoxyribonucleic acid (DNA)**
   It is found in the cell nucleus as the constituent polymer of the chromosomes (and genes) of animals.
2. **Ribonucleic acid (RNA)**

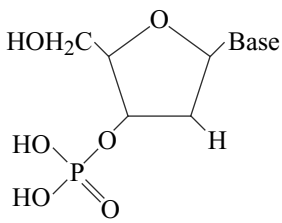
It occurs in ribosomes of all cells and also in many cases, in the cell nucleus of some viruses, phages and plants.

Structure

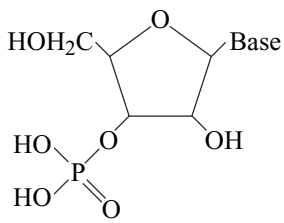
DNA and RNA are closely related in their chemical structures (but differ at some point). The basic monomeric units, which are linked to give nucleic acids, are called nucleotide.

DNA: monomeric unit – deoxyribonucleotide

RNA: monomeric unit – ribonucleotide



Deoxyribonucleotide



Ribonucleotide

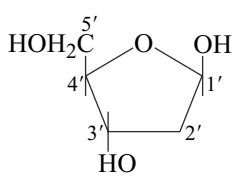
Complete hydrolysis of nucleic acids show that

1. DNA constituents are:

(a) H_3PO_4

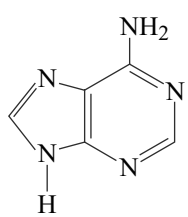
Phosphoric acid

(b)



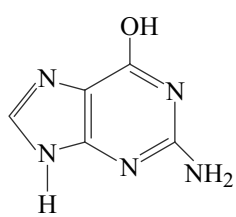
2-Deoxyribofuranos

(c)



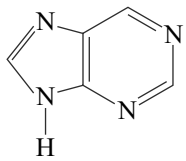
Adenine

(d)



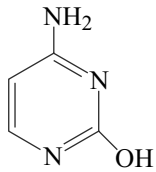
Guanine

The bases adenine and guanine contain purine nucleus.



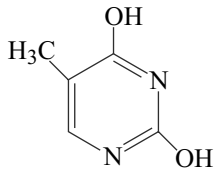
Purine

(e)



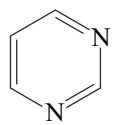
Cytosine

(f)



Thymine

The bases cytosine and thymine contain pyrimidine nucleus.



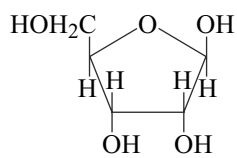
Pyrimidine

2. RNA constituents are:

(a) H_3PO_4

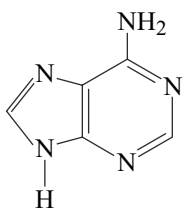
Phosphoric acid

(b)



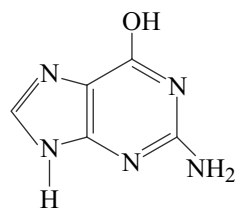
Ribose

(c)



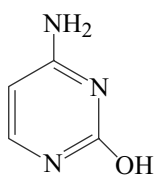
Adenine

(d)



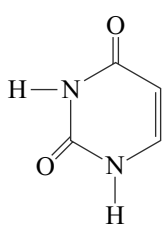
Guanine

(e)



Cytosine

(f)

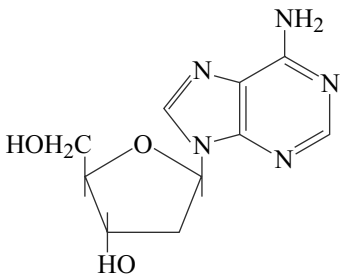


Uracil

The base uracil also contains pyrimidine nucleus.

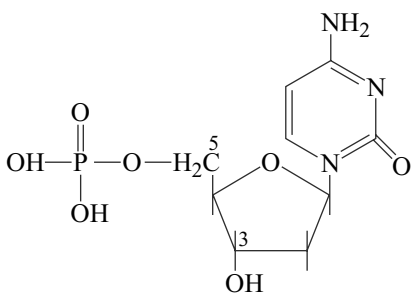
Under milder conditions, nucleic acids degrade to a relatively simple molecule called nucleotide. It is found to contain a purine or pyrimidine base, a phosphate residue and a pentose unit. Furthermore, very careful hydrolysis nucleotides give out phosphoric acid as well as another class of compounds known as *nucleosides* (sugar + base).

Nucleosides (sugar + base)



Adenine deoxyriboside
(a nucleoside)

Nucleotides (phosphate + sugar + base)



Cytosine deoxyribonucleotide
(a nucleotide)

DNA structure

Chemical studies show that DNA is a long chain of polymer made of alternating phosphate and nitrogen base-substituted sugar residue

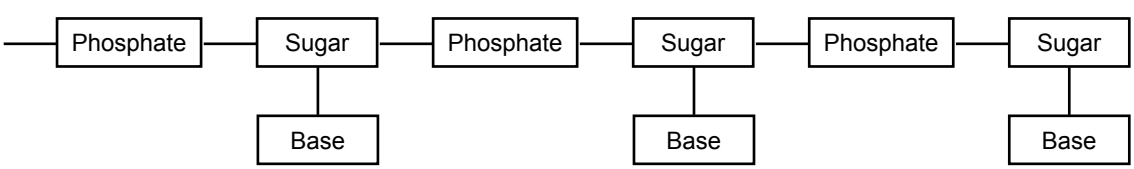
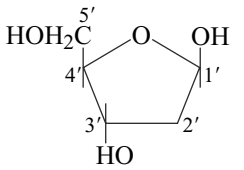


Fig. 18.5

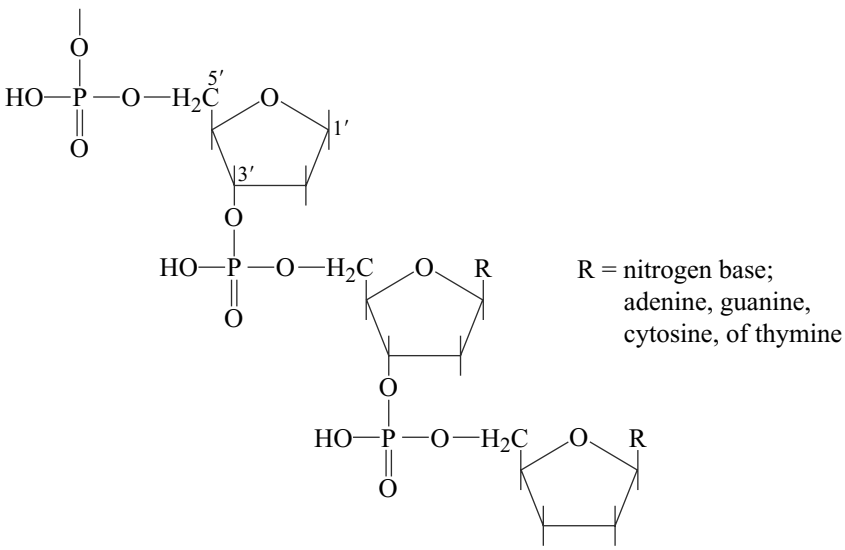
The sugar is D-2-deoxyribofuranose and each sugar residue is bonded to two phosphate groups by ester links involving the 3′ and 5′ hydroxyl groups.



2-Deoxyribofuranos

Each of the sugar residues of DNA is also bonded at the 1′ position to one of the four bases, adenine (A), guanine (G), cytosine (C) and thymine (T) through an N-glycoside linkage (β-linkage).

The polymer has a strand-like structure as shown below:



The ribonucleotides and RNA consists of the bases adenine (A), guanine (G), cytosine (C) and uracil (U). Thus, the basic chemical differences between DNA and RNA are:

Table 18.5

	DNA	RNA
Sugar	D-2-deoxyribofuranose	D-ribofuranose
Bases	Cytosine, thymine, adenine, guanine	Cytosine, uracil, adenine, guanine

This means, adenine, guanine and cytosine are common to both DNA and RNA.

Chain conformation of nucleic acids

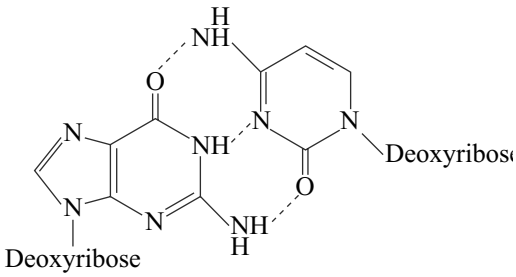
As nucleic acids contain four types of bases, there can be four types of nucleotides. Thus, each nucleic acid differs from another in molecular mass and in the base sequence. Since the chain length is variable, there can be innumerable DNA (also RNA). But DNA found in nature has similar chain conformation (it is not seen in RNA).

DNA

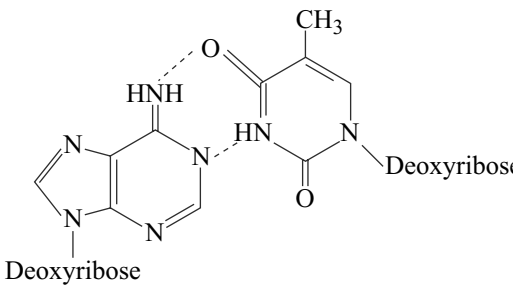
Chargaff observed that in DNA molecules, the base compositions are remarkably regular, that is

1. the amount of adenine (A) = the amount of thymine (T)
2. the amount of guanine (G) = the amount of cytosine (C)
3. the A + G / C + T ratio is close to unity

This means, A = T, G = C and A + G = C + T. It was also found that of the DNA bases A forms H-bonds with T and G, specifically H-bonds with C. It is an important factor for chain structure of DNA and is known as *complementary base pairing*. These H-bonds are responsible to link two strands of DNA.



Guanine–cytosine



Adenine–thymine

Taking into account the above facts and X-ray diffraction data, Watson and Crick (1953) suggested a double-stranded helical structure for DNA.

The width of the double helix is about 20 and each turn of the helix is 34 (equivalent of 10 nucleotides).

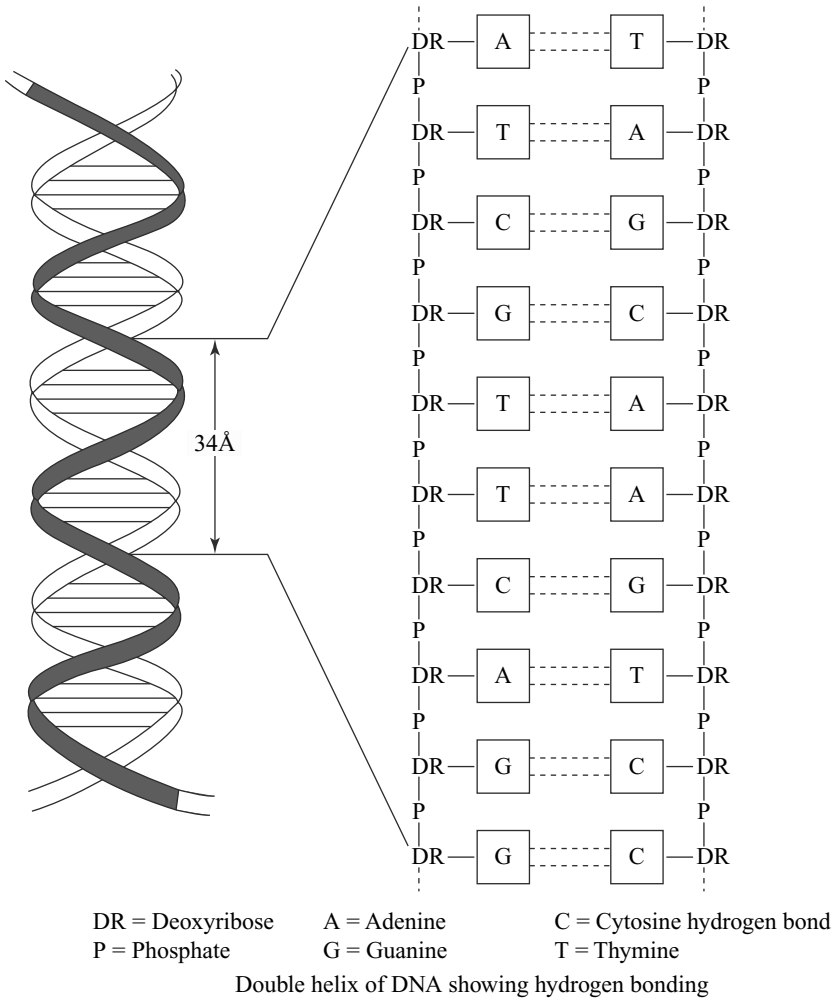


Fig. 18.6 Double helix of DNA showing hydrogen bonding

A from one strand H-bonds with T from the other strand and G, specifically H-bonds with C. H-bonds are a source of stability to and maintain double helix. Another source of stability for the double helix is the dipolar forces between bases along the helix axis.

The base pairing in DNA is complementary, that is if base sequence of one strand is known; the sequence in the other is automatically fixed. It is like a lock and key relation.

Replication

The Watson–Crick model explains physical and chemical properties of DNA. It also gives a clear mechanism for the duplication of the DNA and thus replication of chromosomes and genes. If DNA strands are separated (by heat or chemical effect), each strand works as a mould (or template) for the synthesis of a new DNA strand (from deoxyribonucleotide). If a strand has a base sequence AGCTT… from the free 5′ end on, the new DNA chain will be TCGAA… from its 3′ end on. Thus, each strand produces its complement.

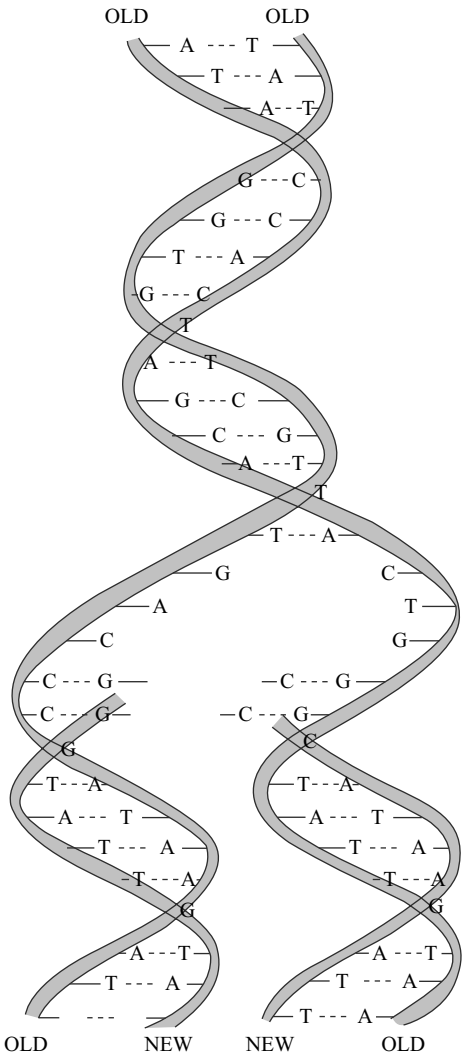


Fig. 18.7 Mechanism of DNA replication

RNA

The base pairing in RNA is between A and U and between G and C. But like DNA, RNA does not maintain A/U, G/C or A + G/U + G constancy. Also, RNA is a single-stranded chain with none of the Watson–Crick regularity. The RNA chain is randomly found in folded form with some AU and GC pairing.

