III Year

Major 1 – ORGANIC CHEMISTRY – II

CONTENTS

UNIT – I STEREOCHEMISTRY

Stereoisomerism – definition – classification into optical and geometrical isomerism. Projection Formulae – Fischer, Sawhorse and Newman projection formulae – Notation of Optical isomers – D-L notation – Cahn – Ingold – Prelog rules – R-S notations for optical isomers.

Optical isomerism – optical activity- optical and specific rotations – conditions for optical activity – asymmetric centre – chirality – achiral molecules – meaning of (+) and (-) Elements of symmetry – Racemisation – methods of recamisation. Resolution – methods of resolution (mechanical, seeding, biochemical and conversion to diastereoisomers).

Optical activity in compounds not containing asymmetric carbon atoms.Biphenyls.allenes and spiranes.

Geometrical isomerism – cis-trans, and E-Z notations – Geomertical isomerism in maleic and fumaric acids – Methods of distinguishing geometrical isomers using melting point, dipole moment, dehydration and cyclisation.

UNIT – II POLYNUCLEAR HYDROCARBONS

Isolatedsystems

Preparation of dipheny1, dipheny1 methane, tri phenyl methane and stilbene.

Condensed system

Synthesis, reactions, structure and uses of naphthalene.Preparation and reactions of naphthols, naphythylamine and naphythaquione.

Synthesis.Reactions, structure and uses of anthracene – Preparation and reactions of anthraquione.

Synthesis.reactions and structure of phenanthrene.

UNIT – III HETEROCYCLIC COMPOUNDS.

Preparation, properties and uses of furan, pyrrole&thiophene – aromatic character.Synthesisand reactions of pyridine and piperidine – comparative study of basicity of pyrrole, pyridine and piperidine with amines.

Condensed five and six membered heterocyclics – preparation and reactions of indole, quinolone and isoquinoline – Fischer indole synthesis, Skraup synthesis and Bischer-Napieralski synthesis-Electrophilic substitution reactions.

UNIT – IV ALKALOIDS AND TERPENOIDS

Alkaloids – classification – isolation – general methods of determination of structure of alkaloids – synthesis and structural elucidation of coniine, piperine and nicotine.

Terpenes – definition, classification – isolation – isoprene rule-synthesis and structural elucidation of citral, geraniol menthol and dipentene.

UNIT – V ORGANIC SPECTROSCOPY

UV spectroscopy – chromophore – auxochrome – blue shift, red shift – hypochromic shift, hyperchromic shift – applications for studying functional groups, cis-trans isomerism and nature of double bonds- Woodward-Fischer rules as applied to conjugated – enes and alpha and beta unsaturated ketones.

IR spectroscopy – characteristics of IR absorption frequencies – intermolecular and intramolecular hydrogen bonding – functional group detection.

NMR Spectroscopy – interpretation of NMR spectra of ethanol, acetaldehyde acetone, benzaldehydy and mesitylene.

REFERENCE BOOKS:

1. K.S. Tewari, N.K. Vishil, S.N. Methtra – A text book of org. chem – Ist edition, Vikas Publishing House Pvt Ltd., 2001, New Delhi.
2. P.L. Soni, Text Book of Organic chemistry, Sultans chand, 1991, New Delhi.

Unit – I STEREOCHEMISTRY

CONTENTS

1.0 Aims and objectives

After studying this lesson, you should be able to

- Explain the different configurations
- Describe the Geometrical Isomerism
- Discuss the optical activity of compounds
- Draw the different projection fomulae for the various compounds.

1.1 Stereochemistry:

It is the branch of Chemistry that deals with the study stereoisomers. (Stereo = Spatial or three dimensional)

Stereoisomerism is a type of isomerism inwhich compounds have same molecular structure but different spatial arrangement of atoms or groups in the molecule such isomers are known as stereoisomers.

Stereoisomerism is mainly classified into

(i) Optical isomerism

(ii) Geometrical isomerism.

1.2 Projection formulae :-

The three dimensional configuration may be represented on a two-dimensional paper by

(i) Fischer's Projection formula

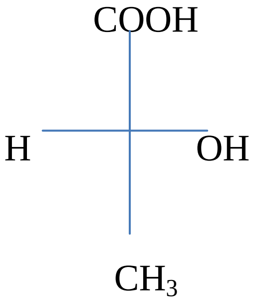
(ii) Sawhorse formula

(iii) Newman's projection formula

(i) Fischer's Projection formula

It is a planar projections formula of three dimensional molecular model. For example, the three dimensional configuarion of **lactic acid** can be represented by the planar Fischer Projection formula as follows.

Example – 1

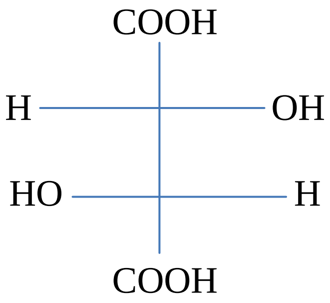


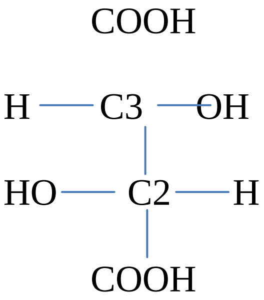
Lactic acid

The groups drawn on either side of the vertical line (-H, -OH gps) are considered to be below or behind the plane. The groups drawn over a horizontal line (CH_3 COOH gps) are considered to be above or infront of that plane.

Example - 2

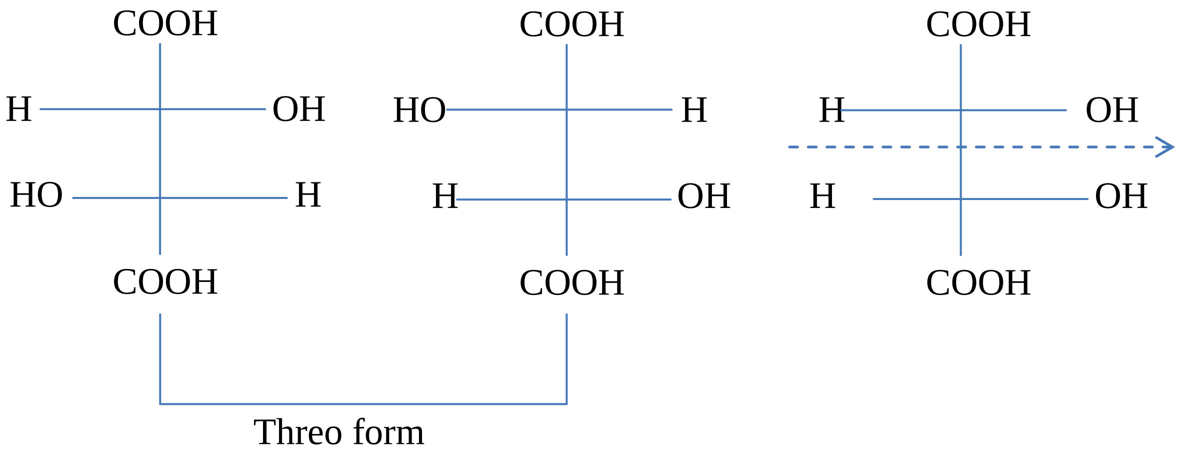
Tartaric acid





Tartaric acid has two chiral centres (C2, C3). The lower chiral centre (C2) is nearer to us. (lie above or infront of the plane). The upper chiral centre (C3) is farther from us (lies below or behind the plane)

The different configuration of tartaric acid molecule are



(+) Tartaric aid (-) Tartaric aid Erythro form

Mesotartaric aid

For the Erythro form, the Fischer Formula shows same or similar groups in the same side. For the threo form, the fischer formula shows same or similar groups in the opposite.

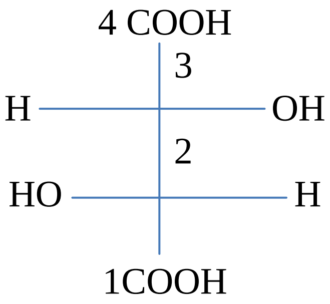
The Fischer projection formula shows only the eclipsed form.

(ii) Newman Projection formula

It represents the spatial arrangement of bonds on two adjacent atoms in a molecule. This is obtained by viewing the molecule along the bond joining the two atoms

.

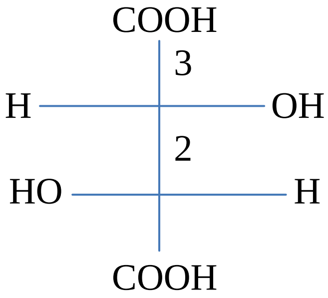
(Eg) Meso Tartaric acid



In the eclipsed form, the –OH, COOH, -H forms of front carbon lie exactly eclipsed with other atoms of rear carbon.

In the staggered form, the atoms of front carbon are anti to the atoms of rear carbon atom.

(Eg) (+) Tartaric acid



Meso – tartaric acid is more stable than (+) and (-) forms of tartaric acid i.e. Meso form is in the anti conformation.

(iii) Sawhorse the spatial arrangement of all the bonds as two adjacent atoms. (Eg) Meso – tartaric acid.

(+) - Tartaric acid

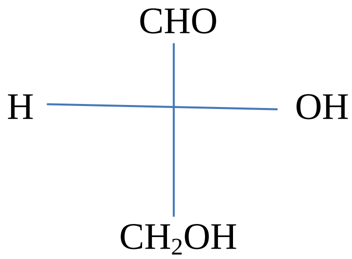
1.3 Notation of optical Isomers:

For studying the configuration of organic compends two types of rotations are used.

(i) D.L notation
(ii) R.S. notation

(i) D.L. notation

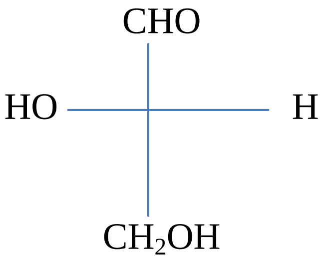
Relative configuaration is named as D.L. notation.Glyceraldehyde was chosen as the standard because of its relationship to carbohydrates. Two forms of glyceraldehyde are labeled as D(+) and L (-) glyceraldehyde.



$$\begin{array}{ccc} & CHO & \\ H & \text{—}\!+\!\text{—} & OH \\ & CH_2OH & \end{array}$$

D (+) Glyceraldehyde
D = Configuration

(+) = Sign of rotation



$$\begin{array}{ccc} & CHO & \\ HO & \text{—}\!+\!\text{—} & H \\ & CH_2OH & \end{array}$$

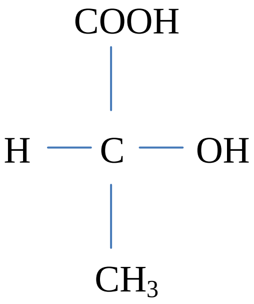
L (-) Glyceraldehyde
L= Configuration

(-) = Sign of rotation.

D – Configuration → The –OH group is present at the right side of the asymmetric carbon atom.

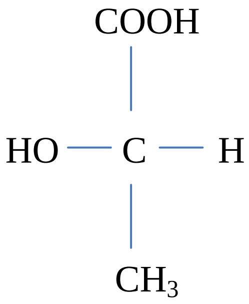
L- Configuration → The – OH group is present at the left side.

Examples (i)



$$\begin{array}{ccc} & COOH & \\ & | & \\ H\ — & C & —\ OH \\ & | & \\ & CH_3 & \end{array}$$

D (-) Lactic aid



$$\begin{array}{ccc} & COOH & \\ & | & \\ HO\ — & C & —\ H \\ & | & \\ & CH_3 & \end{array}$$

D (-) Lactic aid

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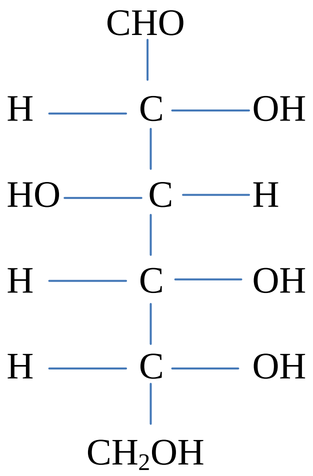
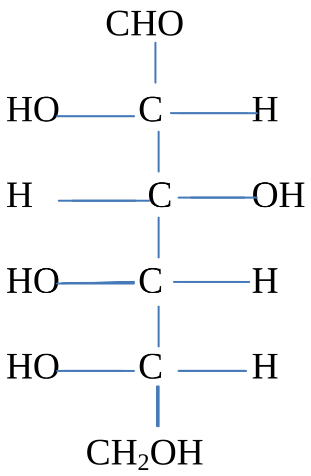


D (+) Glucose



L (-) Glucose

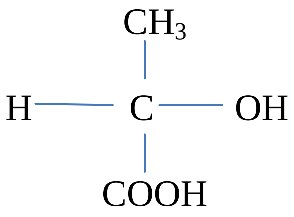
1.4 Optical isomerism – Optical activity – chirality

(iv) Optical isomerism

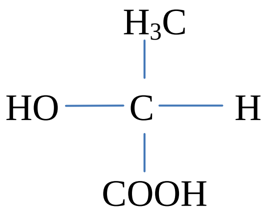
It is a type of stereoisomerism in which compounds having same structural formula, but different configuration & with equal and opposite character towards plane polarized light. These compounds are called optical isomers or enantiomers.

(Eg) (+) Lactic acid and

(-) Lactic acid



(+) Lactic acid



(-) Lactic acid

R.S. notation:- Absolute configuration is named as R-S. notation. It is used for specifying the configuration of chiral carbon atoms.