Types of RNA

RNA that occur in living cells are:

1. Soluble RNA (s-RNA) or transfer RNA (t-RNA)

   It is found in cytoplasm. Its chain length is small and is of less than 100 ribonucleotides in the chain

2. Ribosomal RNA (r-RNA)

It is a part of the ribosomes along the endoplasmic reticulum. Its molecular mass is very high.

3. Messenger RNA (m-RNA)

It is formed in the cell nucleus and is generally 1500 nucleotides long.

Innumerable RNA varieties are possible (like DNA) differing in chain length and in the sequence of the bases A, G, C and U. DNA and RNA have great importance in the genetics of the living cells.

PROBLEMS

Objective-Type Questions

1. Zwitter ion is a
(a) neutral species
(b) singly charged species
(c) doubly charged species
(d) multifunctional species

2. At low pH, an amino acid exists as

(a) $H_3\overset{+}{N}CHRCOOH$

(b) $H_3\overset{+}{N}CHRCOO^-$

(c) $H_2NCHRCOO^-$

(d) $H_2NCHRCOOH$

3. At high pH, an amino acid exists as

(a) $H_3\overset{+}{N}CHRCOOH$

(b) $H_3\overset{+}{N}CHRCOO^-$

(c) $H_2NCHRCOO^-$

(d) $H_2NCHRCOOH$

4. Thymine is
(a) 5-methyl uracil (b) 4-methyl uracil
(c) 3-methyl uracil (d) 1-methyl uracil

5. At pH = 4, glycine exists as

(a) $H_3\overset{\oplus}{N}–CH_2–COO^s$

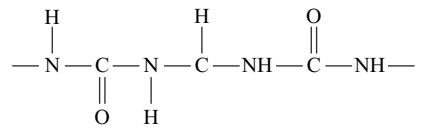
(b) $H_3\overset{\oplus}{N}–CH_2–COOH$

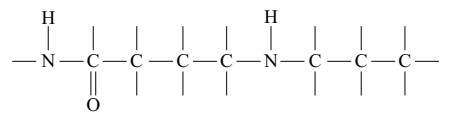
(c) $H_2N–CH_2–COOH$

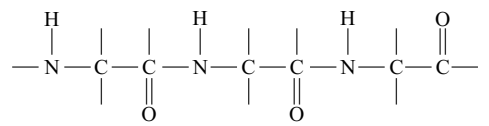
(d) $H_2N–CH_2–COO^S$

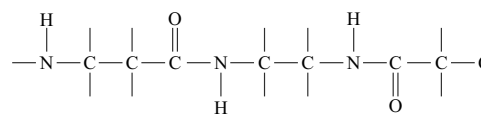
6. The α-amino acid that contains the aromatic side chain is
(a) proline (b) tyrosine
(c) valine (d) tryptophane

7. Which of the following structures represent the peptide chain?

(a) 

(b) 

(c) 

(d) 

8. Which of the following is not an essential amino acid?
(a) Valine (b) Arginine
(c) Lycine (d) Serine

9. The amino acid that contains sulphur is
(a) cystine (b) glutamine
(c) lycine (d) threonine

Which of the following is an achiral amino acid?
(a) Ethylalanine
(b) Methyl glycine
(c) Tryptophan
(d) 2-Hydroxymethyl serine

11. The functional groups found in amino acids are
(a) –COOH (b) $–CH_3$
(c) $–NH_2$ (d)

12. The amino acid that can be synthesized in the body is
(a) lysine (b) valine
(c) histidine (d) alanine

13. The main structural feature of protein is
(a) ester linkage (b) ether linkage
(c) peptide linkage (d) all the three above

14. Antibodies are
(a) lipids (b) enzymes
(c) carbohydrates (d) proteins

15. In DNA, the complementary bases are
(a) uracil and adenine:cytocine and guanine
(b) adenine and thymine:guanine and cytocine
(c) adenine and thymine:guanine and uracil
(d) adenine and guanine:thymine and cytocine

16. The helical structure of protein is stabilized by
(a) dipeptide bond (b) peptide bonds
(c) ester linkage (d) H-bond

17. Sanger's reagent is used for the identification of
(a) N-terminal of a peptide chain
(b) C-terminal of a peptide chain
(c) side chain of amino acids
(d) number of amino acids in a peptide chain

18. What structural feature distinguishes praline from other natural α-amino acids?
(a) It is optically inacline.
(b) It contains two amino groups.
(c) It is a dicarboxylic acid.
(d) It has secondary amine groups.

19. The number of tripeptides formed by three different amino acids are
(a) six (b) five
(c) four (d) three

20. Which functional group participates in disulphide bond formation in proteins?
(a) Thioester (b) Thioether
(c) Thiol (d) Thiolactone

21. According to Chargaff, in DNA the
(a) amount of adenine is equal to that of thymine and the amount of guanine is equal to that of cytosine.
(b) amount of adenine is equal to that of guanine and the amount of thymine is equal to that of cytosine.
(c) amount of adenine is equal to that of cytosine and the amount of thymine is equal to that of guanine.
(d) amounts of all bases are equal.

22. Phospholipids are esters of glycerol with
(a) three carboxylic acid residues.
(b) two carboxylic acid residues and one phosphate group.
(c) one carboxylic acid residue and two phosphate groups.
(d) three phosphate groups.

23. The human body does not produce
(a) vitamins (b) hormones
(c) enzymes (d) DNA

24. During the process of digestion, the proteins present in food materials are hydrolyzed to amino acid. The two enzymes involved in the process

$$\text{Proteins} \xrightarrow{\text{Enzyme (A)}} \text{Polypeptides} \xrightarrow{\text{Enzyme (B)}} \text{A mino acids,}$$

are respectively.
(a) diastase and lipase
(b) pepsin and trypsin
(c) invertase and zymase
(d) amylase and maltase

25. Which base is present in RNA but not in DNA?
(a) Uracil (b) Cytocine
(c) Guanine (d) Thymine

26. The pyrimidine bases present in DNA are
(a) cytocine and adenine
(b) cytocine and guanine
(c) cytocine and thymine
(d) cytocine and uracil

27. An alteration in the base sequence of nucleic acid molecule is
(a) duplication (b) replication
(c) mutation (d) dislocation

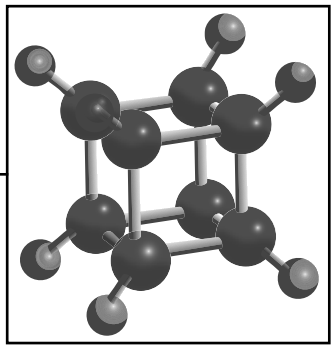
28. Which of the following statements is true for β-structure of protein?
(a) It has no H-bonding support.
(b) N-terminals and C-terminals are always anti-parallel.
(c) N-terminals and C-terminals may be anti-parallel.
(d) Steric factor is absent.

29. The biomolecule, which is insoluble in water, is
(a) haemoglobin (b) adenine
(c) ribonuclease (d) α-keratin

Answers

1. (c)	2. (a)	3. (c)	4. (a)	5. (b)
6. (d)	7. (c)	8. (d)	9. (a)	10. (d)
11. (a, c)	12. (d)	13. (c)	14. (d)	15. (b)
16. (d)	17. (a)	18. (d)	19. (a)	20. (c)
21. (a)	22. (d)	23. (a)	24. (b)	25. (a)
26. (c)	27. (c)	28. (c)	29. (d)	

CHAPTER 19



Polymers

POLYMERS

Polymers are macromolecules. They are made up of small repeating units known as monomers. Thus, a polymer is a high molecular weight substance obtained by recurring structural units (monomers). Monomers may be the same or different compounds.

Polymerization

The reaction by which many small molecules (or monomers) are joined together to form a very large molecule is known as *polymerization*. For example,

$$n\mathrm{CH_2{=}CH_2} \xrightarrow[\text{High pressure}]{\text{High temp.}} -\!\left[\mathrm{CH_2{-}CH_2}\right]_n-$$

Ethene (monomer) → Polythene

$$n\mathrm{CH_3{-}CH{=}CH_2} \longrightarrow -\!\left[\mathrm{C(CH_3){-}CH_2}\right]_n-$$

Propene (monomer) → Polypropene

$$\mathrm{H_2N{-}(CH_2)_6{-}NH_2} + \mathrm{HOOC\,(CH_2)_4{-}COOH} \longrightarrow \left[\mathrm{C(=O)(CH_2)_4.C(=O){-}N(H){-}(CH_2)_6{-}N(H)}\right]_n + \mathrm{H_2O}$$

Hexamethylene diamine + Adipic acid → Nynol (66)

Classification

Polymers can be classified into several different ways, such as, occurrence, structure and physical properties.

Source and Classification

(a) Natural polymers
They are found in plants and animals. For example:
(i) Polysaccharides—starch and cellulose, which provide food, clothing and shelter.
(ii) Nucleic acids—which control heredity at molecular level.
(iii) Proteins—which are part of the animal body, hold it together and run it.
(iv) Silk, wood, etc.

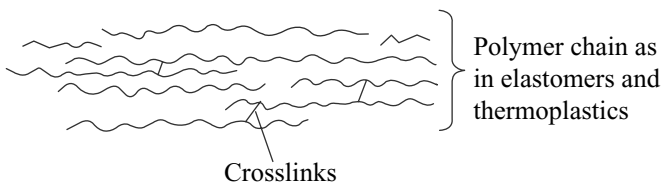
(b) Synthetic polymers
They are man-made polymers (by chemical reactions). These include plastics, synthetic rubbers and fibres. They find diverse use, such as in clothing, substitute for wood, metal and electric fittings, and have no natural counterparts.

(c) Semisynthetic polymers
Chemical derivatives of naturally occurring polymers are semisynthetic polymers. For examples:
(i) Cellulose acetate (acetylation product of cellulose) that is used in making threads, films and glasses.
(ii) Gun-cotton (cellulose nitrate) that is used in making explosives.
(iii) Vulcanized rubber

Physical Properties (or Force) and Classification

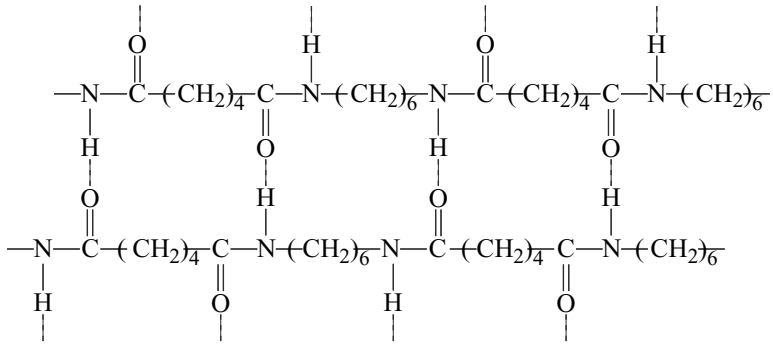
Physical properties like elasticity, toughness and tensile strength (which determines utility) of a polymer depend upon intermolecular forces like van der Waals or dispersion forces and H-bonding. On this basis, polymers are classified as follows:

(a) Elastomers
They have very weak intermolecular forces of attraction between polymer chains. The weak forces permit the polymer to be stretched. Elastomers have a few chemical bonds as crosslinks between the chains. The crosslinks help the polymers to return to its original position.



Natural rubber, vulcanized rubbers are the best-known elastomers.

(b) Fibres
These are polymers, which have relatively stronger intermolecular forces like H-bonding. It is especially important in polyamides, example Nylon-66.



Hydrogen-bonded structure of Nylon-66

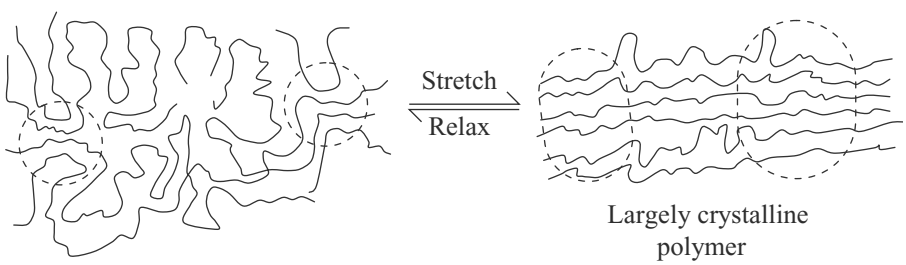
Because of strong forces, chains close pack imparting crystalline nature to polymer. Thus, these polymers have sharp melting points.

(c) Thermoplastics

Thermoplastic polymers have intermolecular forces intermediate between elastomers and fibres. They can be easily moulded by heating, that is it softens on heating and becomes hard on cooling. Polythene, polystyrene, poypropene, etc., are thermoplastic polymers.

(d) Thermosetting

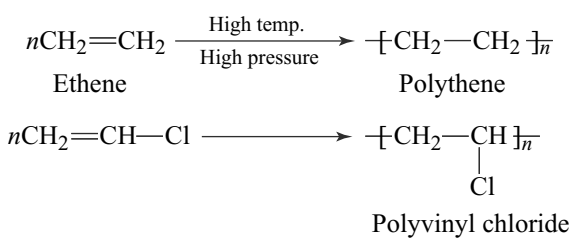
These polymers have extensive crosslinks, that is, strong force among polymer chains. They are made from low molecular weight semi-fluid substances by heating. Heating causes extensive crosslinking among polymer chains giving a three-dimensional network structure. Bakelite (phenol and formaldehyde polymer) is a well-known example.



Monomeric Units and Classification

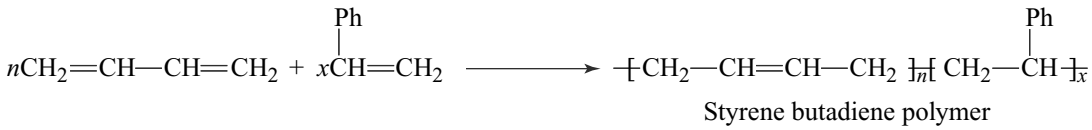
(a) Homopolymers

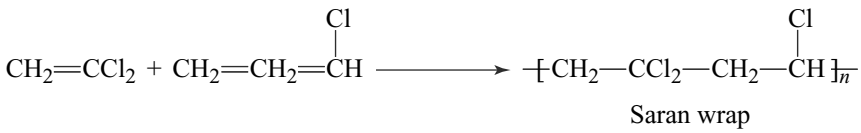
Polymers, which contain only one type of monomeric units, are called homopolymers, example polythene and polyvinyl chloride.