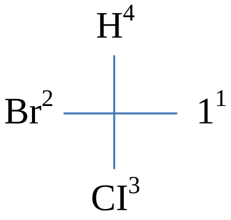
Cahn – Ingold – Prelog rules

(v) 1.26 Cahn – Ingold – Prelog rules

In order to over come the limitation of DL-notation, Cahn, ingold and Prelog proposed a new systemsfor specifying the configuration of chiral carbon atoms. This is known as absolute configuration or RS-notation. The procedure involves the following steps.

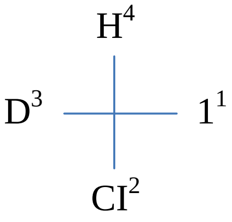
Step 1: The four different atoms or groups attached to the chiral carbon atom are numbered 1, 2, 3 and 4 and are ranked according to the following sequence rules of priority.

Sequence rule 1: The groups or atoms are arranged in the decreasing order of the atomic number of the atom directly bonded to the chiral carbon.



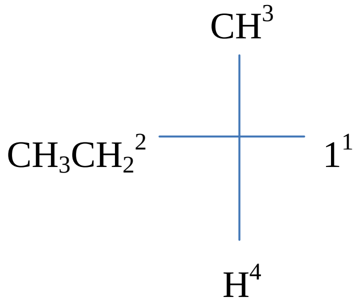
Priority order : 1 > Br > C1 > H

Sequence rule 2 : In the case of isotopes, priority is given to the heavier isotope.



Priority order : 1 > C1 > D > H

Sequence rule 3: If two groups possess same first atom there priority must be given on the basis of the next atom. This process goes on till the selection is made.



Priority order : 1 > $CH_3 – CH_2$> CH_3> H

Sequence rule 4 :

A double or triple bonded atom is equivalent to two or three such atoms.

- COOH ≡ (2'O' + 1' O)
- CH = CH_2≡(2 'C' + 1'H)
- CHO ≡ (2'O + 1'H')
- C≡ N ≡(3N)

b) Step 2: After assigning priority the molecule is viewed from the side opposite to the group of lowest priority.

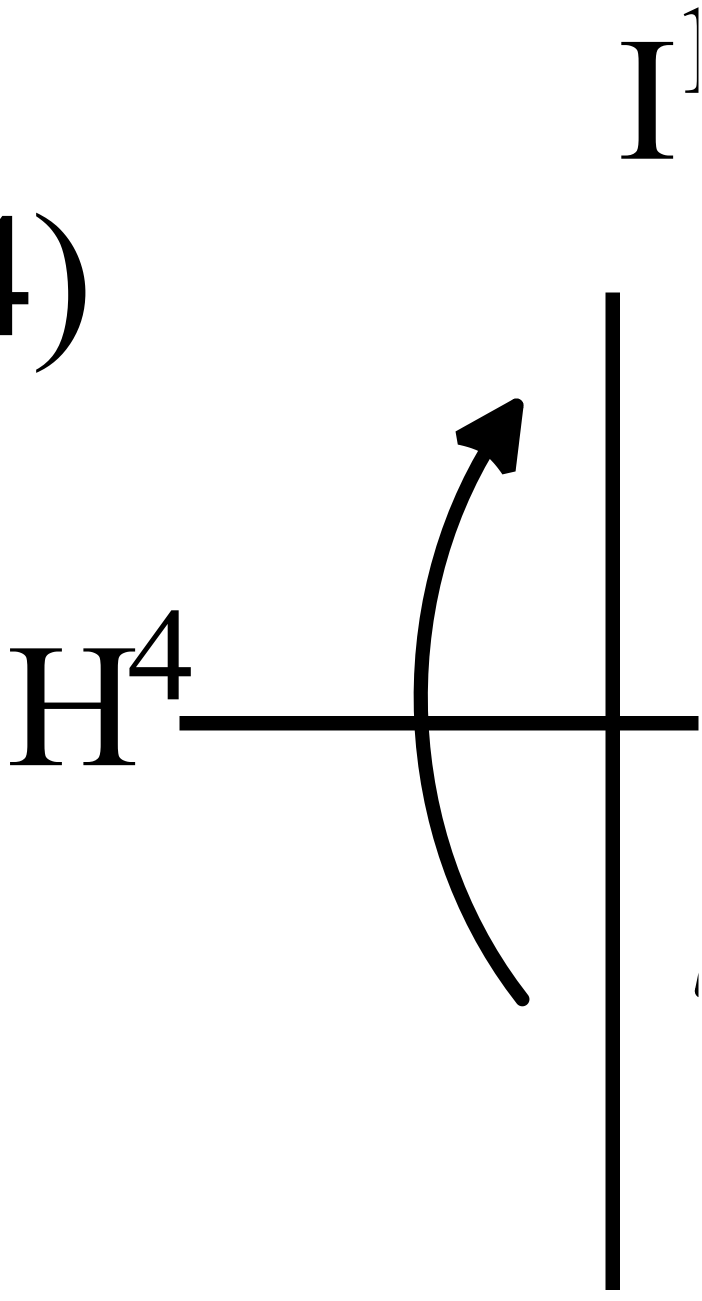
c) Step 3: The priority sequence of the remaining three groups 1→ 2→ 3 is determined. If the sequence is anti-clockwise, the symbol (S) is used (sinister = left) to designate the configuration.

In the above figures the molecules are visualized as steering wheel of a car with lowest priority group as steering rod and other three groups around the wheel.

d) Step 4 : In order to assign R,S configuration for Fischer projection formula, first the atom with the lowest priority should be brought to the bottom. This should be done by effecting any two exchanges among the groups. Then look for the order of the priority sequence.

Examples :

(4)



1.4 Optical activity

Substances which rotate the plane of polarized light are said to be optically active and this property is known as optical activity. Substances which can rotate the plane of polarized light to right are called dextro – rotatory and indicated by sign 'd' or (+). But substances which can rotate the plane of polarized light to left are called levo – rotatory and indicated by sign '1' or (-).

Example : (+) Lactic acid is an optically active compound.

a) Optical and specific rotation

When the plane polarised light (p-p light) is passed through certain substances or solutions, the emerging light is found to be vibrate in a different plane. This is called **optical rotation**.

The measurement of optical activity is reported in terms of specific rotation. This specific rotation is a constant for a particular substance. For example specific rotation of

i) Sucrose is + 66.5 ii) phenyl lactic aid is + 52.0^0

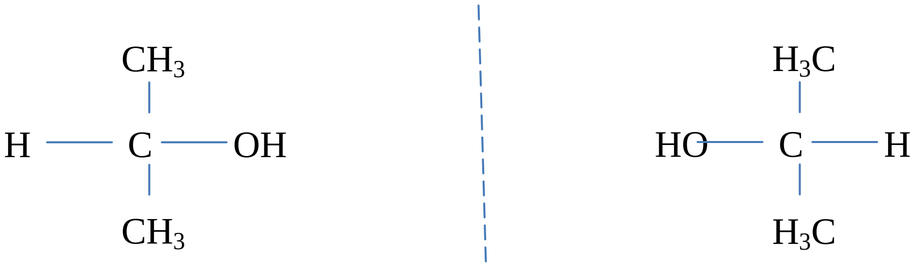
b) Condition for optical activity (Chiral molecule, Chirality)

A molecule that is not superimposable on its mirror image is said to be dissymmetric or asymmetric molecule. This property is known as asymmetry or chirality. Such molecules are also called as chiral molecules. Example : (+) and (-) lactic acid.

Chirality is the condition, criterion or the cause of optical activity.

c) Achiral molecule

A molecule that is superimposable on its mirror image is known as achiral molecule, Example : 2-propanol. It does not have chiral centre.



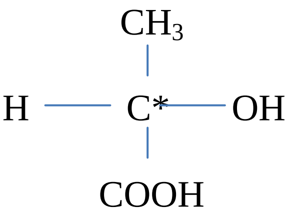
$$\begin{array}{ccc} & CH_3 & \\ & | & \\ H - & C & - OH \\ & | & \\ & CH_3 & \end{array} \qquad \begin{array}{ccc} & H_3C & \\ & | & \\ HO - & C & - H \\ & | & \\ & H_3C & \end{array}$$

Superimposable (Achiral molecule)

d. Chiral centre or asymmetric centre

A carbon atom surrounded by four different atoms or groups is known as chiral centre or asymmetric centre atom.

Example : Carbon atom (C*) in (+) lactic acid.



$$\begin{array}{ccc} & CH_3 & \\ & | & \\ H - & C^* & - OH \\ & | & \\ & COOH & \end{array}$$

(C* = Chiral centre)

1.5 Element of symmetry (Symmetry elements)

Symmetry elements of a molecule are of four types.

i) Plane of symmetry ii) Centre of symmetry

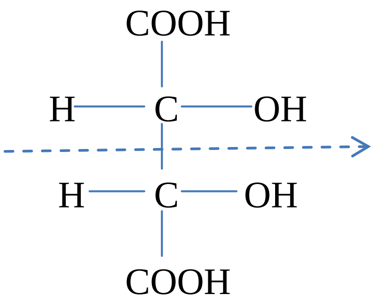
iii) Axis of symmetry iv) Alernating axis of symmetry

i) Plane of symmetry:

A plane of symmetry, is a plane that cuts the molecule into two equal halves which are the mirror images of each other.

Example :Mesotartaric acid.

(Plane of symmetry)

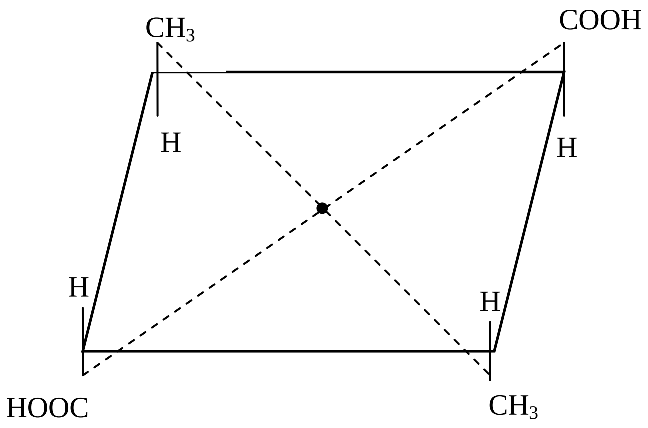


Mesotartaric acid

Centre of symmetry:

A centre of symmetry is a point from which lines, when drawn on one side and produced an equal distance on other side, will meet identical points in the molecules.

Example : 2, 4 – Dimethy1 cyclobutane – 1, 3 – dicarboxylic acid



(Molecule with a centre of symmetry)

ii) Axis of symmetry:

Axis of symmetry is an axis through which one complete rotation (360^o) of a molecule will result in more than one identical structure.

Example :

a) H_2O has a two fold

(C_2) axis of symmetry.

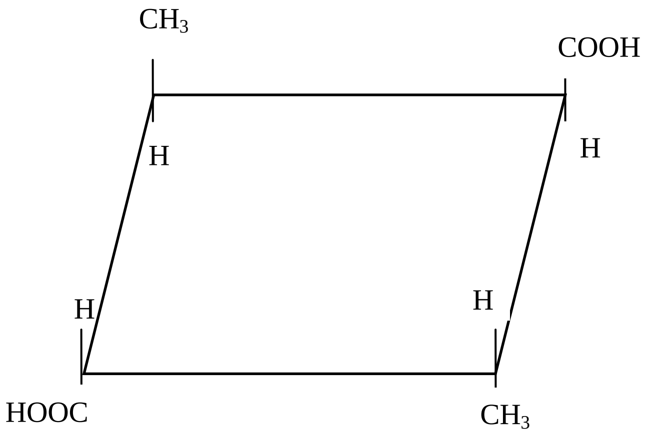
b) NH_3 has a three fold

(C_3) axis of symmetry.

iii) Alternating axis of symmetry:

It is an axis through which if the molecule is rotated by a certain angle and then reflected across a plane at right angles to the axis, another identical structure is obtained. One fold alternating axis corresponds to plane of symmetry. Two fold alternating axis corresponds to centre of symmetry.

Example : 2,4 – Dimethy1 cyclobutane – 1, 3 – dicarboxylic– acid



(A Molecule with two fold alternating axis of symmetry)

Check Your Progress

Fill in the blanks :

1) .... has two fold axis of symmetry

2) The total numbers of stereoisomers in tartaric acid is ....

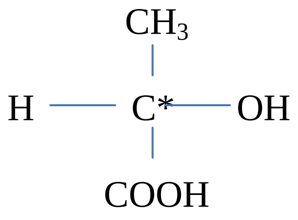
3) Lactic acid is ....

1.6 Racemisation and Resolution

Chiral centre or asymmetric centre

A carbon atom surrounded by four different atoms or groups is known as chiral centre or asymmetric centre atom.

Example : Carbon atom (C*) in (+) lactic acid.



$$\begin{array}{ccc} & \mathrm{CH_3} & \\ & | & \\ \mathrm{H} - & \mathrm{C^*} & - \mathrm{OH} \\ & | & \\ & \mathrm{COOH} & \end{array}$$

(C* = Chiral centre)

e. Racemisation

Definition :

i) The process of converting an optically active compound into the racemic modification is known as racemization.

f. Methods or racemization

Racemisation occurs through intramolecular rearrangements caused by heat, light or catalysts. Some compounds racemisespontaneoulsly at room temperature. This is called auto-racemisation.

a) Recemization using catalyst: Racemisation occurs readily in compounds in which the asymmetric carbon atom is joined to a hydrogen atom and can undergo tautomeric change. For example, racemization of (-) lactic and occurs in aqueous NaOH through enolization as follows.

b) Recemization by heating : Tartaric acid on heating is converted to racemic as well as meso form.

1.13 Resolution

Definition:

Resolution is the process of separation of racemic modification into its two enantiomers. When the two enantiomers are separated in unequal amounts, it is known as partial resolution.

1.14 Methods of resolution

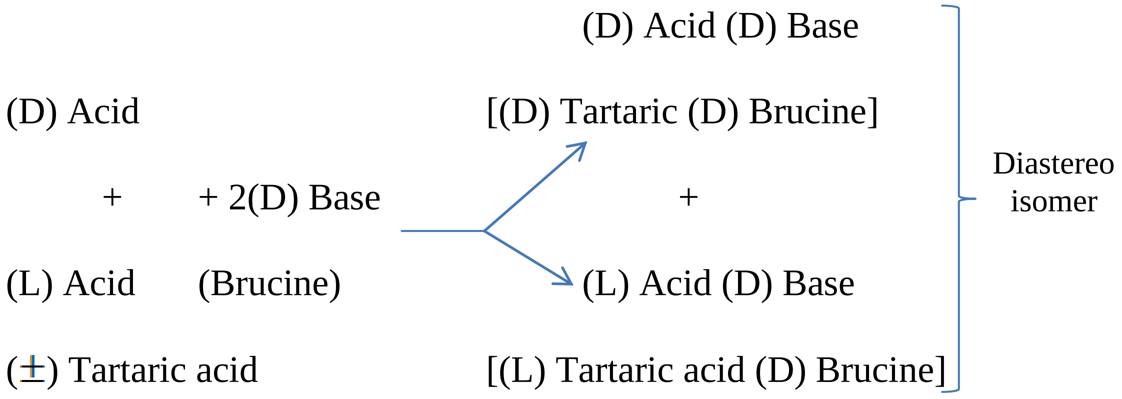
The following are the important methods of resolution.

i) Biochemical separation: Certain bacteria or moulds when grown in a dilute solution of a racemic modification, destroy one enantiomer more rapidly than the other.

Example :*Penicilliumglaucum* when grown in a solution of racemic ammonium tartrate, attacks the (+) form and leaves the (-) form.

ii) Conversion into diastereoisomer:

In this method the enantiomers of the racemic modification are converted to diastereoisomers by treating with optically active substances. The diastereoisomers are separated by fractional crystallization. The racemic acids are separated by opticallyactive bases and vice-versa.



iii) Mechanical separation:

This method can be applied to solid mixtures which consists of two types of welldefined crystals. By this method Pasteur separated the (+) and (-) crystals of sodium ammonium tartarate. He crystallized the racemic solution of (±) sodium ammonium tartarate below 27^{o}C and separated the two kinds of crystals by 'hand picking'.

iv) Preferential crystallization (seeding):

In this method a supersaturated solution of a racemate is treated (inoculated) with a crystal (seed) of one of the enantiomers. Not this enantiomer preferentially crystallisesout. By this method (±) glutamic acid and (±) aspartic acid can be separated.

Seeding can also be done by another optically active isomorphous substance. For example, resolution of (±) sodium ammonium tartarate can be achieved by seeding with (-) asparagine.

1.7 Optical activitiy in compounds not containing asymmetric carbon atoms.

Compounds like allenes, spiranes and biphenyls do not possess any asymmetric carbon atom. However optical isomerism is observed in such compounds due to molecular dissymmetry.

Biphenyl

Biphenyls have no asymmetric carbon atom. But a number of ortho substituted bipheyls are found to exhibit optical activity due to molecular dissymmetry. It is caused by restricted rotation about the C-C bond. This type isomerism is called atropisomerism.

Eg: 2.2'- Diamino 6.6' – dimethyl biphenyl

i) When the ortho, ortho positions are occupied by bulky groups, the free rotation about the single bond is not possible.

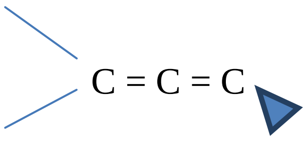
ii) The two phenyl rings are not co planar.

iii) The mirror images are not superimposable.

Thus the substituted biphenyl are optically active.

Allenes

Allenes are compounds which have the general structure.

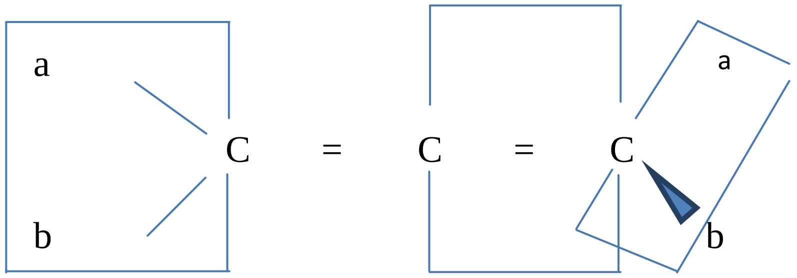


Theallenes exhibit optical isomerism provided the two groups attached to each terminal carbon atom are different.

Example

1,3 - Diphenyl

In allenes the two groups attached to one terminal carbon atom lie in the plane of the paper and other terminal carbon atom lie in the plane peripendicular to the plane of the paper.

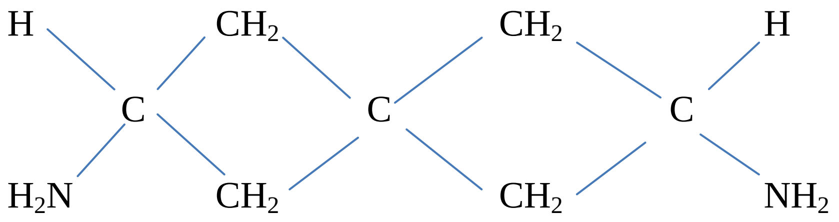


So the molecule does not possess a plane of symmetry. The mirror images are not superimposable. Thus the molecule is **chiral** and hence the allenes are optically active.

Spiranes

The two double bonds of allenes are replaced by rings the bicyclic ring system formed is called spiranes.

Eg.: 1.7 Diaminospirocycloheptane



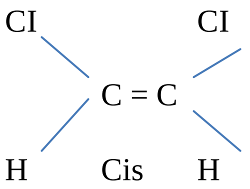
The two rings in spiranes are not coplanar. Hence the whole molecule has no plane of summetry. It is chiral in nature. The mirror images are not superimposable. Thus the spiranes are optically active.

1.8 Geometrical isomerism (Cis-trans isomerism)

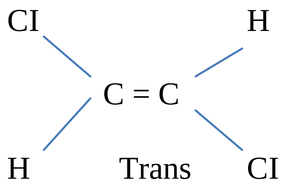
Definition:

Geometrical isomerism is a kind of stereoisomerism it which compounds have same structural formula but different configurations around the double bond. Such compounds and called geometrical isomers or cis-trans isomers.

Esample :**i) 1,2 – Dichloroethene**

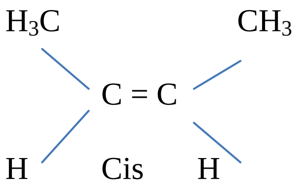


Cis

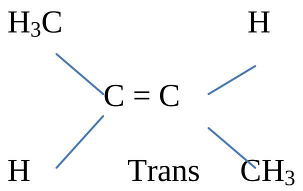


Trans

ii) 2 –Butene

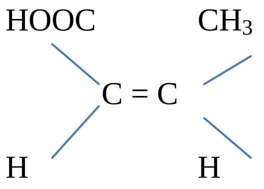


Cis

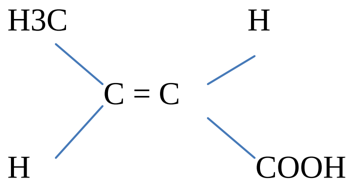


Trans

iii) Crotonic and isocrotonic acid:

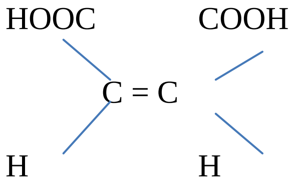


Crotonic acid (Cis)

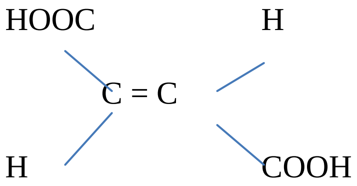


Isocrotonic acid (Trans)

iv) Maleic acid and fumaric acid:

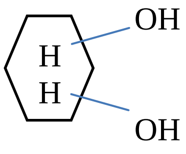


Maleic acid (Cis)

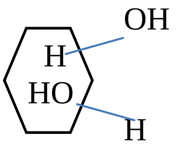


Fumaric acid (Cis)

v) l :



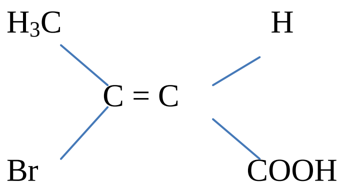
Cis



Trans

1.30 E-Z notation

'Cis – trans' system of nomenclature may not be suitable for many tri or tetrasubstitutedolefins. For example, we can not decide whether the following compound is cis or trans, because no two groups are same.



This difficulty can be overcome by the use of the following newer system based on priority of groups i.e. CIP (Cahn-Ingold-Prelog) convention. This system is called the (E-Z system, applies to alkene diastereoisomers. If the two groups of the higher priority are on the same side of the double bond, the alkene is designated 'z' (German word 'zusammen' mean together). If the two groups of high priority are on opposite side of the double bond, the alkene is designated 'E' (German world 'entgegen' means opposite). For fixing the priority of substituent the sequence rules given by CIP system should be followed.

1.9 Geometrical isomerism in Maleic acid and Fumaric acid

	Property	**Maleic acid**	**Fumaric acid**
1.	Structure	H-C-COOH H-C-COOH	HOOC-C-H H-C-COOH
2.	Geometry	Cis-isomer	Trans-isomer
3.	Melting point	Lower (130^{o})	Higher (287^{o}C)

4.	Boiling Point	Higher	Lower
5.	Dipolemoment	2.54D (Diethy1 maleate)	2.38 D (Diethyl fumarate)
6.	Acidity	More acidic	Less acidic
7.	Stability	Less stable	More stable
8.	Action of heat	Forms cyclic anhydride	No action
9.	Formation of solid solution	Does not from solid solution with succinic acid	Forms a solid solution with succinic acid
10.	Hydroxylation with $KMnO_4$	Meso-tartaric acid	(±) Tartaric acid
11.	Hydroxylation with H2O2 catalysed by SeO_2	(±) Tartaric acid	Meso-tartaric acid

1.10 Methods of distinguishing Geometrical isomers.

Configuration of geometrical isomers can be determined using the following methods.

i) Dehydration:

Intramolecular reactions are possible only, when the reacting groups are closer together in a molecule. in maleic acid both the COOH groups are nearer to each other. Therefore on heating maleic acid undergoes dehydration and gives cyclic anhydride readily. But fumaric acid does not form an anhydride of its own.

Thus maleic acid is the cis isomer and fumaric acid is the trans isomer.

ii) Method of cyclization:

2-Bromo-5-nitroacetophenone oxime exists in two isomeric forms. The $\propto$-oxime of 2-bromo-5-nitroacetophenone is unaffected by NaOH, whereas the β-isomer undergoes ring closure to form 3-methyl-5-nitrobenziso-oxazole. Thus the$\propto$ –oxime is the syn-methloy1 isomer (A) and the β –oxime the anti-methyl isomer (B).

iii) Dipole moment studies:

Dipole moment is a vector quantity. In the trans isomer bond moments cancel each other. Therefore in general cis-isomer always has higher dipole moment than the trans-isomer. For example there are two isomeric 1,2dichloro ethane. The isomer which has 'zero' dipole moment is 'trans' and the other one is 'cis'.

iv)Melting point:

The melting point or cis-isomer is lower than than of the trans-isomer.

Example : i) Melting point of maleic acid (cis) is 130^{o}C.

ii) Melting point of fumaric acid (trans) is 287^{o}C.

Check Your Progress

Fill in the blanks

1) E.Z. isomers are .... isomers

2) Compound has the .... configuration

3) has .... configuration

1.11 Let us Sum up

Stereoisomerism is a isomerism in which compounds have same molecular structure but different arrangements. It is classified into optical and Geometrical isomerisms. The isomers are assigned by R.S, E.Z and Fischer’s, Sawhorse and Newman’s projections formula.

1.12 Key words

R.S: Absolute configuration of organic compounds are named by R.S notation.

E.Z: E - entgegen - opposite

Z - Zusammen - together

This system is applied to alkene diastereoisomers.

1.13 Questions for Discussion

1) Explain the elements of symmetry with suitable examples.

2) Give the following projection formulae using Tartaric acid as an example

(a) Fischer (b) Newman (c) Sawhorse

3) Write notes on Racemisation

4) Give an account of Resolution.

5) Discuss the sequence rules with examples for R, S notations.

6) Discuss the various methodsto distinguish between is -trans isomers.

7) What is atrop isomerism? Give example

8) Explain the optical isomerism of allenes and spiranes

9) Explain the optical isomerism of biphenyls

10) Write a note on optical isomerism.

Check Your Progress : Model Answers

CYP 1

1) Water molecule

2) 3

3) Optically active

Check Your Progress : Model Answers

CYP 2

1) Geometrical isomers

2)E

3) S

1.14 Suggested Readings

[1] Bahl and Arun Bahl - Organic chemistry

[2] P.L. Soni Text Book of organic chemistry

UNIT – II

Polynuclear Hydrocarbons

2.0 Aims and objectives

2.1 Introduction

2.2 Isolated System

Preparation of diphenyl, diphenyl methane, triphenyl methane and stilbene.

2.3 Condensed System

Synthesis, reaction, structure and uses of naphthalene.Preparation and reactions of naphthols, naphthylamine and naphthaquinone.