(b) Copolymers

Polymers made up of different monomers are known as copolymers, example styrene and 1,3-butadiene polymer, polystyrene and methyl methacrylate polymer and saran wrap.





Type of Reactions and Classification

Type of reaction leading to formation of polymer may also be used to classify polymers. Two types are common:

(a) Addition polymerization

When monomers (the same or different) add together to form a polymer, the process is called addition polymerization. The monomers for such polymerization must be unsaturated species like alkenes, alkadienes or their derivatives. This proceeds in stages and each stage produces reactive intermediate for further reaction. Thus, it is often called *chain growth polymerization*.

The polymerization reaction may involve free radicals or ionic species (cation or anion). Thus, an addition polymerization may be

(i) a free-radical addition polymerization.

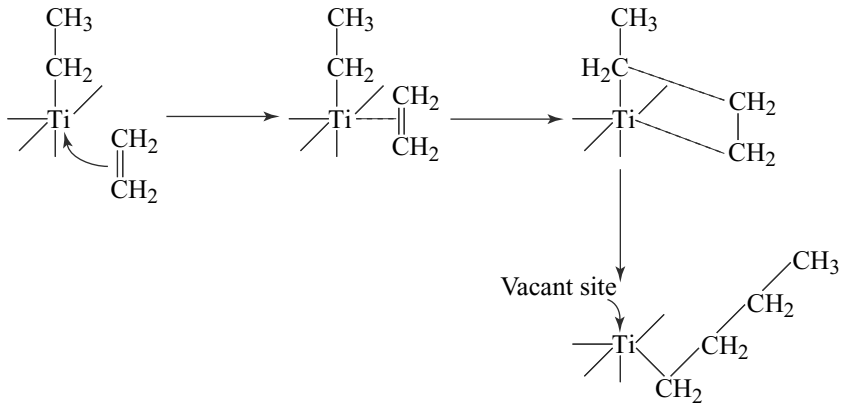
(ii) a cationic addition polymerization.

(iii) an anionic addition polymerization.

In addition to the above transition, metal catalysts may also cause polymerization. The most common is Zeigler–Natta (Z–N) catalyst, $[TiCl_4 + (C_2H_5)_3Al]$. Such polymerizations are termed as *coordination polymerization*, as the transition metal site acts as a coordinating centre for the monomer.

(b) Coordination polymerization

Ethene polymerizes rapidly to polythene at atmospheric pressure and room temperature (in alkane solvent) in the presence of Z–N catalyst. The Z–N catalyst $[TiCl_4 + (C_2H_5)_3Al]$, a fibrous material, is partially alkylated. The titanium is coordinatively unsaturated and acts like a Lewis acid accepting C_2H_4 as ligand. The reaction is believed to proceed as follows:



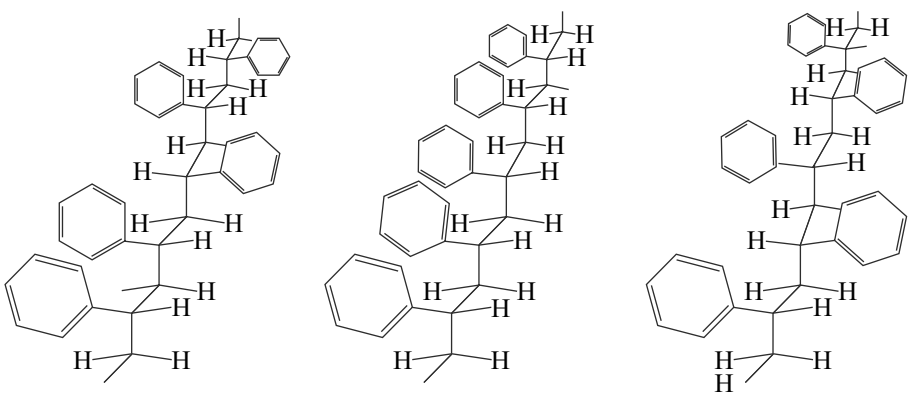
The alkyl group (here CH_2–CH_3) migrates to the coordinated ethene. It again generates a vacant site, which then bound to ethene, and the process is repeated. This polymerization gives a straight-chain polymer.

Propene (or styrene) produces stereoregular polypropene (isotactic) in the presence of Z–N catalyst. The Z–N catalyst can effect copolymerization as well. An important copolymer of styrene, butadiene, and 1,4-hexadiene is synthetic rubber.

Stereochemistry of polymer

Coordination polymerization has stereochemical control. For example, styrene (or propene) can polymerize in three different arrangements, example

1. **Isotactic**
   It has all phenyl groups located at one side of the chain.
2. **Syndiotactic**
   It has the side chain groups (Ph) oriented alternately on one side and then the other.
3. **Atactic**
   In this polymer, phenyl groups are distributed at random (It is easily made by free-radical polymerization).



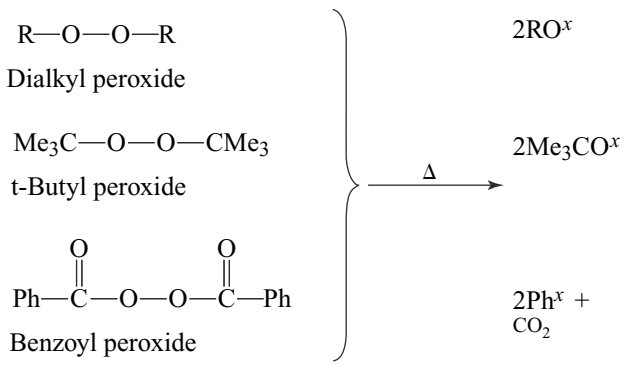
Atactic Isotactic Syndiotactic

By arrangement of proper experimental conditions—catalyst, temperature and solvent etc.,—each of the above polymers can be produced. Full discussion is beyond our scope.

Atactic polymers are generally soft and elastic. Both isotactic and syndiotactic are highly crystalline (example polypropene).

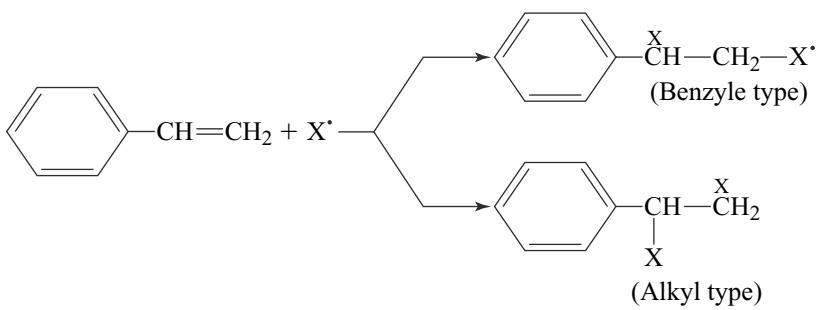
Free radical addition polymerization

A polymerization that proceeds through radicals is called radical polymerization. The radicals are generated by initiators, which decompose easily to form radicals, example peroxides and azo compounds.



Addition of initiator radicals to monomer produces a growing-chain radical. It combines with successive monomers, which ultimately results into the formation of a polymer.

In general, the direction of addition of an initiator to an unsymmetrical monomer takes place in a way to give most stable radical.



Here, $X^{\bullet}$ preferably adds to CH_2 instead of CH as it produces a benzyl-type radical, which is more stable (due to resonance) than alkyl-type radical.

Chain termination occurs either by combination or disproportionation of two radicals.

Polymerization of ethene

Initiation

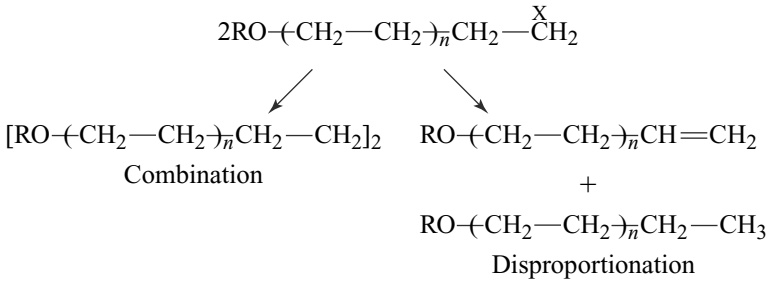
$$R—O—O—R \longrightarrow 2RO$$

Propagation

$$RO^{X} + CH_2{=}CH_2 \longrightarrow RO—CH_2—\overset{X}{C}H_2$$

$$RO—CH_2—\dot{C}H_2 + nCH_2{=}CH_2 \longrightarrow R—O-[-CH_2—CH_2-]_n-CH_2—\overset{X}{C}H_2$$

Termination

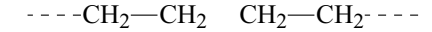


Low-density polythene

Polythene obtained at high temperature (~200°C) has highly branched structure. It is known as low-density polythene. It is chemically inert and tough but flexible and non-conducting. It is used in insulation of electric wires, bottles, pipes and toys.

High-density polythene

Polymerization of ethene at low temperature on atmospheric pressure and in the presence of catalyst gives a polymer having linear structure. It is called high-density polythene.



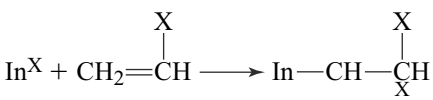
It is chemically inert, hard and tough having high tensile strength. It is used in the manufacturing of pipes, containers, house wares and bottles etc.

Vinyl polymerization

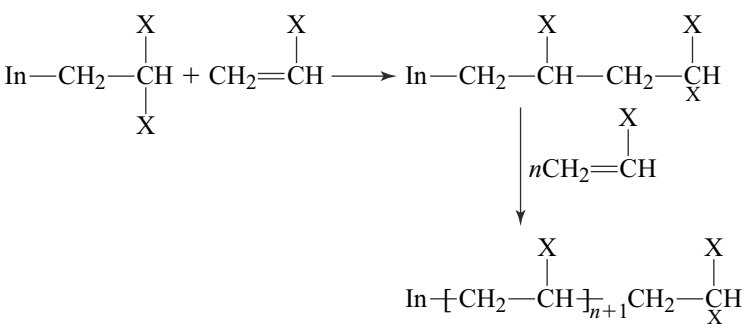
The vinyl group is CH_2=CH–. The monosubstituted ethene derivatives are vinyl compounds, such as vinyl chloride, acrylonitrite and styrene. In general, the compounds can be represented as CH_2=CH–X.

Most of the commercial addition polymers are vinyl polymers. The steps in this polymerization are as follows:

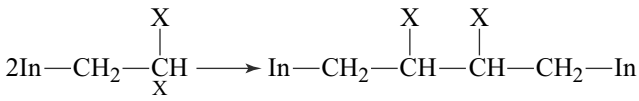
Initiation

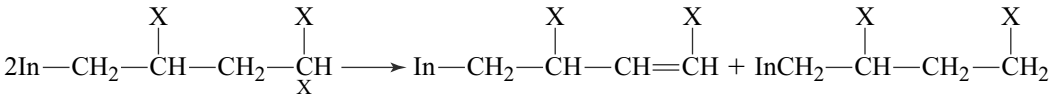


Propagation

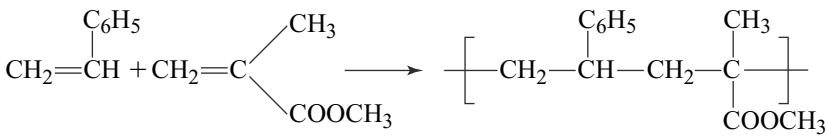


Termination
It proceeds either by radical coupling or disproportionation.



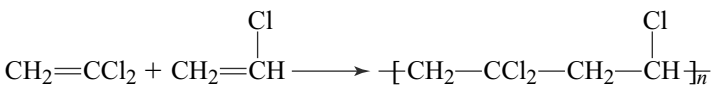


Copolymerization may also proceed in the above way. A common example is a polymer made from styrene and methyl methacrylate.



Styrene Methylmethacrylate Polymer

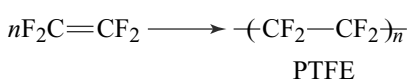
Another example is saran wrap, a copolymer, obtained from vinyl chloride and vinylidene chloride.



Vinylidene chloride Vinyl chloride Saran wrap

Teflon (Polytetrafluoroethylene), PTFE

It is a polymer of tetrafluoroethylene.



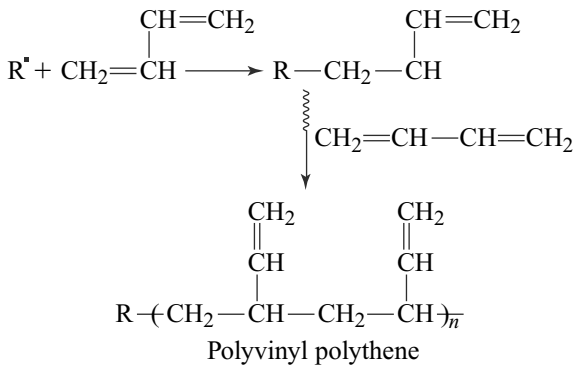
PTFE

Teflon is very inert. It is used as lubricant and electrical insulator. Its coefficient of friction is very low, which still decreases with rise in temperature. For this property, teflon is used for coating of cookwares (non-sticks cookwares).

Polymerization of conjugated diene

Conjugated dienes (1,3-butadiene) may also undergo polymerization. But it may involve 1,2- or 1,4-addition to the monomer.

1,2-polymerization
The polymerization through 1,2-addition (at C-1 and C-2) produces polyvinyl polythene, that is a branched polymer.

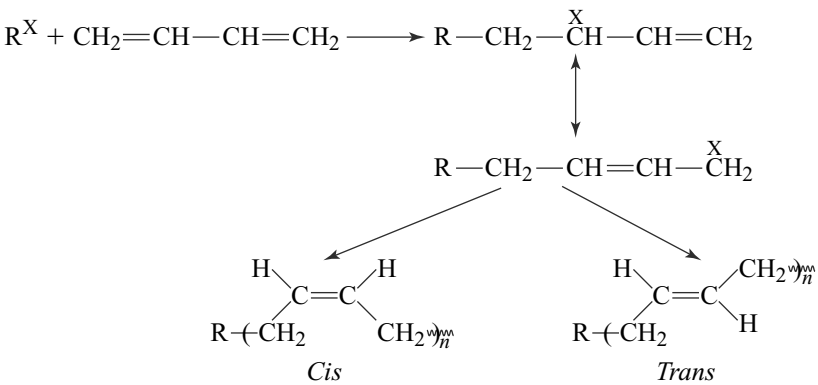


Polyvinyl polythene

The double bond in this polymer can further react with other chemicals. It modifies properties of the original polymers. This reaction is used in the formation of rubbers.

1,4-Polymerization

The polymerization through 1,4-addition produces unbranched polymer. This polymer has double bond. Therefore, the polymer can be *cis*-polybutadiene or *trans*-polybutadiene or a mixture of both.



Cis *Trans*

Many derivative of 1,3-butadiene like isoprene and chloroprene also enter into above type of polymerization. Natural rubber is *cis*-polyisoprene. Synthetic rubbers also include 1,3-butadiene nucleus. We shall take this up later on, in this chapter.

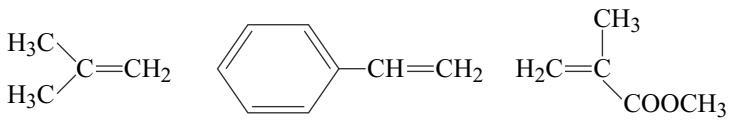
Cationic Addition Polymerization

Cationic polymerization is initiated by acids [H_2SO_4, HF (BF_3 + Small amount of water) etc.]. Polymerization involves intermediate growing-chain cation.

Important aspects of this polymerization are as follows:

1. Acid provide cation, the $H^{\oplus}$.
2. Monomer adds H^+ to form the intermediate growing-chain cation.
3. For the intermediate to be stable, the monomer (alkene) must carry electron-donating group at unsaturated carbon atom.
4. Ethylene fails polymerization by this method as it has no electron-donating group to stabilize the cation.

5. Isobutene, styrene and methyl methacrytate etc. are better monomers.

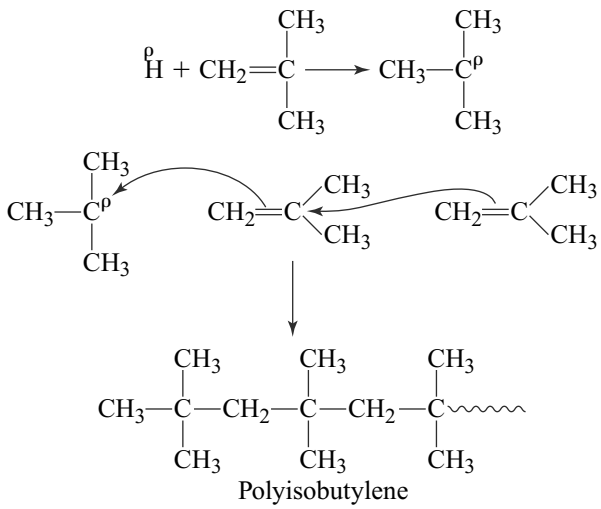


Isobutene Styrene Methyl methacrylate

All the above can stabilize the cationic intermediate by electronic effect (I-effect or resonance).

6. Chain is terminated by an anion.

The polymerization is depicted below:



Polyisobutylene

The polymers of particular molecular weights are very tacky and are used as adhesives for pressure sealing tapes. Copolymerization with a little isoprene gives butyl rubber.

Anionic Addition Polymerization

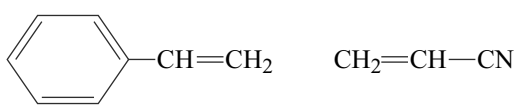
Anionic polymerization is initiated by anions (that is bases like $K^{\rho}N^{\sigma}H_2$ and n-$Bu^{\sigma}Li^{\rho}$).

Important aspects of this polymerization are as follows:

1. Bases provide anion (that is $NH\overline{2}$ or R^{σ}).

2. Monomer adds anion to generate carbanion, which is a chain-growing intermediate.

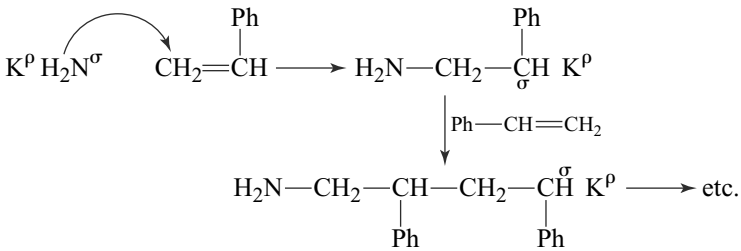
3. Ethenes with strong electron-attracting groups are better monomers. (Example, styrene and acrylonitrile).



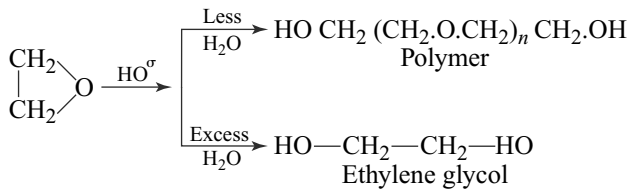
Styrene Acrylonitrile

4. The chain reaction can be terminated by proton acids.

Polymerization of styrene to polystyrene in the presence of KNH_2 is a common example.



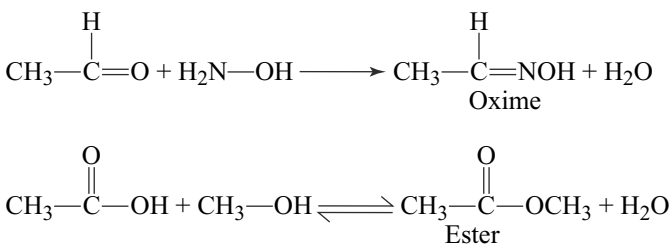
Ethylene oxide may also polymerize in anionic condition. The polymers and polyethylene glycol can be liquids or waxy solids depending upon the molecular weight.



The polymers are water-soluble. This property makes them valuable for preserving archeological objects (or relics). They also find use in cosmetics, pharmaceuticals and lubricants.

Condensation Polymerization

A condensation reaction is that in which two molecules react to split out H_2O (or other simple molecule) and product.

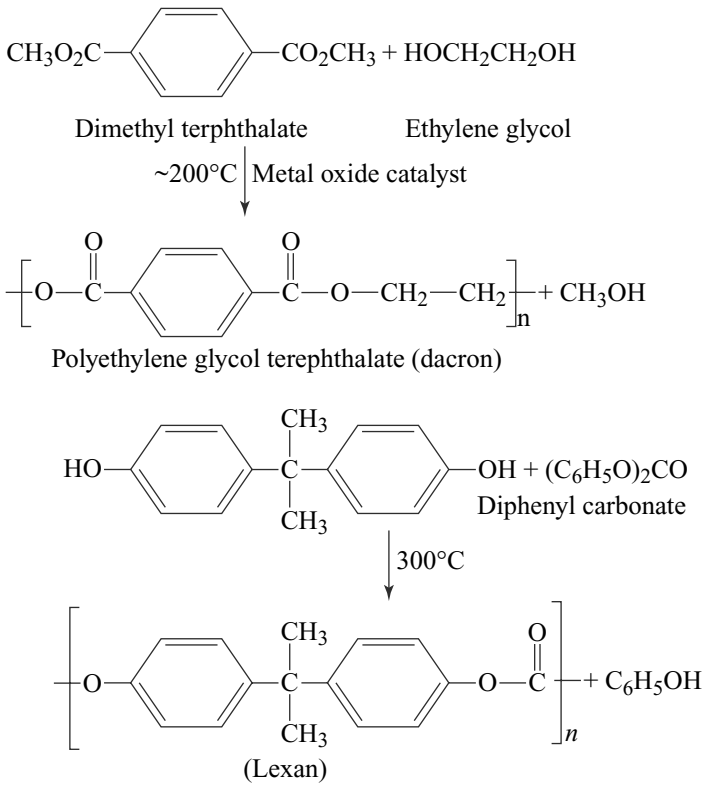


When both reactants are bifunctional (example dicarboxylic acid and diols), the reaction may proceed stepwise to form a polymer. Hence, condensation polymerization is *step–growth polymerization*.

POLYESTERS

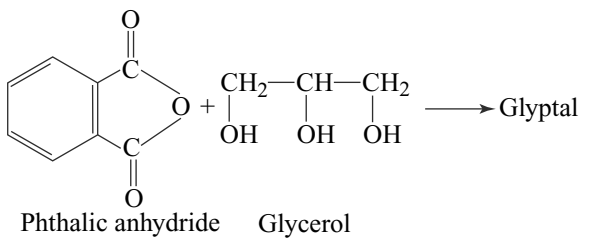
Polyesters are condensation polymers of dicarboxylic acid and diols. For example, dacron, lexan and glyptal.

Synthesis of Dacron and Lexan

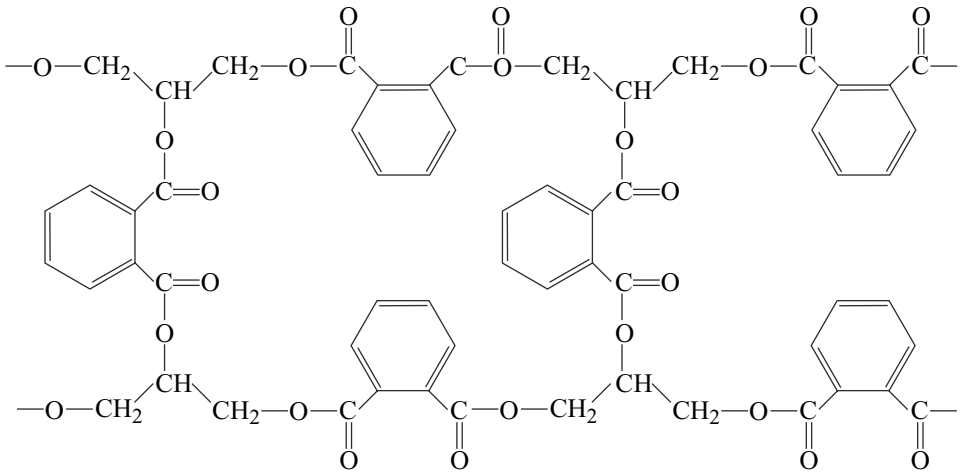


Poly (ethylene terephthalate) is very important, as from it most of the polyester fibres are made, example terylene and dacron. These are crease resistant and mainly used in making wash and wear garments. Terylene-blended wool is highly crease and wrinkle resistant.

However, if either reactant has three or more reactive sites, then formation of a three-dimensional polymer is possible. For example, glyptal, a thermosetting space-network polymer is formed by reaction between glycerol and phthalic anhydride.



Glyptal Resin

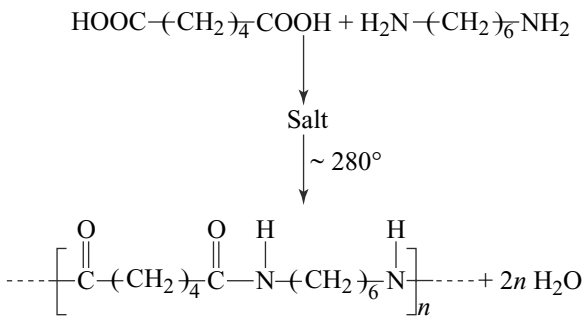


Polyamides

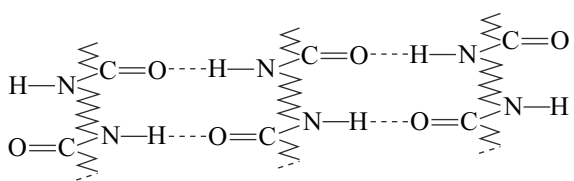
Polyamides are made by heating salts of diamines and dicarboxylic acids. *Nylons* (nylon-66 and nylon-6) are polyamides. Nylons can form fibres and they are stretchable. The intermolecular H-bonding between >NH and >C=O groups of nylon molecules makes them stretchable.

Nylon-66

It is made by heating the pure salt of acipic acid and hexamethylenediamine.

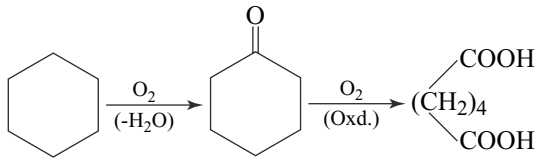


The designation (66) shows that both diamine and dicarboxylic acid contain six C atoms. It is widely used as a fibre, fire cords, ropes and moulded products.

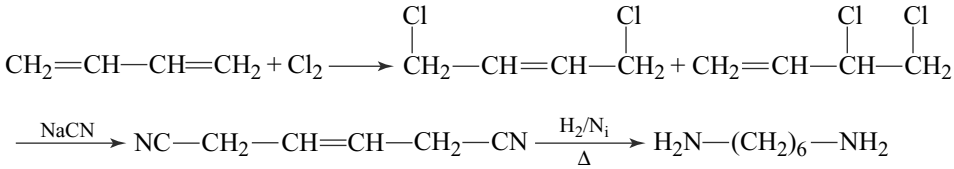


The starting material for nylon-66 are manufactured as follows:

Adipic acid



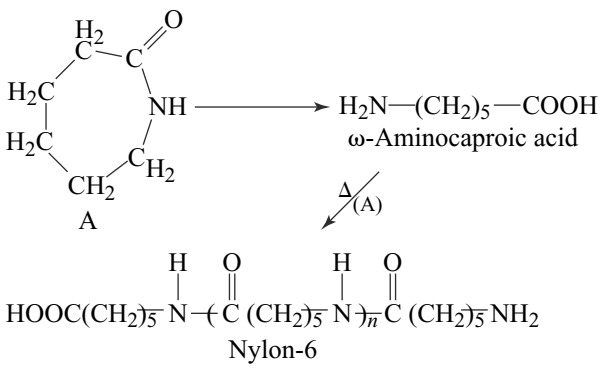
Hexamethylenediamine

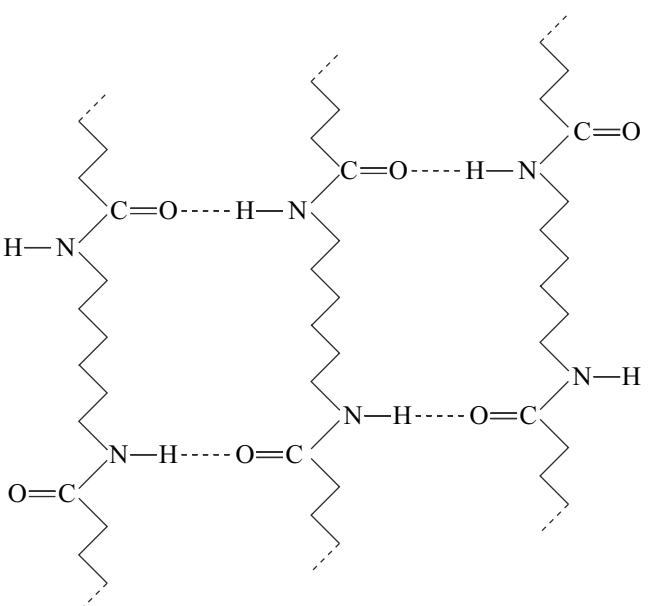


Both, the 1,4 and 1,2-dichlorides give the same product with NaCN.

Nylon-6

Nylon-6 is made from ∈-caprolactum. Caprolactum is first hydrolyzed by heating with water to ω-aminocaproic acid. This acid has six C atom that is incorporated in the name of the polymer (nylon-6).