2.4 Syntheses, Reactions, Structure

Synthesis, Reactions, Structure and uses of anthracene.Preparation and reactions of anthraquinone.

2.5 Synthesis, Reactions

Synthesis of phenanthrene

2.6 Let us Sum up

2.7 Key words

2.8 Questions for Discussion

2.9 Suggested Readings

Polynuclear Hydrocarbons

2.0 Aims and objectives

After studying this lesson, you should be able to :

- Explain the preparation, reactions and structure of polynuclear hydrocarbons.
- Describe overview of various types of napthalene compounds

2.1 Introduction

Compounds containing more than two benzene rings are known as Polynuclear hydrocarbons. They are of two types.

(i) Isolated system

Compounds in which the rings are linked by one or more carbon atoms are known as isolated system.

Example :Diphenyl, Diphenyl methane, Di benzyl etc.

(ii) Condensed System

Compounds in which two or more benzene rings are fused together in ortho positions are known as condensed systems.

Example : Naphthalene, Anthracene, Phenanthrene etc.

2.2 Isolated Systems

Preparation of Diphenyl or Biphenyl

a) Fittings reaction:

$$C_6H_5\boxed{Br + 2Na + Br}H_5C_6 \xrightarrow{Ether} C_6H_5 - C_6H_5 + 2NaBr$$

bromobenzene Diphenyl

Bromobenzene reacts with sodium in ether solution to give diphenyl.

b) Utlmann reaction:

C_6H_5 I + 2Cu + I H_5C_6 $\xrightarrow{\Delta}$ $C_6H_5 – C_6H_5$ + 2CuI

Iodobenzene Diphenyl

Iodobenzene is heated with copper powder in a sealed tube diphenyl is formed.

c. It is also prepared by refluxing bromobenzene with hydrazine in alcoholic KOH in the presence of Palladium Catalyst.

$2C_6H_5$ Br $\xrightarrow{NH_2\text{-}NH_2/pd}$ $C_6H_5 – C_6H_5$ + 2HBr

Diphenyl.

d. Manufacture :Industrially it is prepared by passing benzene vapours through heated iron tubes.

$2C_6H_6$ $\xrightarrow{\Delta/\ Fe}$ $C_6H_5 – C_6H_5 + H_2$

Diphenyl.

II. Preparation of diphenyl methane

a) Friedel – Crafts reaction

C_6H_5 CH_2Cl + C_6H_5 $\xrightarrow{AlCl_3}$ $C_6H_5 – CH_2–C_6H_5$ + Hcl

Benzylchloride Diphenylmethane

Diphenyl methane is prepared by the Friedel craft's condensation between benzyl chloride and benzene.

b) Diphenylmethane is prepared by

Grignard reaction

C_6H_5MgBr+ $C_6H_5CH_2Cl$ → $C_6H_5CH_2C_6H_5$ + MgBrcl

c) Two molecules of benzene condensed with formaldehyde in the presence of conc. H_2SO_4 gives diphenylmethane.

$2C_6H_6 + HCHO \xrightarrow{H_2SO_4} C_6H_5 - CH_2 - C_6H_5 + H_2O$

III. Triphenyl methane

a) Friedel – Crafts reaction

$2C_6H_6 + C_6H_5CHCl_2 \xrightarrow{AlCl_3} (C_6H_5)_3 - CH + 2Hcl$

Benzylchloride Triphenylmethane

It is prepared by the condensation between benzal chloride andbenzene.

b) $3C_6H_6 + CHCl_3 \xrightarrow{AlCl_3} (C_6H_5)_3 - CH + 3Hcl$

The condensation between benzene and chloroform gives triphenyl methane.

c) $C_6H_5CHO + 2C_6H_6 \xrightarrow{ZnCl_2} (C_6H_5)_3CH + H_2O$

The condensation between benzaldelyde and benzene also gives triphenyl methane.

IV. Stilbene

a) Stilbene is prepared by reducing benzoin with zinc amalgam and ethanolic solution of Hcl.

$C_6H_5CHOHCOC_6H_5 \xrightarrow[C2H5OH]{Zn/Hg} C_6H_5CH = CHC_6H_5$

Benzoin Stilbene

b) Stilbene is also obtained by heating $\propto$- phenyl cinnamic acid in quindine in the presence of copper chromite.

$C_6H_5CH = C\text{-}(C_6H_5)COOH \xrightarrow[\text{Copper}]{\Delta}$

Chromite

$C_6H_5CH = CH\text{-}\ C_6H_5$

Stilbene

Stilbene exhibits geometrical isomerism as follows.

Trans – stilbene Cis-stilbene

Stable Unstable

2.3 Condensed system

Synthesis of Naphthalene

a) Synthesis from 4-Phenyl – 1- butane

b) Syntheris from Petroleum

The middle and heavy oil fractions of petroleum contain small amounts of methyl and dimethyl naphtalenes. There are passed over a heated copper catalyst at $680^{o}C$ in the presence of hychogen, naphthalene is obtained.

$C_{10}H_7CH_3 + H_2 \longrightarrow C_{10}H_8 + CH_4$

Methyl napthalene napthalene

$C_{10}H_7(CH_3)_2 + 2H_2 \rightarrow C_{10}H_8 + 2CH_4$

Dimethyl naphthalene napthalene

Reactions of Naphthalene

a) Addition reactions:

(i) When reduced with sodium and ethanol, naphthalene gives 1,4 – dihydronaphthalene (1,4 – dialin)

(ii) When reduced with sodium and isoamyl alcohol, it forms tetralin.

(iii) On Catalytic reduction with H_2 and nickel, decalin is formed.

(b) Oxidation reaction:

(i) Naphthalene on oxidantion with acidified $KMnO_4$, gives phthalic acid

(ii) Oxidation with air in the presence of V_2O_5 catalyst, Naphthelene gives phthalic anhydride.

(iii) Oxidation of naphthalene with chromic acid gives 1,4 – naphthaquinone

(c) Substitution reaction:

Substitution in naphthalene occurs mostly at the ∝(1) position.

(i) Chlorination

Naphthalene on chlorination with S_2cl_2/$Alcl_3$ gives 1-chloronaphthelene and 1,4 – dichloro naphthalene

(ii) Nitration

Naphthalene on nitration with conc H_2SO_4 and conc HNO_3 gives 1-nitronaphthalene

(iii) Friedel – craft's reaction :-

Naphthalene onFriedel – crafts alkylation, naphthalene gives 1 and 2-methly naphthalene.

Structure of Naphthelene

1. The Molecular formula of naphthalene is $C_{10}H_8$.
2. Like benzene, naphthalene undergoes halogenation, nitration etc.
3. Like benzene, its nuclear hydroxy compounds are phenolic.
4. Naphthalene shows unusual stability.
5. On vigorous oxidation, it gives phthalic acid. It proves the presence of one ring and two side chains in ortho position to each other.

6. Naphthalene on nitration gives nitronaphthalene which on oxidation gives 3-nitro phthalic acid.
7. The nitro naphthalene on reduction gives amino naphthalene which on oxidation gives phthalic acid.

8. Reaction 6,7 proposed that naphthalene contains two benzene rings fused to each other in ortho position as follows.

9. Naphthalene is considered to be the resonance hybrid of the following 3 structures.

10. Finaly the structure of naphthalane is proved by Haworth synthesis.

Uses of naphthalene

It is used

(i) as an insecticide

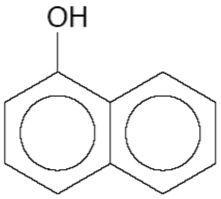
(ii) in the manufacture of important compounds.

(iii) in the preparation of dyes.

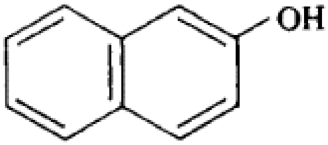
Preparation of naphthols

There are 2 isomeric naphthols

a) .



b)



1- napthol 2- napthol

(i) Fusion of naphthalene – 1 – sulphonic acid with NaOH gives 1 – naphthol.

(ii) Fusion of naphthalene – 2 – sulphonic acid with NaOH gives 2 – naphthol.

Reactions of naphthols

1) Substituion reactions

Napthols undergo sulphonation

2) Reduction :Naphthols are reduced by sodium and isoamyl alcohol to yield tetrahydronaphthols.

3) Oxidation: Naphthols are oxided by alkaline $KMnO_4$ to give phthalonic acid.

Preparation of naphthyl amines

There are two isomeric naphthyl amines

(i) 1 – Naphthyl amine

(ii) 2 - Naphthyl amine

(i) (a) 1 – Naphthyl amine is prepared by heating 1 – naphthol with NH_3 and $ZnCl_3$ at 250°C

(b) 1 – Naphythyl amine is manufactured by the reduction of 1-nitro naphthalene with iron and Hcl.

Bucherer Reaction

(ii) 2 – Naphthylamine is manufactured from 2-naphthol.

Reactions of napthylamines

(a) **Oxidation** 1 and 2 Naphthyl amines on oxidation with acidified $KMnO_4$ gives phthalic acid.

b) Reduction : 1- Naphthylamine is reduced with Na and Isoamyl alcohol to give Tetrahydro – 1 – naphthylamine

2- Naphthylamine is reduced with Na and Iso-amyl alcohol to give tetra hydro – 2 – naphthylamine.

Naphthaquiones

There are three isomeric napthaquinones

Preparation

a) 1,2 – naphthaquinone is prepared by the oxidation of 1-amino – 2 – naphthol with $FeCl_3$ / Hcl.

b) 1, 4 – naphthaquinone is prepared by the oxidation of Naphthalene with CrO_3/ CH_3COOH

c) 2,6 – Naphthaquinone is prepared by the oxidation of 2,6 – dihydroxy naphthalene with PbO_2.

Reaction of naphthaquinone

Reducion:

i) 1,4 – Naphthaquinone is reduced by Zinc and Hcl, it gives 1,4 – dihydroxynaphthalene

ii) 1, 4 –Naphthaquinone is oxidised with Nitric acid, it gives phthalic acid

iii) On reaction with nitrous acid 1,4–naphthaquinone is converted to 1,3 – diketohydrindene.

Check Your Progress I

1) ....belongs to condensed system

2) Atrop isomerism is given by ....

3) Naphthalene on oxidation with V_2O_5 gives ....

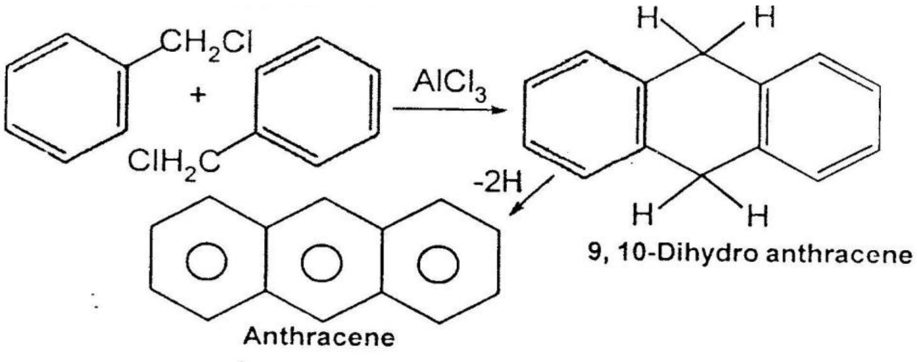
2.4 Anthracene

It is a tricyclic system containing three benzene rings fused together in a linear pattern as given below.

Synthesis of Anthracene

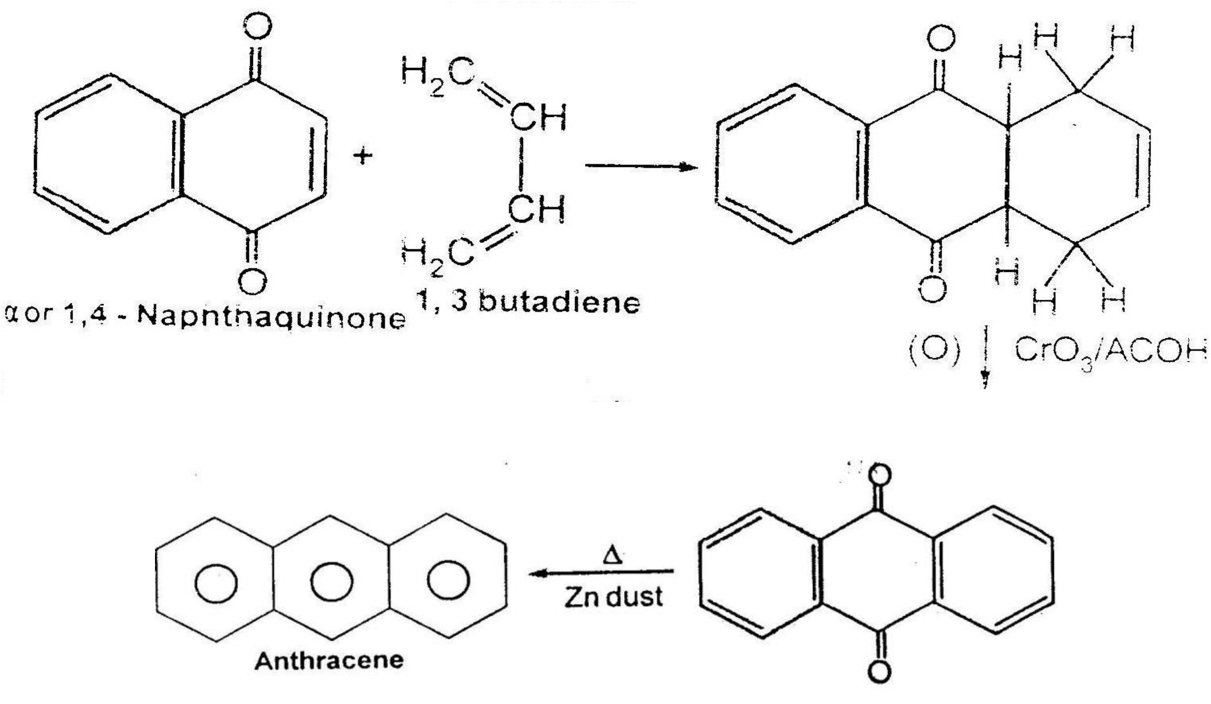
i) **By Friedel – Craft's reaction:**

Anthracene is synthesized from Benzyl chloride by Friedel-Craft's reaction as follows.