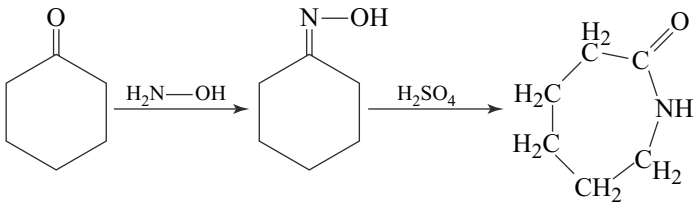




Nylon-6 has important uses in synthetic fibre industry. It is insoluble in common solvents, absorbs little moisture and is strong. The fibres are used in making garments, ropes, tyres and carpets.

ϵ-caprolactum

The starting material for the manufacture of Nylon-6 is prepared by the Backmann rearrangement of cyclohexanone oxime.

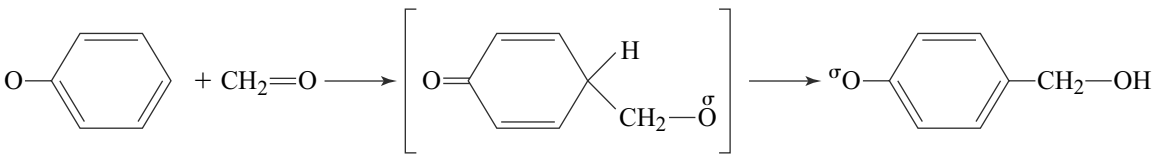


Caprolactum

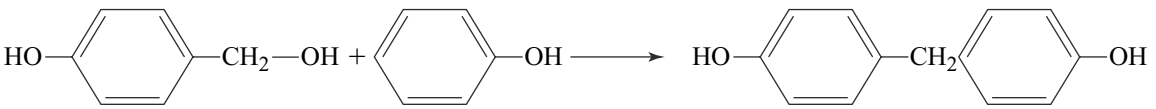
Phenol–Formaldehyde Resins (Bakalite)

Bakalites are the oldest-known thermosetting synthetic polymers. They are made by condensation of phenol with formaldehyde using basic (or acidic) catalysts.

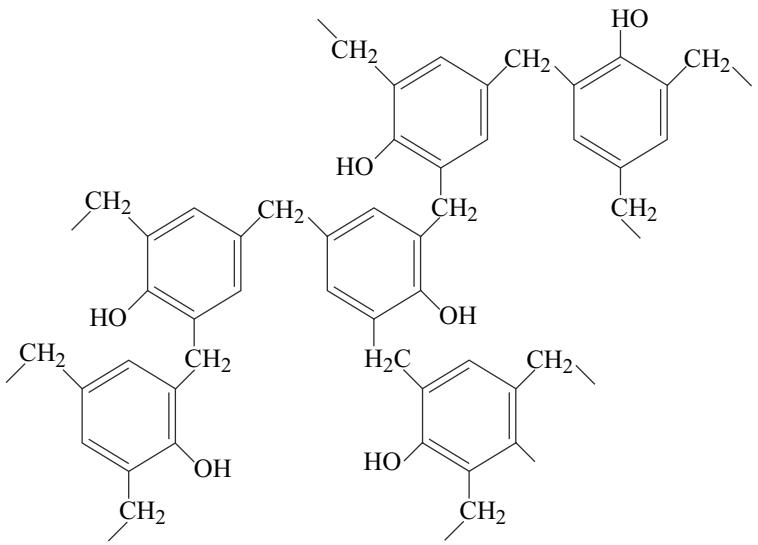
The first stage in the base-induced reaction of formaldehyde and phenol produces *o*– or *p*– hydroxy benzyle alcohol (the *p*- isomer is shown here).



The next step in the condensation is the formation of a dihydroxydiphenyl methane.



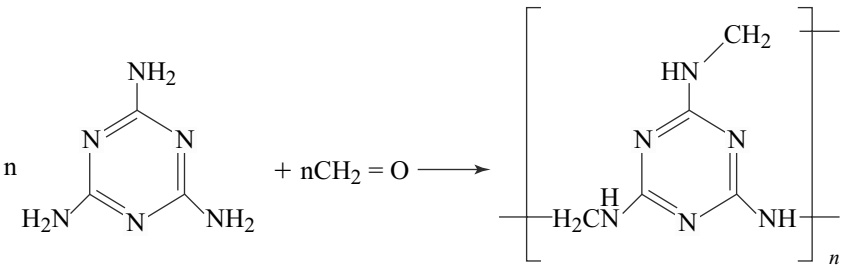
Continuation of these reactions to all the available ortho and para positions (that is three) of phenol leads to the polymer. Thus, the polymer is a cross-linked rigid three-dimensional space-network polymer.



Backlite is widely used for the manufacture of electrical appliances such as switches, plugs, cabinets of TV and radio.

Melamine–Formaldehyde Resin

Melamine and formaldehyde copolymerize to form a polymer known as *Melmac*. It is widely used in kitchenware (cups, plates, etc., that are unbreakable).



The starting material melamine is prepared as

$$6\ NH_2—CO\ NH_2 \xrightarrow[100\ atm]{\sim 300°C} \text{Melamine} + 6NH_3 + 3CO_2$$

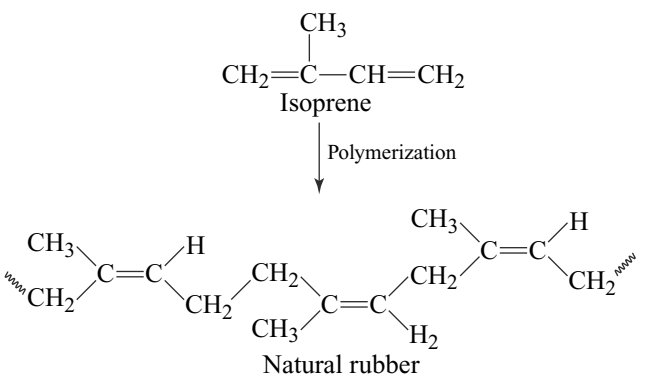
RUBBERS

Rubbers are addition polymers. Natural as well as synthetic rubbers are known.

Natural Rubber

Natural rubber (an elastomer) is a gum that is obtained from the latex of the rubber tree. It is found in South India, Indonesia, Malaysia, Sri Lanka, South America, etc.

Structurally rubber is *cis*-1,4-polyisoprene. Isoprene is 2-methyl-1,3-butadiene.



(*cis*-1,4-Polyisoprene)

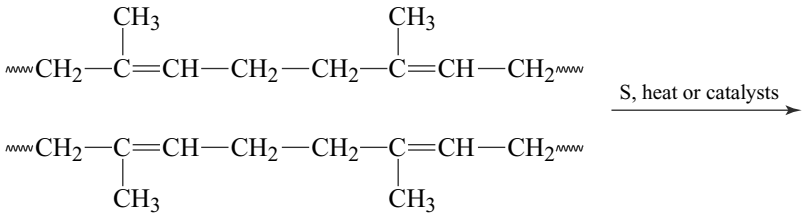
The double bonds in the polymer are present between C-2 and C-3 of isoprene units. These double bonds permit *Vulcanization* (explained ahead).

There are no polar groups in rubber structure. Hence, intermolecular attraction is weak Van der Waals' force. The *cis* configurations around double bonds do not allow polymer chains come close enough. It makes weak van der Waals' force still weaker. Thus, the polymer is not a straight-chain rather it has a coiled structure. It makes rubber a good elastomer.

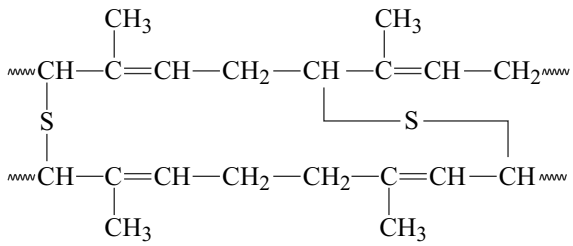
Vulcanization of Rubber

Natural rubber softens at moderate temperature and hardens quickly to a brittle mass. It is water sensitive, attacked by oxidizing agents, non-resistant to non-polar solvents etc. These weaknesses of rubber can be removed by vulcanization.

Rubber (natural or synthetic) has double bonds in its structure. It provides reactive allylic hydrogens and helps in vulcanization. This reaction leads to the formation of S bridges between carbon chains that removes tackiness and strengthens rubber.



Natural rubber



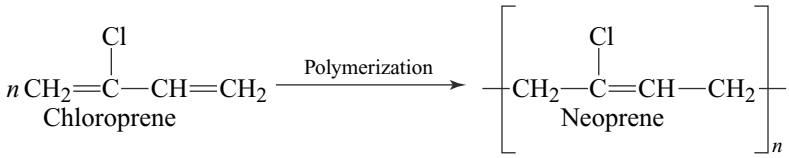
Vulcanized rubber

The strength of vulcanized rubber depends upon S added. For example, about 5 per cant S is added for making tyre rubber but about 30 per cant S is used for making battery case rubber.

Synthetic Rubbers

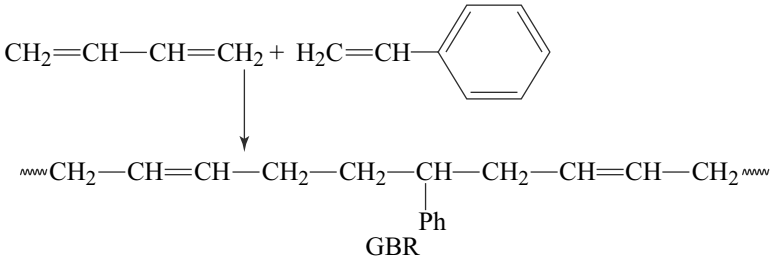
Synthetic rubbers are substitutes for natural rubber. They are either homopolymers of butadiene derivatives or coplymers of butadiene and other substances. Synthetic rubbers also have double bonds in their chains and so they can be vulcanized. Some examples are as follows:

1. **Polychloropene (neoprene)**
   It is a polymer of chloroprene (2-chloro-1,3-butadiene).



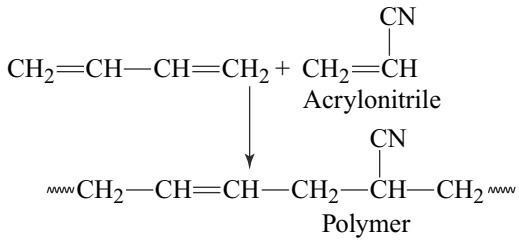
Chloroprene Neoprene

2. **Buna-S or SBR (styrene-butadiene rubbers)**
   It is a copolymer of 1,3-butadiene and styrene. Presently, most of the tyre threads contain this rubber.



GBR

3. **Buna-N (nitrile rubber)**
   It is a copolymer of 1,3-butadiene and acrylonitrile.

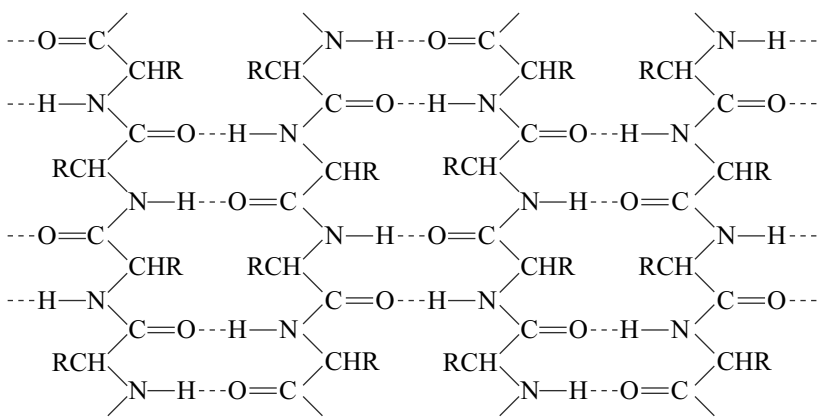


SILK

Silk fibroin is a polypeptide. Its composition varies according to the source of larva. The principalis that the amino acids are glycine (~46 per cant) and another 38 per cant are alanine and serine. Others are small in amount.

The fibroin has oriented-crystalline structure. The polypeptide chains occur in the sheet in anti-parallel arrangement. The chains are H-bonded.

Figure 19.1 H-bonded structure of silk fibroin



WOOL

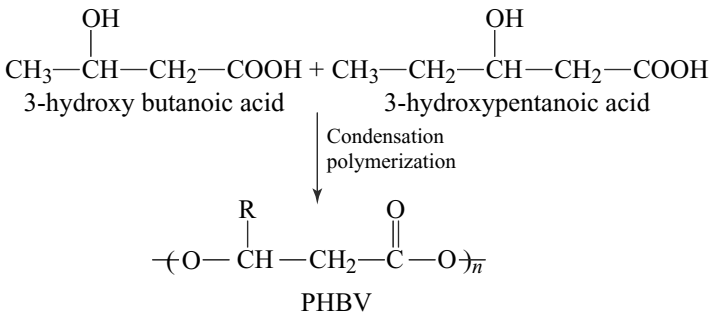
Wool is also a polypeptide but its structure is more complicated. It is because wool contains considerable quantity of cystine that provides disulphide crosslinks between the peptide chains.

BIODEGRADABLE POLYMERS

Synthetic polymers are highly inert. They do not degrade under environmental conditions. They pose a great problem for management of polymeric wastes. The wastes pollute environment heavily. To get rid of this pollution problem, biodegradable synthetic polymers, that is synthetic polymers, which degrade in environment conditions, have been developed. Some examples are as follows:

Polyhydroxybutyrate-Co-β-Hydroxyvalerate (PHBV)

It is a copolymer. The monomers are 3-hydroxybutanoic acid and 3-hydroxypentanoic acid. The monomers are linked through ester linkage.

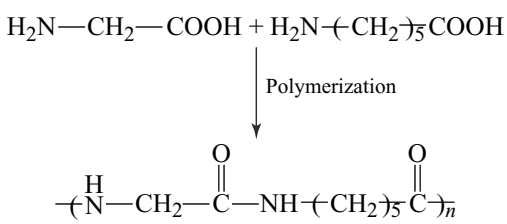


$R = C_2H5, CH_3$

The polymer is degraded by the bacteria in the environment. It is used in orthopaedic devices, capsule for drug and specific packaging etc.

Nylon-2–Nylon-6

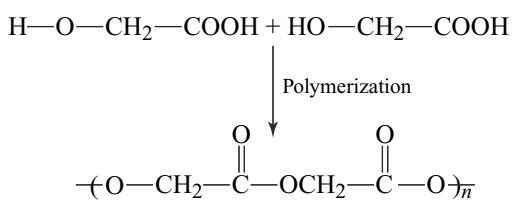
It is a polyamide. The monomers are glycine and amino hexanoic acid. The monomers are alternately present in the polyamide. The -2 and -6 in the polymer shows the number of carbon atoms in the monomers.



Poly (Glycolic Acid) and Poly (Lactic Acid)

These are polyesters (sutures) that are biodegradable. Dextrin (thread) is the first biodegradable suture. It is made from these polyesters that is used for post-operative stitches.

Polymerization proceeds as both the acids are bifunctional.



Monodispersity and Polydispersity

Monodispersity

Polymers in which all the chains are identical chemically as well as in size are known as monodispers samples. This property is monodispersity. Natural polymers possess monodispersity.

Polydispersity

Polymers that contain molecules of different chain lengths are called polydisperse samples. This property is polydispersity. Synthetic polymers generally possess polydispersity.

Mass of Polymers

Polymers may have molecules of different chain lengths. Thus, molar mass of polymers has a range. In these cases, experiments give different molar masses. Thus, average mass of the polymer is determined by the following two types:

1. Number average molar mass, $<M>n$.
2. Weight average molar mass, $<M>w$

For a polymer, containing n_1 molecules of molar mass M_1, n_2 molecules of molar mass M_2, etc., the number of average molar mass

$$< M >_n = \frac{n_1 M_1 + n_3 M_3 + \cdots\cdots\cdots}{n_1 + n_2 + n_3 + \cdots\cdots} = \frac{\sum n_i M_i}{n_i}$$

Weight average molar mass

$$< M >_w = \frac{n_1 M_1^2 + n_2 M_2^2 + n_3 M_3^2 + \cdots\cdots\cdots}{n_1 M_1 + n_2 M_2 + n_3 M_3 + \cdots\cdots} = \frac{\sum n_i M_i^2}{\sum n_i M_i}.$$

For natural polymers (which are monodisperse samples), $<M>n = <M>w$.

But for synthetic polymers, $<M>w$ is always greater than $<M>n$. However, both may be equal if the polymer is carefully purified to the level of monodispersity.

Polydispersity Index (PDI)

The ratio of the weight and number of the average molecular masses is known as the polydispersity index (PDI), that is

$$PDI = \frac{< M >_w}{< M >_n}.$$

For some natural polymers, which are monodisperse, $PDI = 1$, but for synthetic polymers PDI is greater than unity. It is because synthetic polymers are polydisperse.

Polymers of Ethylene and Substituted Ethylene

Table 19.1 Addition polymers

Monomer(s)	Formula	Polymer	Structure	Uses
Ethylene or ethene	$CH_2{=}CH_2$ $CH_2{=}CH_2$	Polyethylene Polythene	$-(CH_2-CH_2)_n-$	Film, containers, packaging, piping, etc.
Propene	$CH_3-CH_2{=}CH_2$	Polypropene	$-(CH_2-CH(CH_3))_n-$	Fibres, moulded articles, rope, etc.
Vinyl chloride	$CH_2{=}CH-Cl$	Polyvinyl chloride (PVC)	$-(CH_2-CH(Cl))_n-$	Insulation, film, pipes, raincoat, bags and plastic
Styrene	$CH_2{=}CH-C_6H_5$	Polystyrene	$-(CH_2-CH(C_6H_5))_n-$	Foam, toys, combs, insulator, false roofing, etc.
Acrylonitrile	$CH_2{=}CH-CN$	Polyacrylonitrile (orlon)	$-(CH_2-CH(CN))_n-$	Fibres, carpets, synthetic wool, etc.
Tetrafluoethene	$F_2C{=}CF_2$	Polytetrafluoethene (teflon)	$-(CF_2-CF_2)_n-$	Valves, gaskets, lubricant, coatings, etc.
Methyl methacrylate	$CH_2{=}C(CH_3)-CO_2CH_3$	Polymethyl methaacrylate (plexi glass)	$-(CH_2-C(CN)(CO_2CH_3))_n-$	Aircraft window, dentures coatings, optical lenses, etc.
2-Chloro-1,3 butadiene	$CH_2{=}C(Cl)-CH{=}CH_2$	Neoprene	$-(CH_2-C(Cl){=}CH-CH_2)_n-$	Insulator, conveyer belt and printing rollers
Ethyl acrylate	$CH_2{=}CH-CO_2C_2H_5$	Polyethyl acrylate	$-(CH_2-CH(C_6H_5))_n-$	Films, pipes and finishing fabrics
1,3-butadiene styrene	$CH_2{=}CH-CH{=}CH_2$ $CH_2{=}CH-C_6H_5$	Styrene butadiene rubber (Buna-S or SBR)	$-(CH_2-CH{=}CH-CH_2-CH(C_6H_5)-CH_2)_n-$	Tyres and foot wears
1,3-butadiene acrylonitrile	$CH_2{=}CH-CH{=}CH_2$ $CH_2{=}CH-CN$	Nitrile rubber (Buna-N)	$-(CH_2-CH{=}CH-CH_2-CH(CN)-CH_2)_n-$	Oil seals, manufacture of tank linings and hoses

Table 19.2 Polyesters (condensation polymers)

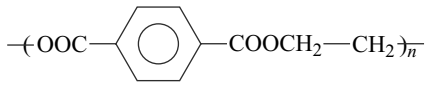
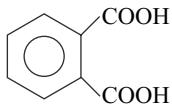
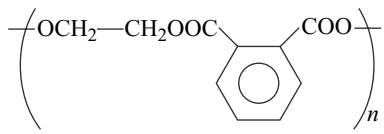
Monomer(s)	Formula	Polymer	Structure	Uses
1. Ethylene glycol 2. Terephthalic acid	$HOCH_2.CH_2.OH$ 	Terylene (Dacron)		Fibres, tyre, cord, tents, safety belts, etc.
1. Ethylene glycol 2. Phthalic acid	$HOCH_2—CH_2—OH$ 	Glyptal		Binder in paints and mixed plastic

Table 19.3 Polyamides

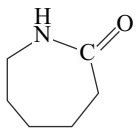
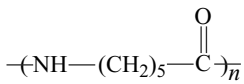
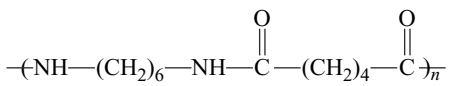
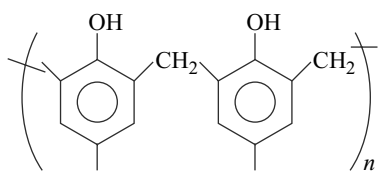
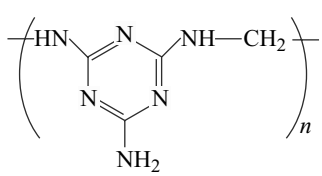
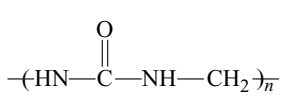
Monomer(s)	Formula	Polymer	Structure	Uses
Carprolactum		Nylon-6		Fibres, plastic, ropes, tyre cords, etc.
1. Caproic acid 2. Hexamethylene diamine	$HOOC—(CH_2)_4—COOH$	Nylon-66		Fibres, brushes, ropes, carpets and parachutes

Table 19.4 Resins

Monomer(s)	Formula	Polymer	Structure	Uses
1. Formaldehyde 2. Phenol	HCHO $C_6H_5.OH$	Bakelite		Protective coating, gears, radio, TV, cabinets and electrical fittings
1. Formaldehyde 2. Melamine	HCHO	Melamine formaldehyde resin		Plastic, unbreakable cups, plates, etc.
1. Formaldehyde 2. Urea	HCHO H_2NCONH_2	Urea formaldehyde resin		Unbreakable crockery and laminated sheets

PROBLEMS

Objective-Type Questions

1. Which one of the following monomers gives the polymer neoprene on polymerization?
(a) $CH_2=CHCl$
(b) $CCl_2=CCl_2$
(c) $CH_2=\underset{\displaystyle Cl}{\underset{|}{C}}-CH=CH_2$
(d) $CF_2=CF_2$

2. Which of the following is a fully fluorinated polymer?
(a) Neoprene (b) Teflon
(c) Thiokol (d) PVC

3. Which of the following is a chain-growth polymer?
(a) Orlon (b) Terylene
(c) Nylon-6 (d) Glyptal

4. Which of the following is a step-growth polymer?
(a) Orlon (b) Terylene
(c) Teflon (d) Styron

5. The monomer of synthetic rubber is
(a) butadiene
(b) chloroprene
(c) 2-methyl-1,2-butadiene
(d) 2–methyl-1,3-butadiene

6. Which of the following is a copolymer?
(a) Natural rubber (b) Synthetic rubber
(c) Gutta-percha (d) Saran

7. The monomer of teflon is
(a) FClC=CClF (b) $Cl_2C=CCl_2$
(c) $F_2C=CF_2$ (d) $FClC=CF_2$

8. Which of the following has amide linkages?
(a) Nylon (b) Bakelite
(c) Terylene (d) PVC

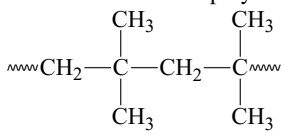
9. Polymerization of caprolactam yields
(a) terylene (b) nylon-6
(c) nylon-66 (d) bakelite

10. Which of the following is an elastomer?
(a) Bakelite (b) Polyethylene
(c) Nylon-6 (d) Natural rubber

11. Which of the following is a fibre?
(a) Bakelite (b) Polyethylene
(c) Nylon-6 (d) Natural rubber

12. The monomers of Buna-S polymers are
(a) vinyl chloride and vinylidene
(b) styrene and butadiene
(c) acrylonitrile and butadiene
(d) isobutylene and isoprene

13. The monomer of the polymer



polymer <artwork>is
(a) $CH_2=C(CH_3)_2$
(b) $CH_3–CH=CH–CH_3$
(c) $CH_3–CH=CH–CH_3$
(d) $(CH_3)_2C=C(CH_3)_2$

14. $\sim\!\!\sim NH(CH_2)NHCO(CH_2)_4CO\sim\!\!\sim$ is a
(a) addition polymer (b) thermosetting polymer
(c) homopolymer (d) copolymer

15. Which of the following is used to make non-stick cookware?
(a) Poly (ethylene terephthalate)
(b) Polystyrene
(c) Poly tetrafluoro ethylene
(d) PVC

16. Which of the following is used for the formation of nylon-66?
(a) Adipic acid
(b) Sulphurous acid
(c) Sulphur hexafluoride
(d) Phthalic acid

17. Terylene is a condensation polymer of ethylene glycol and
(a) phthalic acid (b) benzoic acid
(c) terephthalic acid (d) salicylic acid

18. Natural rubber is a polymer of
(a) butadiene (b) ethyne
(c) styrene (d) isoprene

19. Which of the following is a biodegradable polymer?
(a) Polystyrene (b) Neoprene
(c) Suture (d) Orlon

20. Which of the following is a copolymer?
(a) Natural rubber (b) PVC
(c) Teflon (d) Buna-S

21. Natural rubber is
(a) *trans*-1,4-polyisoprene
(b) 1,4-polyisoprene
(c) *cis*-1,4-polyisoprene
(d) *cis*-1,3-polyisoprene

22. Isotactic polystyrene has
(a) all phenyl groups at one side of the chain
(b) phenyl groups oriented alternately
(c) phenyl groups distributed randomly
(d) two phenyl groups on one side then the next two in the other side

23. Which of the following is a thermosetting polymer?
(a) Nylon-66 (b) Bakelite
(c) Glyptal (d) Polystyrene

24. The polymer, which is a polyamide, is
(a) glyptal (b) teflon
(c) nylon-6 (d) dacron

25. Which of the following is a chain-growth polymer?
(a) PVC (b) Dacron
(c) Bakelite (d) Nylon-66

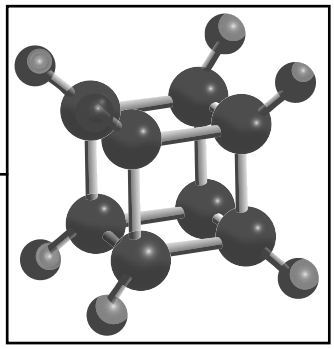
26. In Ziegler–Natta catalyst ($TiCl_4$ + Et_3Al) titanium acts as a
(a) Lewis base (b) Lewis acid
(c) Bronsted base (d) Bronsted acid

27. Which of the following is not expected to polymerize through cationic addition polymerization method?
(a) Isobutene (b) Styrene
(c) Ethylene (d) Methyl methacrylate

Answers

1. (c)	2. (b)	3. (a)	4. (b)	5. (b)
6. (d)	7. (c)	8. (a)	9. (b)	10. (d)
11. (c)	12. (b)	13. (a)	14. (d)	15. (c)
16. (a)	17. (c)	18. (d)	19. (c)	20. (d)
21. (c)	22. (a)	23. (b)	24. (c)	25. (a)
26. (b)	27. (c)			

CHAPTER 20



Column Matching Problems

COLUMN MATCHING

1. Match list I with list II and select the correct answer using the codes given below.

List I		List II
A. $R_2C{=}O + RNH_2$	$\longrightarrow$	M. A Phenyl hydrazone
B. $RCH{=}O +$	$\xrightarrow{H^+}$	N. Schiff's base
C. Phenyl hydrazine	$\xrightarrow[\text{gas}]{\text{Dry HCl}}$	O. Benzaldehyde oxime
D. $PhCHO + NH_2OH$	$\xrightarrow{H^+}$	P. An acetal

Codes	(A)	(B)	(C)	(D)
(a)	N	P	M	O
(b)	M	P	N	O
(c)	O	N	P	M
(d)	N	O	M	P

2. Organic compound in list I are oxidized by HIO_4. The list II includes oxidized products. Match list I with list II using codes.

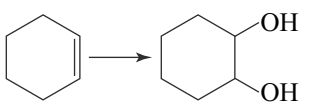
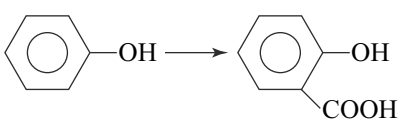
List I	List II
A. CH_3COCHO	1. $PhCH = O + HCOOH$
B. 1,2-cyclohexane dione	2. $CH_3CH_2CHO + HOOCCH_3$
C. $PhCH(OH)CHO$	3. $HOOC(CH_2)_4COOH$
D. $CH_3CH_2CH(OH)COCH_3$	4. $CH_3COOH + HCOOH$

Codes	(A)	(B)	(C)	(D)
(a)	4	3	1	2
(b)	4	3	2	1
(c)	3	4	1	2
(d)	3	2	1	4

3. Match list I with list II.

List I	List II
A. $C_6H_5—CHO \longrightarrow$	1. Rosenmund reduction
B. $C_6H_6 + CH_3Cl \xrightarrow[AlCl_3]{Anhy.}$	2. Kolbe–Schmidt reaction
C. $R—COCl + H_2 \xrightarrow[BaSO_4]{Pd}$	3. Friedel–Crafts reaction
D. $C_6H_5—OH + NaOH \xrightarrow[BaSO_4]{Pd}$	4. Cannizzaro reaction

4. Match the reactions in list I with the reagents in list II.

List I	List II
A. 	1. $CHCl_3/NaOH$
B. $CH_3—CH=CH_2 \longrightarrow CH_3—CH_2—CH_3$	2. $O_3/Zn, H_2O$
C. 	3. $KMnO_4$
D. $C_2H_5—CH=C(CH_3)_2 \longrightarrow C_2H_5CHO + CH_3—COCH_3$	4. Pd/H_2

5. Match the species in column I with properties given in column II.

Column I	Column II
A. $CH_2{=}CH{-}CH_2$	1. Resonance
B. CH_3^-	2. Pyramidal
C. $CH_3{-}CH_2$	3. Electrophile
D. $CH_3{-}CH{=}CH{-}COCH_3$	4. Nucleophile

6. Match statements made in column I with facts in column II.

Column I	Column II
A. Ether	1. Neutral $FeCl_3$
B. Phenol	2. Williamson's synthesis
C. Tert-alcohol	3. $AgNO_3$/aq. NH_3
D. $R{-}C{\equiv}CH$	4. Lucas reagent

7. Match the compounds (or ions) in column I with properties (or reactions) in column II.

Column I	Column II
A. $R{-}C{\equiv}CH$	1. gives precipitate with $AgNO_3$.
B. CN^-	2. is a nucleophile.
C. $C_6H_5{-}CHO$	3. gives precipitate with 2,4-dinitrophenylhydrazine.
D. I^-	4. is involved in cyanohydrine formation.