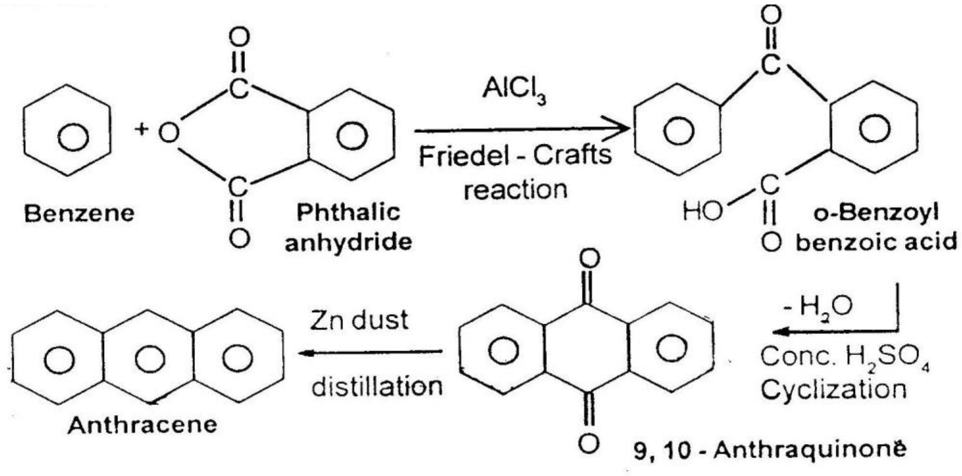
ii) Diel's Alder reaction:

Anthracene is also synthesized from 1,4naphthaquinone by Diel's - Alder reaction as follows.



iii) Haworth synthesis:

Benzene reacts with phthalic anhydride in the presence of $A1C1_3$ to give o-benzoyl benzonic acid. This on cyclization gives 9, 10-anthraquinone which on distillation with Zn dust gives anthracene.



Reactions of anthracene

a) Reduction

i) Anthracene is reduced by Na/amy1 alcohol into 9,10dihydro anthracene.

b) Oxidation

Anthracene is oxidises by chromic acid to 9,10Anthraquinone

c) Substitution Reaction

i) Anthracene undergoes Bromination to give anthracenedibromide which on heating gives 9-bromo anthracene.

ii) Nitration : Nitration of anthracene in acetic anhydride at 15-20^{o}c gives a mixture of 9-nitro anthracene and 9,10-dinitroanthracene.

Structure of Anthracene

1) The molecular formula of anthracene is $C_{14}H_{10}$.

2) This molecular formula suggests that anthracene may be related to benzene and naphthalene.

$$\underset{\text{Benzene}}{C_6H_6} \xrightarrow[\substack{+4C \\ +2H}]{\qquad\qquad} \underset{\text{Naphthalene}}{C_{10}H_8} \xrightarrow[\substack{+4C \\ +2H}]{\qquad} \underset{\text{Anthracene}}{C_{14}H_{10}}.$$

3) It is similar to benzene and naphthalene, because of its substitution reactions.

4) Brominationreaction suggest the presence of atleast two benzene rings in anthracene.

Oxidation reaction proves the presence of

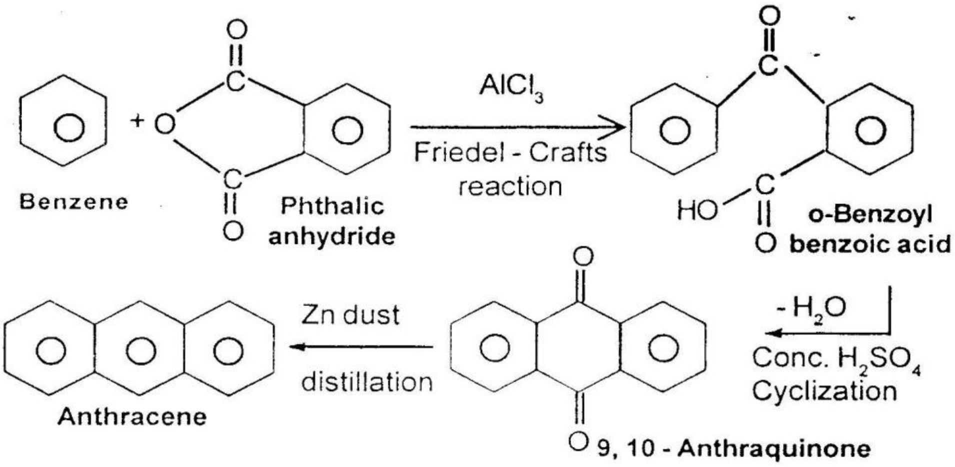
6) Anthracene is a resonance hybrid of the following 4 structures.

7) Finally the structure of anthracene is proved by Haworth synthesis.

Study from the preparation

Finally the structure of anthracene is proved by Haworth synthesis:

Benzene reacts with phthalic anhydride in the presence of A_1C1_3 to give o-benzoyl benzoic acid. This on cyclization gives 9,10 – anthraquinone which on distillation with Zn dust gives anthracene.

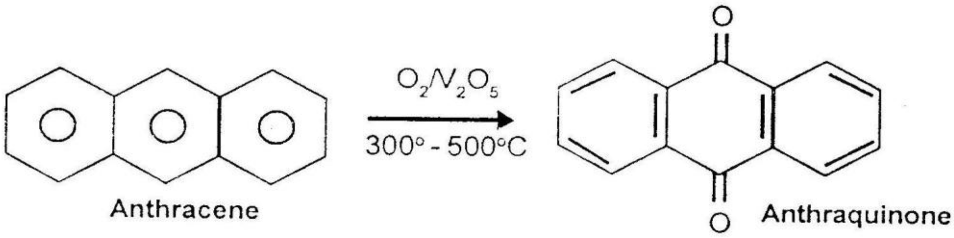


Uses of anthracene

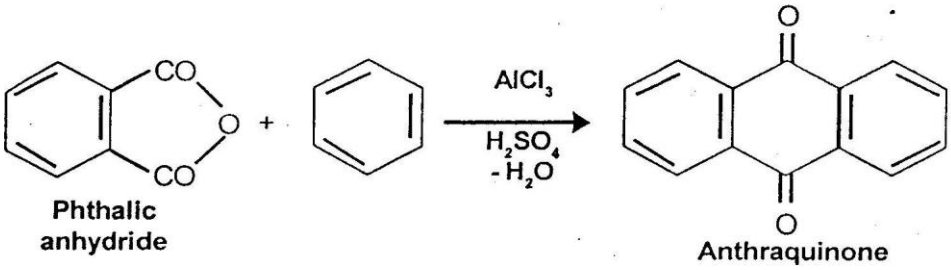
It is used in the preparation of anthraquinone dyes such as alizarin.

Preparation of anthraquinone

1) **From anthracene:** It is manufactured by the vapour phase air oxidation of crude anthracene.



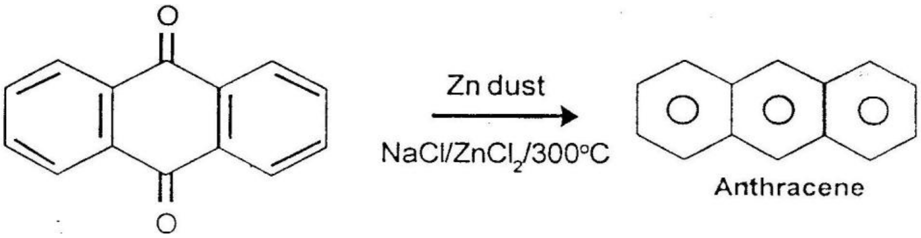
2) **Synthetic method:**Friedel – Craft condensation of phthalic anhydride with benzene in the presence of $A1C1_3$ forms an intermediate which on heating with H_2SO_4 cyclizes to give anthraquinone.



Reactions of anthraquinone

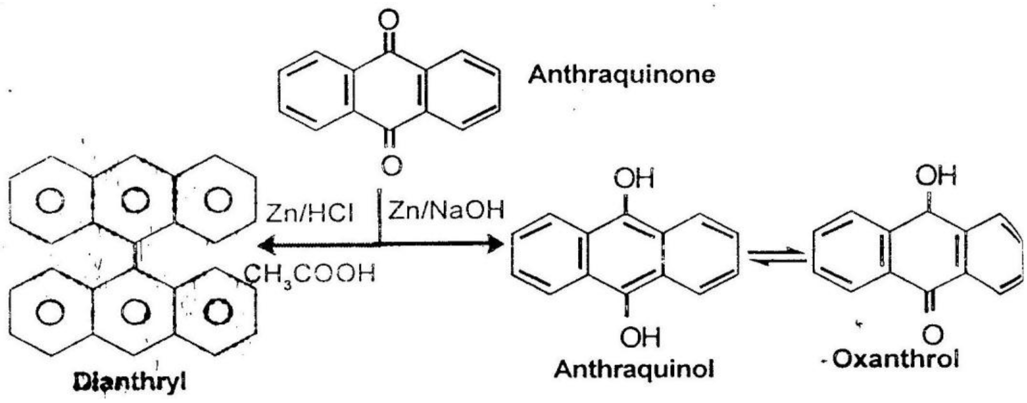
i) Distillation with zinc dust:

It forms anthracene on distillation with $ZnC1_2$/NaCl/Zn dust at 200-300°C.



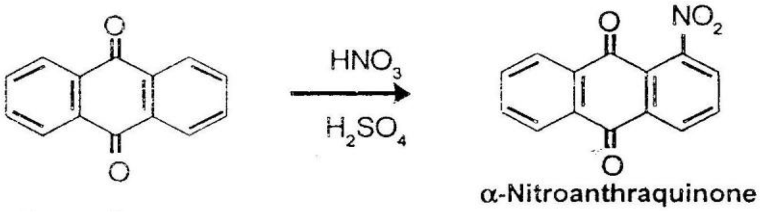
ii) Reduction:

With tin and HCI in acetic acid it forms anthrone; with Zn/HCI in acetic acid the main product is dianthryl; with Zn and NH_4OH it gives 9, 10-dihydroanthrol; and with zinc and NaOH the main product is anthraquinol which is tautomeric with oxanthrol.



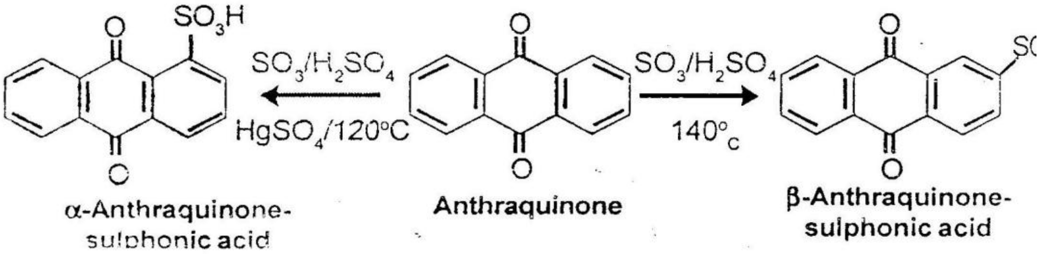
iii) Nitration:

Nitration of anthraquinone gives 1-or a-nitro-anthraquinone.



iv) Sulphonation:

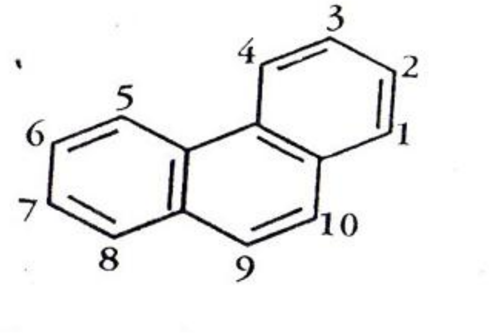
Anthraquinone on sulphonation with oleum in presence of catalyst mercuric sulphate at 120°C gives mainly ∝- anthraquinone-sulphonic acid, whereas in the absence of catalyst at 140°C the main product is β- anthraquinonesulphonic acid.



2.5 Synthesis, Reactions and structure of phenanthrene

5. Phenanthrene

Phenanthrene is an isomer of anthracene. The three benzene rings are fused in angular fashion. The structure and numbering of the carbon atoms of phenanthrene are shown below:



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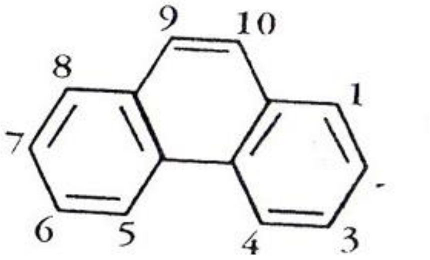


Isolation from Coal-tar

Phenanthrene, along with anthracene, occurs in the green oil (anthracene oil) fraction of coal –tar. On cooling the oil, a solid mass crystallises out. It contains anthracene, phenanthrene and carbazole. The crystals are treated with solvent naphtha when phenanthrene goes into solution. Evaporation of this solution yields crude phenanthrene. It is purified by recrystallization of the picrate from ethnol.

Haworth synthesis

Phenanthrene is obtained from naphthalene and succinc anhydride by

Haworth's synthesis.

Properties

Like anthracene, phenanthrene undergoes addition and substitution reactions. Substitution occurs preferentially at 9 and 10 positions.

1. Addition reactions

i) Addition of Hydrogen (Reduction)

Phenanthrene undergoes reduction with sodium and iso-amyl alcohol to yield 9,10 – dihydrophenanthrene.

ii) Addition of Chlorine :Phenanthrene reacts with chlorine in CCI, at room temperature to give 9, 10 – dichloro, 9-10 dihydrophenanthrene

2. Substitution reactions

i) Halogenation : When heated with $C1_2$ in CCI_4.

Phenanthrene yields 9-chlorophenanthrene.

ii) Nitration :Phenanthrene is nitrated with conc. HNO3 and conc. H2SO4 to yield 9-nitrophenanthrene.

iii) Sulphonation :Phenanthrene reacts with conc. H_2SO_4 at 120^oC to give a mixture of 2-phenanthrene-sulphonic acid and 3-phenanthrenesulphonic acid.

iv) Friedel – Craft's reaction : In the presence of anhydrous $AICI_3$, phenanthrene reacts with acetyl chloride to form 9 – acetylphenanthrene.

3. Oxidation

Phenanthrene is oxidized with acidified $K_2Cr_2O_7$ to give 9, 10 – phenanthraquinone which on further oxidation with H_2O_2 in acetic acid yields diphenic acid.

Structure

Phenanthrene is a resonance hybrid of the following structures:

Structure of phenanthrene

1) The molecular formula of phenanthrene is $C_{14}H_{10}$.

2) Phenanthrene is isomeric with anthracene.

3) Phenanthrene oxidation gives phenanthraquinone, which on further oxidation gives diphenic acid.

4) This Diphenic acid on decarboxylation gives diphenyl.

5) Thus phenanthrene must contain the skeleton as follows.

6) Phenanthrene is a resonance hybride of the five structures.

7) The structure is finally proved by Haworth synthesis.

Study from the preparation.

Check Your Progress II

1) Alizarin is synthesied from ....

2) Electrophilic substitution reaction takes place in anthracene at position ....

3) The total number of isomeric naphthols ....

2.6 Let us Sum up

Polynuclear hydrocarbons are compounds containing more than one aromatic ring. They may be divided into isolated and condensed system. Diphenyl, Diphenyl methane and Dibenzyl are examples of isolated system. Napthalene, Phenanthrene, Anthracene are examples of condensed system.

2.8 Key words

Isolated system :	Aromatic rings are directly linked to carbon atoms.
Condensed system:	Two or more aromatic rings are fused together.

2.8 Questions for Discussion

1) Write the Oxidation and Reduction reactions of naphthalene.

2) Explain any two methods of preparation of diphenyl

3) Discuss the various methods of preparation of phenanthrene.

4) Discuss the various reactions of phenanthrene.

5) Explain the structure of Naphthalene.

6) Outline the Haworthis Synthesis of anthracene.

7) Give the reactions of naphthols.

8) Give the reactions of naphthaquinone.

9) Explain the structure of Anthracene.

10) Explain the preparation and reactions of anthraquinone.

Check Your Progress Model Answers

CYP 1

1. Naphthalene
2. Substituted diphenyl
3. Phthalic anhydride

CYP2

1. Anthrquinone
2. C_9 and C_{10}
3. 2

2.9 Suggested Readings

[1] K.S. Tewari N.K. Vishil. S.N Mehotra organic chemistry.

[2] P.L. Soni. Text Book of organic chemistry.

UNIT III

HETEROCYCLIC COMPOUNDS

CONTENTS

3.0 Aims and objectives

After studying this leson, you should be able to

- Describe Heterocyclic compounds.
- Explain the different examples
- Describe the classification of compounds
- Explain the uses of different heterocyclic compounds.

3.1 Perparation, properties and uses of furgan

Heterocyclic compounds are stable cyclic compounds with the ring containing carbon and Oxygen, Nitrogen and Sulphur. These are usually five or six membered cyclic compounds exhibiting aromatic character.

Example : Furan, pyrrole, thiophene and pyridine.

Furan is a 5 membered heterocyclic compound containing oxygen as the hetero atom.

Preparation

1) Dry distillation of mucic acid gives furoic acid. This on heating gets decarboxylated to give furan.

2) Manufacture

Furan is manufactured by the catalytic decomposition of furfural in steam in the presence of CaO Catalyst

3) Synthesis - Paul Knorr Synthesis

Derivatives of furan are obtained by heating acetonyl acetone with P_2O_5

Reactions of furan

a) Reduction reaction:

Furan is reduced with hydrogen in the presence of RaneyNi to give Tetrahydrofuran.

b) Oxidation

Furan on oxidation in oxygen to give succinaldehyde.

c) Diel’s - Alder reaction:

Furan undergoes Diel’s - Alder reaction with maleic anhydride to form adduct.

d) Substitution reaction

i) Furan undergoes Nitration to give 2 Nitro furan

ii) Sulphonation of furan gives furan-2-sulphonic acid

iii) Acetylation of furan gives 2-Acetyl furan

Uses of furan

1) It is used as a starting material for the preparation of dyes, plastics and polymers.
2) It is used in the manufacture of nylon.
3) Tetrahydro furan is used as a solvent.

3.2 Preparation, properties and uses of pyrrole

i) Pyrrole is manufactured by passing a mixture of furgan, ammonia and steam over heated alumina as catalyst.

ii) Pyrrole is synthesised by passing a mixture of acetylene and ammonia through red-hot tube.

Reactions of pyrrole

1) Reduction :

It undergoes reduction in the presence of Ni catalyst at 200°C gives pyrrolidine

2) Oxidation :

Pyrrole is oxidised by Cr_2O_3 in acetic acid to maleinimide.

3) Substitution reaction

a)

b)

4) Friedils Craft reaction

Uses of pyrrole

i) It is used as a solvent
ii) It is used in pharmaceuticels

3.3 Preparation, properties and uses of thiophene

Thiophene

a) Paal - Knorr Synthesis

2,5 - Dimethyl thiophene can be obtained by heating acetonyl acetone with P_2S_5.

b) It may be prepared by paring a mixture of acetylene and H_2S over heated alumina.

c) Thiophene may be prepared by reaction between Furan and H_2S in the presence of Al_2O_3.

Reactions of Thiophene

a) Addition reaction (or) Reduction (or) Birch reduction

Thiophene is reduced with sodium in liquor NH_3, it gives 2,3 dihydro thiophene and 2,5 - dihydro thiophenes.

b) Substitution reaction

1) Thiophene undergoes chlorination at 30°C gives 2-chloro and 2,5 - dichloro thiophene

2)

On nitration thiophene gives 2- Nitro thiophene.

3) Thiophene undergoes Friedel - crafts reaction to give 2 - Acetyl thiophene

4) Thiophene on sulphonation gives thiophene - 2 - sulphonic acid

Uses

1. i) Thiophene derivatives are used in rubber and resin industries
2. ii) It is used to prepare biotin which is a growth factor for yeast
3. iii) Thiophene derivatives are used in pharmaceuticals.

Check Your Progress

Fill in the blanks

1) Furan has as its hetero atom ....

2) When acetylene is heated with ammonia, it yields ....

3) Thiophene has as its hetero atom ....

3.4 Comparison of aromatic character of thiophene, pyrrole and furan.

The order of aromatic character of thiophene pyrrole and furan can be given as follows.

Thiophene > Pyrrole > Furan

$\longrightarrow$

Decrease in the order of aromatic character

The variation in aromatic character among these three heterocyclic compounds in due to the following facts.

a) Variation in the electronegative nature of hetero atoms.
b) Variation in their resonance energy.

a) Electronegative nature of hetero atom :

In pyrrole the hetero atom is nitrogen. The members of the ring (Nitrogen and carbon atoms) undergo sp^2 hybridization to give a flat geometry to pyrrole; N (7) = $1s^2\ 2s^2\ 2p^3$

The lone pair of electorn available in the 2pz orbital is involved in aromatic sextet.

In thiophene the hetero atom is sulphur. The members of the rings (sulphur and carbon atoms) undergo sp^2 hybridization to give a flat geometry to thiophene; S(16) = $1s^2 2s^2 2p^6 3s^2 3p^4$

The lone pair of electron available in $3p_z$ orbital is involved in aromatic sextet.

In furan the hetero atom is oxygen. The members of the ring (oxygen and carbon atoms) undergo sp^2 hybridization to give a flat geomentry to furan; O(8) $1s^2 2s^2 2p^4$

The lone pair of electron available in $2p_z$ orbital is involved in aromatic sextet.

Out of the nitrogen, oxygen and sulphur, oxygen is most electonegative. Thus it attracts its lone pair and destabilises the aromatic sextet. Moreover the lone pair involved in the aromatic sextet of thiophene is available in $3p_z$ orbital. Thus sulphur atom cannot destabilise the aromatic sextet of thiophene.

Therefore the variation in the aromatic character of thiophene pyrrole and furan is due to the relative stability of their aromatic sextet.

b) Resonance energy:

resonance energy stabilises the aromatic compound. The resonance energy of thiophene pyrrole and furan is given in the following table.

Compound	Resoance energy kJ/mole
Thiophene	117
Pyrrole	87.8
Furan	71.7

Since thiophene has more resonance energy it is more aromatic and furan has the lowest resonance energy it is least aromatic.

c) The least aromatic nature of furan is proved by its adduct formation with maleic anhydride (Diel's-Alder reaction).

3.5 Synthesis and reactions of pyridine

Preparation

1) Pyridine is obtined by passing a mixture of acetylene and hydrogen cyanide through a red hot tube

2) Pyridine is produced industrially by heating tetrahydrofurfuryl alcohol with ammonia over alumina (catalyst) at 500°C.

Reactions

1. Basic character

Pyridine behaves as a base because of the presence of a lone pair of electrons on the nitrogen atom. It is freely available for protonation with acids and hence more basic than pyrrole. (In pyrrole, the lone pair is engaged in delocalisation).

2. Addition reactions

i) Hydrogenation : Catalytic reduction of pyridine with hydrogen in the presence of nickel gives hexahydropyridine called piperidine

ii) Addition of Methyl bromide : Pyridine reacts with methyl bromide to form N-pyridinium bromide (quaternary ammonium salt)

3) Electrophilic substitution reactions

Under drastic conditions, pyridine undergoes electophylic substitution reactions at the 3 - or 5- position.

i) Halogenation : Chlorination of pyridine in the presence of $AlCl_3$ gives 3-chloropyridine.

Pyridine may be brominated by passing vapours of pyridine and bromine over heated charcoal at 300°C. A mixture of 3-bromopyridine and 3,5-dibromopyridine is obtained.

ii) Nitration : Pyridine is nitrated to 3-nitropyridine by heating with conc.H_2SO_4 and fuming HNO_3 at 300°C

iii) Sulphonation : When heated with fuming sulphuric acid (oleum) in the presence of mercuric sulphate, pyridine yields pyridine 3-sulphonic acid.

4) Nucleophilic substitution reactions

Pyridine undergoes nucleophilic substitution reactions at the 2-position with strong nuclophiles.

i) Reaction with Sodamide : Pyridine when heated with sodamide in toluene solution forms 2 aminopyridine (Chichibabin reaction).

ii) Reaction with NaOH : Pyridine forms 2-hyroxypyridine when heated with NaOH at 300°C. The hydroxy compound is readily oxidised to pyridone

iii) Reaction with Butyl-lithium : When heated with butyl lithium, pyridine forms 2-butyl pyridine.

3.6 Synthesis and reactions of piperidine ($C_5H_{11}N$)

a) Catalytic hydrogenation :

Piperidine is manufactured by the catalytic hydrogenation of pyridine.

b) Reduction of pyridine :

It is also prepared by the reduction of pyridine using ethanol and sodium.

c) Cyclization reaction :

Piperidine is obtained as a cyclic product by heating pentamethylene diamine hydrochloride.

Reaction of piperidine :

i) Piperidine is a strong base. It behaves as an aliphatic secondary amine. ($Kb = 1.66 \times 10^{-3}$)

ii) Oxidation of piperidine with conc.H_2SO_4 gives pyridine.

iii) Piperidine undergoes ring open reaction with 3% H_2O_2 and gives 5-amino pent-1-al

iv) Piperidine is converted into n-pentane on heating with HI.

v) On Hofmann exhaustive methylation piperidine is converted into penta 1,3-diene.

3.7 Comparative study on baricity

i) Basic nature of nitrogen containing compounds is due to the availability of lone pair of electrons on their nitrogen atom for protonation.

ii) The basic character is measured using their dissociation constant of base (Kb) values.
Kb value for pyridine is 2.3×10^{-9}
Kb value for pyrrole is 2.5×10^{-4}.

3.8 Preparation and reactions of indole, quinoline and isoquinoline.

Indole

Preparation

1. Fischer Indole Synthesis :

Indole is prepared by heating the phenylhydrazone of pyruic acid with $ZnCl_2$ or BF_3 (catalyst).

Reactions :

1. Addition reaction :

Indole is reduced by tin and HCl to 2,3- dihydroindole (Indoline). However, hydrogenation using nickel catalyst yields octahydroindole (Indolidine).

2. Substitution reactions :

Unlike pyrrole, electrophilic substitution in indole occurs at C-3 position. This is due to resonance stabilization of the carbonium ion.