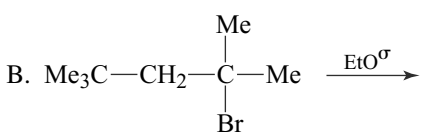
8. Match the chemical species in column I with properties given in column II.

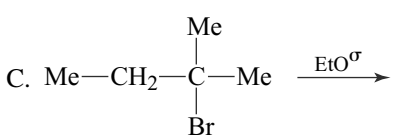
Column I	Column II
A. NO_2^+	1. Trigonal pyramidal
B. CH_3^- Phenol	2. Electrophile
C. CCl_2	3. Nucleophile
D. NH_3	4. Formed by 1,1-elimination reaction

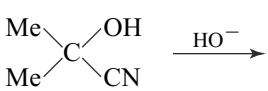
9. Match column I with column II.

Column I	Column II
A.	1. π-deficient aromatic
B.	2. π-efficient aromatic
C.	3. Resonance stabilized
D.	

1. Hoffmann elimination, major reaction

B.  2. E_1CB mechanism

C.  3. Saytzeff elimination major reaction

D.  4. E_1 mechanism

11. Match the chemical substances in column I with type of polymers (type of bonds) in column II.

Column I	Column II
A. Rubber	1. Natural polymer
B. Buna-S	2. Amide linkage
C. Nylon-6	3. Synthetic polymer
D. Starch	4. *cis*–Configuration

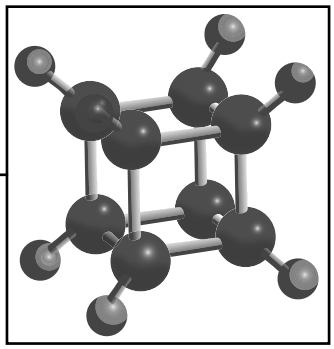
12. Match the facts in column I with column II.

Column I	Column II
A. Nylon-6	1. Condensation polymer
B. Polythene by Zeigler–Natta catalyst	2. H–b bonding
C. Polystyrene	3. Isotactic
D. Bakelite	4. High-density polymer

Answers

1. a	2. a
3. A → 4, B → 3, C → 1, D → 2	4. A → 3, B → 4, C → 1, D → 2
5. A → 1, 3, 4, B → 2, 4, C → 3, D → 1, 3, 4	6. A → 2, B → 1, C → 4, D → 3
7. A → 1, 2, B → 1, 2, 4, C → 2, 3, 4, D → 1, 2	8. A → 2, B → 1, 3, C → 2, 4, D → 1, 3
9. A → 1, 3, B → 2, 3, 4, C → 4, D → 3	10. A → 1, B → 1, 4, C → 3, 4, D → 2
11. A → 1, 3, 4, B → 3, 4, C → 2, 3, D → 1	12. A → 1, 2, B → 4, C → 3, D → 1

CHAPTER 21



Short Answer Problems

SHORT-ANSWER PROBLEMS

1. Which resonance that forms in each of the following set is a major contributor to the real structure? Give reason in one or two sentences.

(i) $CH_2{=}C(CH_3){-}CH{=}CH_2 \longleftrightarrow {}^{\rho}CH_2{-}C(CH_3){=}CH{-}{}^{\sigma}CH_2 \longleftrightarrow {}^{\sigma}CH_2{-}C(CH_3){=}CH{-}CH_2^{\oplus}$

A B C

(ii) $CH_3{-}C(=O){-}CH{=}CH_2 \longleftrightarrow CH_3{-}C(O^{\sigma}){-}CH{=}CH_2 \longleftrightarrow CH_3{-}C(O^{\sigma}){=}CH{-}CH_2^{\oplus}$

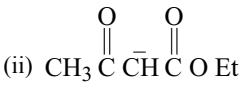
A B C

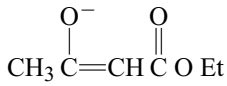
(iii) $CH_3{-}C(=O){-}\ddot{N}H_2 \longleftrightarrow CH_3{-}C(O^{\sigma}){-}\ddot{N}H_2 \longleftrightarrow CH_3{-}C(O^{\rho}){-}\ddot{N}H_2 \longleftrightarrow CH_3{-}C(O^{\sigma}){=}NH_2^{\rho}$

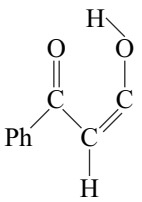
A B C D

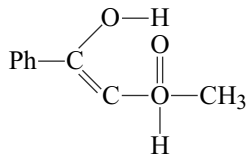
2. Classify the following pairs as resonance contributors or structural isomers.

(i) $CH_3C(=O)CH_2C(=O)OEt$ $\qquad$ $CH_3C(OH){=}CHC(=O)OEt$

(ii) 



(iii) 



3. Define the term 'aromaticity'. How is it related with Huckel rule? Account for the aromaticity of cyclopentadienyl anion and cycloheptatrienyl cation.

4. The cyclopentadienyl cation is an antiaromatic compound, whereas cyclopropenyl cation is an aromatic compound. Explain in brief.

5. How do you explain the instability of vinyl alcohol and stability of phenol, although both contain an OH group linked to sp^2 carbon?

6. Why 8-hydroxyquinoline can be separated from 4-hydroxyquinoline by steam distillation?

7. In the second ionization, fumaric acid is stronger than maleic acid. Explain.

8. Why are the cyanoanilinium ions $(C_6H_4(CN)\overset{+}{N}H)_3$ stronger acids than the anilinium ions $C_6H_5\overset{+}{N}H_3$?

9. Arrange the following compounds in order of increasing acidity (weakest acid first). Give a reason for your answer in short.

(a) *p*-Nitrobenzoic acid (b) 2,4-Dinitrobenzoic acid

(c) 2,4,6-Trimethylbenzoic acid (d) 3,4-Dinitrobenzoic acid

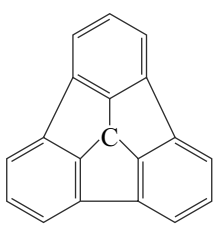
10. Arrange the following sets of compounds in order of increasing acidity (weakest acid first).

(a) 2-Chlorobutanoic acid (b) 4-Chlorobutanoic acid

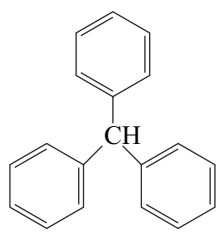
(c) 3-Chlorobutanoic acid (d) Butanoic acid

11. Triphenylmethane is stronger acid than diphenylmethane, which in turn is stronger acid than toluene. Explain.

12. Which of the compound (A or B) is expected to be the stronger acid? Give reasons.



A



B

13. Arrange the following acids in order of increasing acid strength.

Benzoic acid *p*-tert-Butylbenzoic acid *p*-Nitrobenzoic acid

A B C

14. Explain the following in brief.

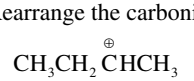
(i) Guanidine is very strong base

(ii) Amides are less basic than amines

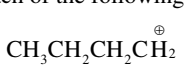
(iii) Pyridine is much weaker base than aliphatic amines

(iv) N,N-dimethyl-o-toluidine is stronger base than N,N-dimethylaniline.

15. Rearrange the carbonium ions in each of the following sets in order of stability (least stable first).

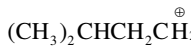


A

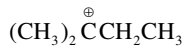


B

C


A

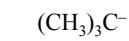
B

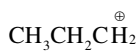

C

16. What is the state of hybridization of carbon in carbonium ion, carbanion, free radical, singlet carbine and benzyne?

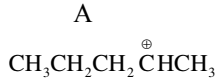
17. Say, which cation will have the tendency to undergo rearrangement for each pair?

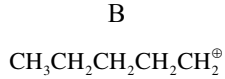
(i)
A


B

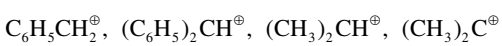
(i) 
A

B

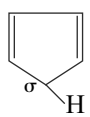
(i) 
A


B

18. Arrange the following carbonium ions in order of increasing stability (least stable first).



19. Arrange the following carbanions in order of decreasing stability (most stability first).


I

II

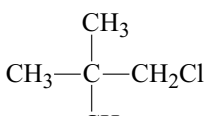
III

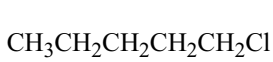
IV

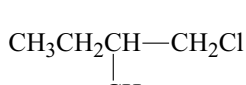
V

VI

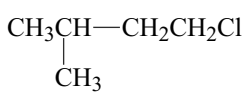
20. Arrange the following compounds in order of decreasing reactivity towards sodium iodide in acetone.

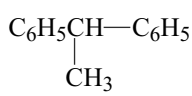

A

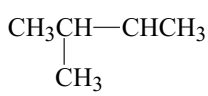

B


C

21. Arrange the following compounds in order of reactivity towards aqueous formic acid (most reactive first).


A


B


C

22. (i) Arrange the following nucleophiles in order of increasing nucleophilicity.

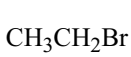
I^{σ} Cl^{σ} Br^{σ}

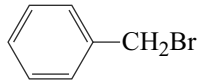
(ii) Explain the fact that allyl chloride (CH_2=CH–CH_2–Cl) undergoes substitution reaction by S_N1 mechanism whereas *n*-propyl chloride ($CH_3CH_2CH_2Cl$) reacts by S_N2 mechanism.

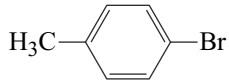
(iii) How do you explain the inertness of chlorine in chlorobenzene and vinyl chloride in substitution reactions?

23. Predict the order of reactivity of the following halides with (a) sodium iodide in acetone and (b) aqueous alcoholic silver nitrate.

I


II


III


IV

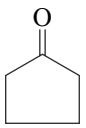
24. Ozonolysis of alkenes A, B, C, D and E gave the following products. Predict the structures of alkenes A through E.

[A] $CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}—H$ (only)

[B] $CH_3\overset{O}{\overset{\|}{C}}CH_3 + CH_3\overset{O}{\overset{\|}{C}}—H$

[C] $CH_3CH_2\overset{O}{\overset{\|}{C}}—H$ (only)

[D] $CH_3\overset{O}{\overset{\|}{C}}—\overset{O}{\overset{\|}{C}}—H$ + 2 moles of $H_3\overset{O}{\overset{\|}{C}}—CH_3$ (only)

[E]  + $H—\overset{O}{\overset{\|}{C}}—H$

25. What are singlet and triplet carbenes? Predict state of hybridization of carbon in them.

26. Which alcohol in each of the following pairs would undergo easy dehydration? Give reason for your answer.

(i) $CH_3CH_2CH_2CH_2OH$ and $CH_3\underset{OH}{\underset{|}{C}}HCH_2CH_3$

A B

(ii) $CH_2\underset{OH}{\underset{|}{C}}H—\underset{CH_3}{\underset{|}{C}}HCH_2CH_3$ and $CH_3\underset{CH_3}{\underset{|}{C}}H—\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}—CH_3$

A B

(iii) $CH_3CH_2\underset{CH_3}{\underset{|}{C}}H—\underset{OH}{\underset{|}{C}}—CH_3$ and $CH_3CH_2\underset{CH_2CH_3}{\underset{|}{C}}H—\overset{OH}{\overset{|}{C}}HCH_3$

A B

27. Predict the structure of alkenes expected from the dehydrohalogenation of the following alkyl halides. In case of isomeric alkenes, predict the major product.

(i) 2-Bbromobutene
(ii) 1-Chlorobutane
(iii) 2-Chloro-3-methylbutane
(iv) 3-Chloro-2-methylpentane
(v) 2-Bromo-3-methylpentane, and
(vi) 2-Chloro-3,3-dimethylpentane

28. Predict the product(s) in the following reactions:

(i) $ClCH_2COOC_2H_5 \xrightarrow[(ii)\ C_6H_5CHO]{(i)\ C_2H_5O^{\sigma}} X \xrightarrow[(ii)\ H^{\oplus}]{(i)\ Base} Y$

(ii) $EtOCO(CH_2)_4COOEt \xrightarrow[H^{\oplus}]{C_2H_5O^{\sigma}}$

29. Arrange the following hydrocarbons in order of decreasing acidity (most acidic first).

$(C_6H_5)_3CH$ (I) $(C_6H_5)_2CH_2$ (II) $(C_6H_5)_3CH$ (III)

30. (i) More than one equivalent of $AlCl_3$ is used in Friedel–Crafts acylation reaction in order to obtain a good yield. Suggest a reason.

(ii) In Friedel–Crafts reactions, nitrobenzene is often used as a solvent. Why does it not compete with the aromatic substrate for this reaction?

31. Predict the major product in each of the following reaction.

(i) Monochlorination of *p*-cymene
(ii) Monobromination of *o*-cresol
(iii) Mononitration of *p*-fluorobromobenzene
(iv) Mononitration of benzotrichloride
(v) Mononitration of *m*-bromochlorobenzene

32. Rank the following free radicals in order of decreasing stability (most stable first).

$C_6H_5\dot{C}HC_6H_5$ (A) $C_6H_5\dot{C}HCH_3$ (B)

$C_6H_5\dot{C}H{-}CH{=}CH_2$ (C) $CH_3CH{=}CHCH_2\dot{C}H_2$ (D)

33. Two alkenes, A and B, on oxidation with $KMnO_4$ yield glycols, which give carbonyl compounds on treatment with periodic acid.

(A) $CH_3{-}\overset{\overset{O}{\|}}{C}{-}CH_3$ (2 moles) and $CH_3\overset{\overset{O}{\|}}{C}CH_2COCH_3$ (1 mole)

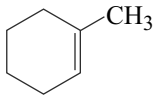
(B) $CH_3(CH_2)_7CHO$ (1 moles) and $CHO(CH_2)_7COOH$ (1 moles)

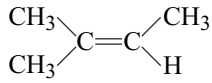
Deduce structures of A and B and write reactions involved.