Attack at C-3

Attack at C-2

If C-3 position is blocked, the substituent enter C-2 position. In case, both 2-and 3- positions are occupied, substitution occurs at C-6 position in the benzene ring.

i) Bromination

ii) Nitration

iii) Sulphonation

iv) Fricdel - Craft's reaction

v) Mannich reaction

3. Oxidation

QUINOLINE

Preparation :

Quinoline is prepared by the following method:

1) Skraup synthesis :

Quinoline is obtained on a large scale when aniline is heated with glycerol, conc.H_2SO_4 and $FeSO_4$ in the presence of nitrobenzene as oxidising agent.

a)

b)

Reactions:

1. Basic character :

Quinoline is weakly basic in nature. It forms salts with mineral acids.

$$C_9H_7N + HCl \rightarrow C_9H_7\overset{+}{N}HCl$$

Quinoline Quinoline hydrochloride

2. Reaction with Methyl Iodide :

Being a tertiary base, it forms a quaternary ammonium salt with one mole of methyl iodide.

$$C_9H_7N + CH_3I \rightarrow C_9H_7\overset{+}{N}CH_3\,I$$

Quinoline N-Methylquinolinium iodide

3. Electrophillc Substitution Reactions

i) Halogenation

ii) Nitration

iii) Sulphonation

4. Nucleophllic Substitution Reactions

i) Reaction with Sodamide (Chichibabin Reaction)

ii) Reaction with phenyllithium

iii) Reaction with Butyllithium

iv) Reaction with Alkall

5. Oxidation

6. Reduction

ISOQUINOLINE

Preparation

1) Bischler-Naplerlaski Synthesis :

When β-Phenyl ethylamide is heated with a dehydrating agent such as P_2O_5 or anhydrous $ZnCl_2$, it undergoes, cyclodehydration to form dihydro isoquinoline, which on dehydrogenation with palladium or selenium yields isoquinoline derivative.

Reactions

1. Electrophilic Substitution Reactions

i) **Nitration**

ii) **Sulphonation**

iii) Bromination

iv) Oxidation

On oxidation with $KMnO_4$, isoquinoline gives a mixture of phthalic acid and cinchomeronic acid.

The action of perbenzoic acid converts isoquinoline into its N-oxide.

v) Reduction

vi) Reduction with Grignard reagent

Check Your Progress

Fill in the blanks

1) In Indole electrophilic substitution occurs at ....

2) Oxidation of quinoline with $KMnO_4$ gives ....

3) On bromination of isoquinoline gives ....

3.9 Let us Sum up:

Heterocyclic compounds are cyclic compounds with the ring containing carbon, oxygen, Nitrogen and sulphur. It is classified into five membered and six membered compounds. The baricity of heterocyclic compounds are compared.

3.10 Key words

Heterocyclic compounds:	Five membered and six membered rings.
Baricity :	Basic nature of nitrogen containing compounds.

3.11 Questions for Discussion

1) How is indole synthesised by Fischer Indole synthesis?
2) Discuss the preparation, properties and uses of thiophene.
3) Explain the properties of furan.
4) Discuss the preparation of pyrrole.

5) Write the synthesis of pyridine.
6) Write the skraup synthesis of quinoline.
7) Write the Bischler- Napieralski synthesis of isoquinoline
8) Write the oxidation products of quinoline and isoquinoline
9) Compare the basic characters of pyrrole, pyridine with amines.
10) Explain the Nucleiophilic subitution reactions of quinoline.

Check Your Progress : Model Answers

CYP I

1) Oxygen

2) Pyrrole

3) Sulphur

CYP II

1) C-3 position

2) Nicotinic acid

3) 4-Bromo isoquinoline

3.12 Suggested Readings

[1] O.P. Agarwal. Chemistry of Organic Natural Products.

[2] Gurdeep Chatwal Chemistry of Organic natural products.

UNIT IV
Alkaloids and Terpenoids

4.0 Aims and objectives

4.1 Alkaloids - Classification - isolation - General methods of determination of structure of alkaloids
4.2 Structural elucidation of piperine
4.3 Structural elucidation of nicotine
4.4 Structural elucidation of Coniine
4.5 Terpenes - Classification isolation - isoprene rule
4.6 Synthesis and structural elucidation of citral
4.7 Synthesis and structural elucidation of geraniol and menthol
4.8 Synthesis and structural elucidation of Dipendene

Alkaloids

4.0 Aims and objectives :

After studying this lesson you should be able to

- Explain the different class of alkeloids
- Discuss the different structure of alkaloids and terepenoids
- Explain the synthesis of alkaloids
- Discuss the uses and different sources of alkaloids

4.1 Definition

Alkaloids are natural plant compounds which contain atleast one nitrogen atom a heterocyclic ring. Example : Piperine, coniine, nicotine etc.

Alkaloids are mainly classified on the basis of the nature of the heterocyclic nucleus.

Class of alkaloid	Heterocyclic nucleus Present	Example
1. Pyridine alkaloid	Pyridine	Piperine, coniine
2. Pyrrolidine alkaloid	Pyrrolidine	Hygrine, stachydrine
3. Pyrolidine – pyridine alkaloid	Pyrrolidine and Pyridine	Nicotine
4. Quinoline alkaloid	Quinoline	Quinine, cinchonine
5. Isoquinoline alkaloid	Isoquinoline	Papaverine, morphine
6. Indole alkaloid	Indole	Reserpine
7. Tropane alkaloid	Condensed system of pyridine and pyrrole	Cocaine, atropine
8. Phenyl ethlamine alkaloid	Not a heterocyclic system	Ephedrine

Isolation

The powdered plant material is extracted, usually in a Soxhlet extractor, with an organic solvent like chloroform. Alternatively, the powered plant material is extracted with water, alcohol or dilute acids. The extract contains the alkaloidal salts present in the plant. Free alkaloids may then be released by treatment with an alkali.

The crude mixture of alkaloids, obtained above is separated into indivual alkaloids, by techniques like fractional crystallisation, precipitation, extraction, chromatography, countercurrent distribution etc.

General methods of structural eleucieation

The structural dertermination of an alkaloid involves the following steps.

i. Determination of molecular formula

The molecular formula is determined by elemental analysis and molecular weight determination.

ii) Detection and estimation of unsaturation

The Presence of unsaturation is detected by decolourisation of bromine water or dilute alkaline $KMnO_4$.

1. **Hydroxyl group :** The hydroxyl group may either be alcoholic or phenolic.
2. **Carboxyl group :** Ester formation and liberation of CO_2 with $NaHCO_3$ shows the presence of carboxyl group
3. **Carbonyl group :** The presence of carbonyl group is indicated by the formation of oximes, phenyl hydrazone and semicarbazones.
4. **Ester group :** Ester and lactone groups are detected by the products of hydrolysis
5. **Methoxy group :** It is detected and estimated by Zeisel mehod.
6. **N-methl group :** It is detected and estimated by Herzig-Meyer method.

Estimation of functional groups

1. **Methoxy group :** It can be estimated by Zeisel method. A known weight of alkaloid is heated with conc. HI. The methyl iodide formed is absorbed in alcoholic $AgNO_3$. The Agl formed is filtered, dried and weighed. From the weight of Agl, the no. of methoxy group present in the alkaloid can be estimated.

$$R(OCH_3)_n + nHI \rightarrow R(OH)_n + n\,CH_3I$$

$$n\,CH_3I + nAgNO_3 \rightarrow nAgl\downarrow + n\,CH_3NO_3$$

Moles of Agl formed	≡	Moles of CH_3I formed	≡	No. of (OCH_3) group

Nature of the ring

The nature of the ring can be known by splitting the complex alkaloid molecule into simple fragments.

a. Hydrolysis : For example, Piperine on hydrolysis breaks into piperic acid and pipeidine.

$C_{11}H_9O_2CONC_5H_{10} + H_2O \rightarrow C_{11}H_9O_2COOH + C_5H_{10}NH$
Piperine Piperic acid Piperidine

b. Oxidation : Alkaloids give a variety of oxidation products depending upon the nature of oxidizing agent. For example, coniine on oxidation gives pyridine 2-carboxylic acid. This proves that coniine is an α-substituted pyridine derivative.

c. Zinc dust distillation : On distillation with zinc dust the alkaloid is degraded into parent hydrocarbon

d. Hofmann’s exhaustive methylation :

Conversion of an amine into a quarternary ammonium salt by treating with CH_3 I is known as exhaustive methylation. The quarternary salt is treated with moist silver oxide to form the

Corresponding hydroxide. This when heated, eliminates water by combining OH^- and the β-hydrogen with respect to nitrogen atom. This results in the formation of an alkene and an amine. This process is repeated till the complete splitting of nitrogen takes place leaving an alkene. The entire process is known as Hofmann's exahaustive methylation.

Physical methods

Physical methods such as UV-visible, IR, NMR, Mass spectroscopic studies, ORD, CD and X-ray diffraction studies reveal the exact structure of the alkaloid.

Finally the structure of an alkaloid is confirmed by its chemical synthesis.

4.2 Piperine

a. Sources : Black pepper, white pepper

b. Structure of Piperine :

i) The molecular formula of piperine is $C_{17}H_{19}O_3N$.

ii) It is hydrolysed by alkali into piperidine (2^o amine) and piperic acid.

$$C_{17}H_{19}O_3N + H_2O \xrightarrow{OH^-} C_{12}H_{10}O_4 + C_5H_{11}N$$

Piperine Piperic acid Piperidine

This suggests that piperine is amide of piperic acid. The base is piperidine.

iii) Structure of Piperidine

1. The molecular formula of piperidine is $C_5H_{11}N$
2. Pyridine on reduction gives piperidine.

Thus piperidine is a heterocyclic secondary amine.

3. This structure of piperidine is further confirmed by Hofmann's exhaustive methylation as follows :

Thus the structure of piperidine is proved by the formation of piperylene in Hofmann's exhaustive methylation.

Structure of Piperic acid

1. The molecular formula of piperic acid $C_{12}H_{10}O_4$.

2. Piperic acid forms tetrahydro and tetrabromo derivatives with H_2 and Br_2 respectively.

$$C_{12}H_{10}O_4 + 2H_2 \xrightarrow{Ni} C_{12}H_{14}O_4$$

Piperic acid Tetrahydro piperic acid

$$C_{12}H_{10}O_4 + 2Br_2 \xrightarrow{CCl_4} C_{12}H_{10}O_4Br_4$$

Tetrabromo piperic acid

These reactions indicate the presence of two (C=C) double bonds in piperic acid.

3. It gives brisk effervescence with sodium bicarbonate. Therefore it contains a carboxyl group. This accounts for two oxygen atoms.

$$C_{11}H_9O_2(COOH) + NAHCO_3 \rightarrow C_{11}H_9O_2COONa + H_2O + CO_2$$

4. On oxidation with $KMnO_4$, it forms piperonal ($C_8H_6O_3$), tartaric acid and oxalic acid.

$$C_{12}H_{10}O_4 \underset{(O)}{\overset{KMnO_4}{\rightarrow}} C_8H_6O_3 \xrightarrow{(O)} C_8H_6O_4$$

Piperic acid Piperonal Piperonylic acid

5. This structure of piperonylic acid is confirmed by its synthesis from protpcatechuic acid and methylene iodide.

7. Piperonal can be formulated as follows.

8. The structure of Piperic acid may be given as follows

11. Finally the above structure of piperic acid may be proved by its synthesis from catechol.

12. Therefore piperine must be the acid amide of piperic acid. Thus the structure of piperine can be assigned as follows.

4.3 Nicotine

i. The molecular formula of nicotine is C_{10} H_{14} N_2.
ii. With HCI it forms the crystalline salt, nicotine dihydrochloride. This proves that nicotine is a diacid base.
iii. On treatment with CH_3I, it forms dimethiodide. This suggests that nicotine is a di-tertiary base
iv. Herzig - Meyer determination proves that nicotine contains one ($-NCH_3$) group.
v. Nicotine on oxidation with $KNnO_4$ or chromic acid gives nicotinic acid (Pyridine – 3-carboxylic acid).

Nicotine can be written as

The reaction shows that the side chain is saturated

vi) The structure of nicotine is also proved by the following reaction. Nicotine when treated with bromine, forms dibromo nicotine. This on heating with barium hedroxide, breaks down to give nicotinic acid, malonic acid and methyl amine.

xi) Synthesis of nicotine:

Finally the above structure of nicotine is confirmed by its synthesis by Spath *et.al*. The synthesis involves the Clasien condensation of ethyl nicotinate with N-mehtyl-2-pyrolidone.

4.4 Coniine

1. The molecular formula of coniine is $C_8H_{17}N$.
2. Coniine on distillation with zinc give conyrine.

$$\underset{\text{Coniine}}{C_8H_{17}N} \xrightarrow[\text{Distillation} - 3H_2]{\text{Zn dust}} \underset{\text{Conyrine}}{C_8H_{11}N}$$

3. Conyrine on oxidation with $KMnO_4$ gives α -picolinic acid (Pyridine 2- carboxylic acid)

The suggests that conyrine is a pyridine derivative containing a side chain at position 2 only.

4. Nature of the side chain

The molecular formula of the side chain can be obtained as follows

$$C_8 H_{11}N \quad - \quad C_5H_4N \quad = \quad C_3H_7$$

(conyrine) (Pyridine derivative) (Side chain)

5. Therefore conyrine may be represented by the following two structure.

6. Since conyrine has six hydrogen atoms less than coniine, the latter is probably the piperidine derivative and may be represented by the following two structures.

7. When heated with HI at 300° under pressure, coniine forms n-octane and not isooctane. This proves that the side chain of coniine is only n-propyl (I) and not isolropyl (II)

8. Therefore coniine can be represented by structure (I).

9. The above structure of coniine is further proved by the formation of conylene (C_8H_{14}) by Hofmann exhaustive methylation.