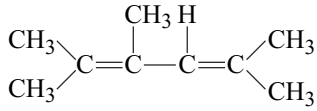
Answers

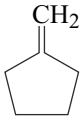
1. 'A' in every set as C atoms having an octet structure.
2. (i) Tautomers, (ii) Resonance structures, (iii) and (iv) Structural isomers, (v) and (vi) Resonance structures
8. (i) The –CN group is electron attracting
(ii) $o-C_6H_4(CN)\overset{\oplus}{N}H_3 > p-C_6H_4(CN)\overset{\oplus}{N}H_3 > m-C_6H_4(CN)\overset{\oplus}{N}H_3$
9. (c) < (a) < (b) < (d)
10. (d) < (b) < (c) < (d)
11. Triphenylmethane > Diphenylmethane > Toluene
12. A > B (anion of A has locked structure, remains planar, so better resonance stabilization. The anion of B may not remain planar because of steric reason).

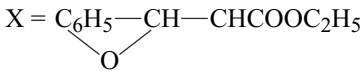
13. B < A < C
15. C > A > B and C > B > A
17. (I) and (II) A ⟶ B (hydride shift), (III) B ⟶ A (shift)
18. ART TK
19. I > II > V > VI > IV > III
20. B > C > A (S_N2 reaction, steric effect)
21. II > III > I (S_N1 reaction, electronic effect, stability of carbocation)
22. (I) $I^{\sigma} > Br^{\sigma} > Cl^{\sigma}$
23. (a) I > II > III > IV (b) III > II > I > IV

24. A = 

B = 

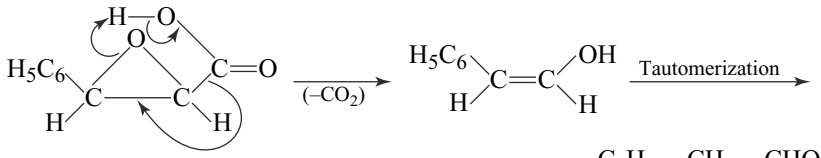
C = $CH_3—CH_2.CH=CH.CH_2.CH_3$ D = 

E = 

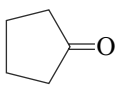
26. (i) B , (ii) B and (iii) A (as these form more substituted alkene).
27. Answer as in 26.
28. (i) X =  Y = $C_6H_5CH_2—CHO$

(Darzens condensation)

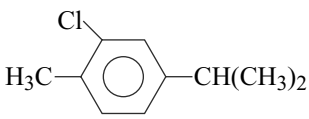
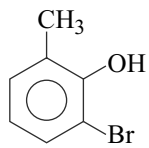
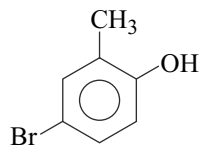
Formation of Y is decarboxylation, which proceeds as given below.

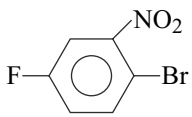
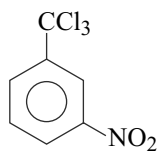


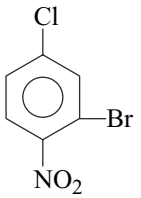
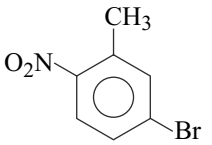
$C_6H_5—CH_2—CHO$

(ii) 

29. D > C > A > B (resonance stabilization)

31. (i)  (ii)  and 

(iii)  (iv) 

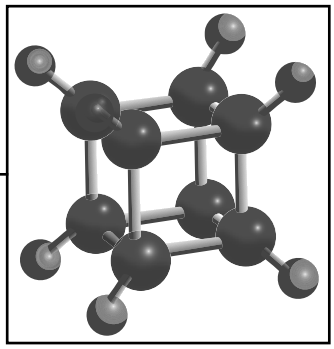
(v)  and 

32. A > C > B > D (resonance and hyperconjugation effect)

33. A = $(CH_3)_2C{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}C(CH_3)_2$

B = $CH_3(CH_2)_7.CH{=}CH(CH_2)_7COOH$

CHAPTER 22



Problems on Structure Determination

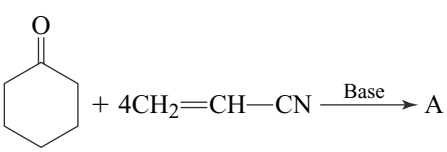
1. An alkane with the molecular formula C_6H_{12} gives only one monochloro derivative. Write its structure.

2. Treatment of $C(CH_2Br)_4$ with Zn yielded a compound A. The molecular formula of A was shown to be C_5H_8. Suggest a structure of A.

3. Two isomeric hydrocarbons A and B have the molecular formula C_6H_{12} and do not show the presence of a double bond. Both these compounds react with chlorine in sunlight to afford the monochloro derivatives having the molecular formula $C_6H_{11}Cl$, whereas only one product is obtained in case A, several different compounds are isolated in case B. Write the structures of A and B.

4. A hydrocarbon that has the molecular formula, C_6H_{12}, was subjected to ozonolysis giving equimolar amounts of ethyl methyl ketone ($CH_3CH_2COCH_3$) and acetaldehyde (CH_3CHO). Assign structure to the hydrocarbons.

5. Predict the product(s) of the following reaction:

(a) 

(b) $CH_3—CH_2—CH_2—CH=CH_2 \xrightarrow[\Delta]{AlCl_3} B$

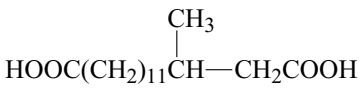
6. An aromatic hydrocarbon of the formula, C_9H_{12}, upon oxidation gives a dibasic acid $C_8H_6O_4$. Nitration of this dibasic acid yields only one mononitro derivative. Suggest the structure for the hydrocarbon.

7. Two isomeric hydrocarbons A and B have the molecular formula C_6H_{12}. Oxidation of A with hot $KMnO_4$ forms an acid C($C_7H_6O_2$), which affords three mononitro derivatives upon ring nitration. Similarly, oxidation of B also forms an acid D ($C_9H_6C_6$), which yields only one mononitro derivative upon nitration. Write the structures of A, B, C and D.

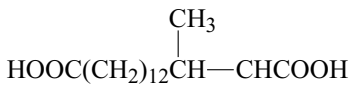
8. How many products do you expect to be formed by the addition of 1 mole of bromine to C_6H_5—CH═CH—CH═CH_2. Write their structures and state, which one is the most stable.

9. A compound M ($C_6H_{14}O$) upon treatment with thionyl chloride gave a compound B. Treatment of B with magnesium in ether afforded the corresponding Grignard reagent that upon treatment with CH_2O followed by usual work-up gave 4-methyl-1-hexanol. Identify M and B.

10. Muscone is a sweet-smelling substance, frequently used in perfumes. It is optically active and has the molecular formula $C_{16}H_{80}O$. Upon oxidation, it yields a mixture of two dicarboxylic acids M and N (having the same number of carbon atoms).

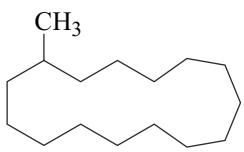


M



N

Clemmensen reduction of muscone gives an optically inactive hydrocarbon whose structure has been established as methyl cyclopentadecane (C).



C

Write a reasonable structure of muscone based upon this data.

11. A dicarboxylic acid A, $C_4H_6O_4$, gave a compound B, $C_6H_{10}O_4$, upon treatment with excess of methanol and a trace of H_2SO_4. Subsequent treatment of B with $LiAlH_4$ followed by usual work-up afforded C ($C_4H_{10}O_2$). Pyrolysis of A yielded D ($C_4H_4O_2$). Assign the structures to A, B, C and D.

12. An unsaturated dicarboxylic acid (A, $C_6H_8O_4$) loses CO_2 on heating and gives another unsaturated acid (B, $C_5H_8O_2$). Upon catalytic reduction, B affords pentanoic acid. Assign the structures to A and B.

13. Two isomeric compounds A and B are ($C_6H_5Br_2N$). Compound A upon diazotization followed by deamination yields a compound C which forms only one mononitro derivative, whereas compound B upon similar treatment gives another solid D which gives three mononitro derivatives. Write the structures of A, B, C and D.

14. A neutral organic substance A is ($C_{10}H_{13}O_2N$). Reduction of A gives another compound B. Treatment of B with $NaNO_2$/HCl gives C, which upon reduction with H_3PO_2 gives a hydrocarbon D. Compound D gives two mononitro derivatives. Oxidation of D with alkaline potassium permanganate affords a dicarboxylic acid E ($C_8H_6O_4$) that forms a cyclic anhydride on heating. Give the structures for A, B, C, D and E.

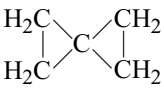
15. Molecular formula of a weakly basic cyclic substance is C_7H_9N. Upon treatment with $NaNO_2$/HCl, followed by treatment of the product with cuprous cyanide it gives a compound B. Hydrolysis of B with

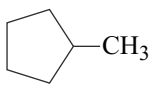
mineral acids gives C. Oxidation of C affords D ($C_8H_6O_4$), which forms only one mononitro derivative. Write the structures for A, B, C and D.

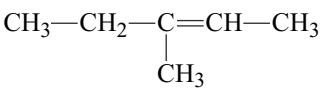
16. The molecular formula of an organic solid is $C_{10}H_7NO_2$. Vigorous oxidation of A gives a dibasic acid, B, $C_8H_5O_6N$. Treatment of A with Sn and HCl followed by oxidation gives another dibasic acid C, $C_8H_6O_4$, which forms a cyclic anhydride upon heating. Identify compounds A, B and C.

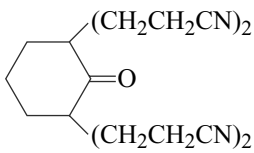
Answers

1. $(CH_3)_4C$

2. 

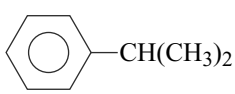
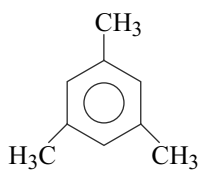
3. A = B = 

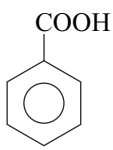
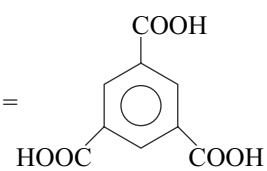
4. 

5. (a) A = 

(b) B = $CH_3—CH_2—CH=CH—CH_3$

6. p = $CH_3.C_6H_4.CH_2—CH_3$

7. A =  B = 

C =  D = 

8. Three products A, B and C are possible, where

A = $C_6H_5—\underset{\displaystyle Br}{\underset{|}{CH}}—\underset{\displaystyle Br}{\underset{|}{CH}}—CH=CH_2$

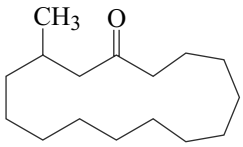
B = $C_6H_5—\underset{\displaystyle Br}{\underset{|}{CH}}—CH=CH—\underset{\displaystyle Br}{\underset{|}{CH_2}}$

C = $C_6H_5—CH=CH—\underset{\displaystyle Br}{\underset{|}{CH}}—\underset{\displaystyle Br}{\underset{|}{CH_2}}$ (Most stable)

9. M = $CH_3—CH_2—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH_2—CH_2—OH$

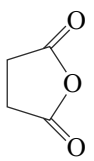
B = $CH_3—CH_2—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH_2—CH_2—Cl$

10.



11. A = $\begin{matrix}CH_2—COOH\\|\\CH_2—COOH\end{matrix}$ B = $\begin{matrix}CH_2—COOCH_3\\|\\CH_2—COOCH_3\end{matrix}$

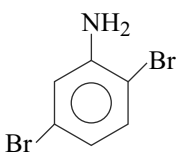
C = $\begin{matrix}CH_2—CH_2—OH\\|\\CH_2—CH_2—OH\end{matrix}$ D =



12. A = $CH_3—CH=CHCH\begin{matrix}\diagup COOH\\\diagdown COOH\end{matrix}$

B = $CH_3—CH=CH.CH_2.COOH$

13. A =



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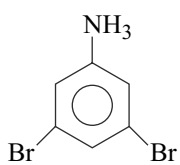

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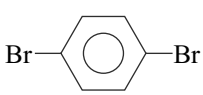

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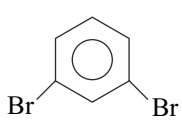
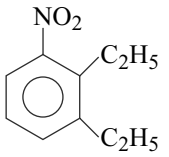
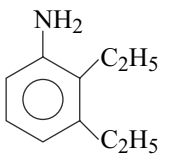
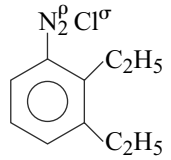
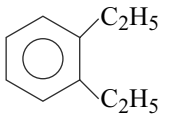
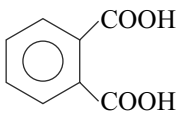


14. A = 

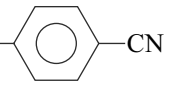
B = 

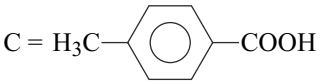
C = 

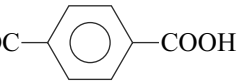
D = 

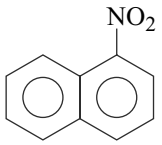
E = 

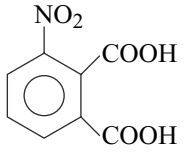
15. A =

B = 

C = 

D = 

16. A = 

B = 

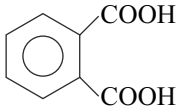
C = 

Table XX Natural α-amino acid

Name	Symbol	Formula	[M]D in °C	Isoelectric point	Solubility in g/100 g water at 20°C
Neutral					
Glycine	Gly		X	6.0	22.5
Alanine	Ala		+1.6	6.0	15.8
Valine*	Val		+6.6	6.0	6.8
Leucine*	Leu		–14.4	6.0	2.4
Isoleucine*	Ileu		+16.3	6.0	2.1
Serine	Ser		–7.9	5.7	4.3
Threonine*	Thr		–33.9	5.6	1.6
Acidic					
Aspartic acid	Asp		+6.7	2.8	0.4
Asparagines	Asp(NH_2)		–7.4	5.4	2.4
Glutamic acid	Glu		+17.7	3.2	0.7
Glutamine	Glu(NH_2)		+9.2	5.7	3.6
Basic					
Lysine*	Lys		+19.7	9.7	Very soluble
Hydroxylysine	Hylys		+14.9	9.15	Very soluble
Arginine*	Arg		+21.8	11.2	Very soluble
Sulphur containing					
Cysteine	CySH		–20.0	5.1	Very soluble
Cystine	CySSCy		–50.9	5.0	0.009
Methionine*	Met		–14.2	5.7	3.0

Aromatic				
Phenylalanine*	Phe	–57.0	5.5	2.7
Tyrosine	Met	–14.2	5.7	3.0
Heterocyclic				
Histidine*	His	–59.8	7.5	4.0
Proline	Pro	–99.2	6.3	154.5
Hydroxyproline	Hypro	–99.6	5.7	34.5
Tryptophane*	Try	–68.8	5.9	1.1

Note: Acids marked with * (asterisk) are essential amino acids.