10. The structure of conine is further proved by the following synthesis from α-picoline.

Check Your Progress

1) Coniine is a .... alkaloid

2) Tobacco leaves contain ....alkaloid

3) All terpenes have the carbon skeleton made up of ....

4.5 TERPENES

Terpenes are isomeric hydrocarbons obtained from the essential oils such as eucalyptus oil, sunflower oil, sandalwood oil, palmrosa oil etc. Their general formula is $(C_5H_8)_n$.

eg : Dipentene, myrcene (Terpenes), citral, geraniol (Terpenoids)

They occur in the fruits, flowers, leaves, stembarks and roots of nearly all the plants that have pleasant smell. This pleasant smell is due to the presence of certain steam volatile oils known as essential oils.

4.9. Classification

Terpenes are classified on the basis of the number of C_5 (isoprene) units present in them.

Class	No. of isoprene units	Example
a) Hemiterpenes	One isoprene unit (C_5)	-
b) Monoterpenes	Two isoprene units (C_{10})	Citral, limonene
c) Sesquiterpenes	Three isoprene units (C_{15})	Farnesol, zinziberene

d) Diterpenes	Four isoprene units (C_{20})	Phytol
e) Triterpenes	Six isoprene units (C_{30})	Squalence
f) Polyterpenes	Several isoprene units $(C_5)_n$	Rubber

4.10 Isolation of essential oils and terpenoids

Essential oils are extracted from plants by any one of the following methods.

i) Expression method

The plant material is cut into small pieces. These pieces are crushed to get the juice. When the juice is centrifuged, the essential oil is obtained as the centrifugate. Nowadays this method is not used.

ii) Steam distillation

The plant material is macerated and then steam distilled. From the steam distillate the essential oil is extracted using pure organic solvents such as light petrol. The solvent is then removed by distillation. This method cannot be used for essential oils which undergo decomposition during steam distillation.

iii) Solvent extraction

The plant material is extracted directly with the solvent such as light petrol at room temperature. When the filtered extract is evaporated under reduced pressure the oil is left as residue. This method is employed for heat sensitive essential oil which cannot be obtained by steam distillation.

4.11 Isoprene rule

1) The C_5 unit of Terpenes is isoprene [2-methyl, 1,3-butadiene].
2) The isoprene units are joined together through C_1 and C_4 positions. That is the isoprene units are joined in a regular head to tail fashion. This is known as **isoprene rule.**

3. The isoprene rule is further proved by the following facts.

Eg : Isoprene may be polymerized to give rubber like product.

$$nC_5H_8 \xrightarrow{Polymerization} (C_5H_8)_n$$

Isoprene Rubber

4.6. Citral

i. The molecular formula of citral given by analytical data and molecular weight determination $C_{10}H_{16}O$

ii. It forms tetrahydro and tetrabromo derivatives with hydrogen and bromine respectively.

Therefore it contains two double bonds.

$$C_{10}H_{20}O \xleftarrow{2H_2} C_{10}H_{16}O \xrightarrow{2\,Br_2} C_{10}H_{16}OBr_4$$

Tetrahydro citral Citral Citral tetrabromide

iii. These reactions confirm that citral contains an aldehyde group.

$$C_{10}H_{18}O \xleftarrow[Na/Hg]{(H)} C_{10}H_{16}O \xrightarrow[(O)]{Ag_2O} C_{10}H_{16}O_2$$

Geraniol Citral Geranic acid

iv. On heating with $KHSO_4$ citral forms p-cymene.

v. Citral on ozonolysis gives acetone, leavulinic aldehyde and glyoxal.

vi. Ozonolysis and dealdolization studies suggest the following structure for citral.

vii. **Synthesis of citral** : Finally the above structure of citral is confirmed by the following synthesis

Evidence to prove that neral is a cis isomer and geranial is a trans isomer:

Usually citral contains a mixture of cis-citral and trans – citral. Therefore this mixture on reduction gives two isomeric alcohols.

4.7 Geraniol

Structrue of geraniol

(i) The molecular formula of geraniol given by analytical data and molecular weight determination is $C_{10}H_{18}O$.

(ii) It forms tetrahydro and tetra bromo drivates withhydrogen and bromine respectively.

Therefore it contains to (C=C) double bonds.

$$C_{10}H_{22}O \xleftarrow{2H_2} C_{10}H_{18}O \xrightarrow{2Br_2} C_{10}H_{18}OBr_4$$

Tetrahy drogeraniol   Geraniol   Geraniol tetrabromide

iii. The structure of geraniol can be designed as follows.

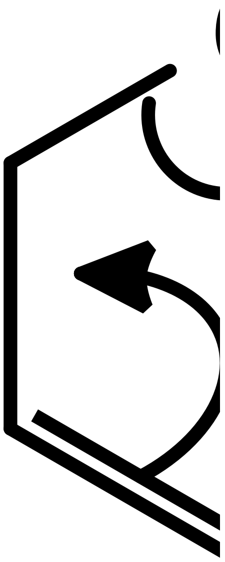
iv. Ozonolysis of geraniol gives l mole each of glycolaldehyde, acetone and 2-keto pentanol.

The above products can be obtained if geraniol has the structure (I).

v. The nature of carbon slaleton of geraniol is confirmed by its dehydrogenation to p-cymene.

vi. Based on the above facts geraniol is assigned the following structure.

vii. **Synthesis of geraniol :** The above structure of geraniol is confirmed by the following synthesis.



4.7 Menthol

Occurance : It occurs in peppermint oil.

Structure of menthol:

i. Molecular formula of menthol given by analytical data and molecular weight determination is $C_{10}H_{20}O$.

ii) Menthol an oxidation with chromi acid gives menthone which is a ketone. This reaction suggests that menthol is a secondary alcohol.

iii. Menthol of reduction with hydroiodic acid gives p-menthane.

iv. Catalytic hydrogenation of thymol gives menthol.

This reaction suggests that the position of –OH group in menthol should be C_3.

v. Dehydration of menthol with $KHSO_4$ gives menthene which on dehydrogenation with sulphur giver p-cymene.

The above reactions prove the following structure of menthol.

vi. **Synthesis of menthol:** The above structure of menthol is further proved by the following synthesis.

4.8 Dipentene

It is an optically active compound. In its optically active form it is known as limonene. The racemic form of limonene (±) is known as dipentene.

Occurance : The limonene form is available in lemon, orange, peppermint oil etc. The dipentence form is available in turpentine oil.

Structure

1) The molecular formula of limonene is $C_{10}H_{16}$.
2) The presence of two double bonds in limonene is proved by its addition reaction with hydrogen and bromine to give tetrahydro and tetrabromo dervatives respectively.
3) On dehydrogenation with sulphur limonene gives p-cymene. This confirms that limonene is having a similar carbon skeleton.

4) On complete reduction limonene gives p-menthane

5) Thus limonene is p-menthane with two double bonds.
6) Limonene on hydration with dil.H_2SO_4 gives α-terpeniol which on dehydration gives back the limonene.

7) Thus the structure of limonene may be either (A) or (B). Limonene is optically active. This is possible only with structure (B). This structure contains the asymmetric carbon atom (⊗). Thus the structure of limonene is

8) Finally the above structure of limonene is proved by the following syntheses.

a) Dehydration of α-terpeniol with $KHSO_4$:

α-Terpeniol on dehydration with $KHSO_4$ gives limonene.

Demerization of isoprene :

When isoprene molecules are heated in a sealed tube, they undergo dimerization to give dipentence.

Check Your Progress

1) The source of citral is ....

2) Which among the following terpenes occurs in turpentine ....

3) Menthol occurs in ....

4.9 Let us sum up

Alkaloids are natural plant compounds containing Nitrogen atom. Alkaloids are classified on the basis of heterocyclic nucleus. Terpenoids are isolated from essential oils. The main unit of terepenoid is Isoprene.

4.10 Key words

Isoprene is 2 methyl 1,3 - butadiene

Isolation of terpenes from natural oils synthesis and structural elucidation of alkaloids and terpenoids.

4.11 Questions for Discussion

1) State and explain isoprene rule
2) Explain 'Hotmann's exhaustive methylation' with an illustration.
3) Outline the synthesis of citral.
4) Discuss the structure of coniine
5) Outline the synthesis of Nicotine.

6) Discuss the structure of Nicotine
7) Discuss the structure of Geraniol
8) Discuss the structure of piperine.
9) Write the synthesis of dipentene.
10) Write the synthesis of Menthol

Check Your Progress

CYP I

1) Pyridine

2) Nicotine

3) Isoprene units

CYP II

1) Lemon

2) Dipentene

3) Pepper mint oil.

4.12 Suggested Readings

[1] O.P. Agarwal. Chemistry of Organic Natural Products

[2] Gurdeep Chatwal. Chemistry of Organic Natural Products.

Unit V
Organic Spectroscopy

Contents

5.0 Aims and objectives

After studying this lesson, you should be able to

- Describe Spectroscopy
- Explain Wood-Ward Fieser rule
- Describe Chemical shift.
- Explain the electronic trantions.
- Describe the different types of shift.
- Draw and explain the nmr spectra of many compounds.

Introduction

The UV spectroscopy arises from the excitation of electrons in a molecule from bonding orbital to antibonding orbital by the absorption of UV radiation energy. Hence UV spectroscopy is sometimes called electronic spectroscopy. It involves radiation ranges from 100-400 nm (1nm = 10^{-7} cm = 10 $\overset{o}{A}$ = 1mμ). The region above 200nm is called near UV or the quartz UV and region below 200 nm is called the far UV or the vacuum UV.

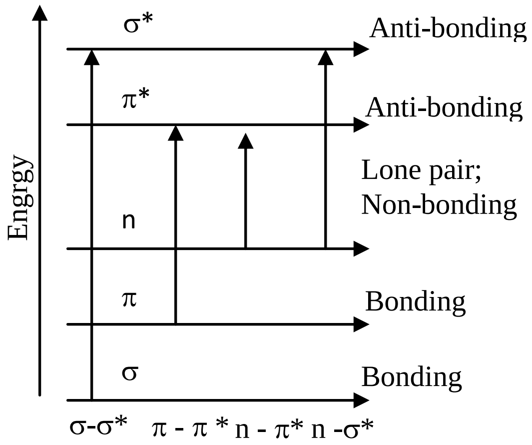
Two informations are obtained from the UV spectrum. The first is the wavelength of the peak maximum (λ_{max}) and the second is the intensity of the absorption peak $(\in_{max})$.

5.1 Types of electronic excitations

The electronic transitions (excitations) in molecules are classified according to the type of the valence electrons in them.

When a molecule is excited by a radiation energy, the electrons can be excited from a bonding (σ^*, π^*), which are vacant in the ground state. This produces $\sigma \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, $n \rightarrow \sigma^*$ and $n \rightarrow \pi^*$ electronic transitions (Fig.5.1). The energy of transition is in the following order.

$\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$



Types of transitions and energy of n,π,σ electrons

(a) $\sigma \rightarrow \sigma^*$ transition:

The transition of an electron occurs from a bonding sigma orbital of a molecule to the higher energy antibonding sigma orbital is known as $\sigma \rightarrow \sigma^*$ transition.

Examples :	Methane	λ_{max}	122 nm
	Ethane	λ_{max}	135 nm

(b) $\pi \rightarrow \pi^*$ transition:

The transition of an electron occurs from π bonding orbital to π* orbital is known as $\pi \rightarrow \pi^*$ transition.

Examples :	1,3-butadiene	λ_{max}	217 nm
	Acetophenone	λ_{max}	240 nm

(c) $n \rightarrow \sigma^*$ transition:

The transition of an electron occurs from the non-bonding orbital of the ground state to the antibonding sigma orbital is known as n-σ* transition.

Examples :	methyl alcohol	λ_{max}	174 nm
	Methyl chloride	λ_{max}	169 nm

(d) $n \rightarrow \pi^*$ transition:

The transition of an electron from the non-bonding orbital of the ground state to the antibonding π^* orbital.

Examples :	Acetone	λ_{max}	270 nm
	Acetaldehyde	λ_{max}	293 nm

Chrmophore

A covalenty unsaturated groups responsible for electronic absorption in the ultraviolet and visible regions are called chromophores.

Examples:

It may or may not give colour to the compound.
There are two types of chromophores.

a) Chromophores which contain both π electrons and undergo $\pi \rightarrow \pi^*$ transitions.

Examples : Ethylene, acetylene, etc.

b) Chromophores which contain both π electrons and n electrons and undergo $\pi \rightarrow \pi^*$ and $n \rightarrow n^*$ transitions.

Examples : Carbonyls, nitriles, azo compounds, nitro compounds

Auxochromes

An auxochrome is a saturated group with nonbonded electrons attached to the chromophore, which shifts the absorption band to a longer wavelength (bathochromic shift). It also increases the intensity of absorption peak. Generally an auxochrome is a group which depends upon the colour of the compound.

Examples : $-NH_2$, $-OH$, $-Cl$, etc.

5.2 Red shift :

Shift of an absorption maximum to a longer wavelength side is called bathochromic shift. It is also called red shift because the absorption is shifted towards the red region of the visible spectrum.

Examples :

Acetone shows $n \rightarrow \pi^*$ transition at 264.5 nm in water as the solvent, whereas it shows absorption at 279 nm in hexane as the solvent.

Hypsochromic shift or blue shift :

Shift of an absorption maximum to a shorter wavelength side is called hypsochromic shift. It is also called blue shift because the absorption is shifted towards the blue region of the visible spectrum.

Hypsochromic shift can also be produced when an auxochrome is attached to the double bonds where non bonding, ‘n’ electrons are available (e.g: $>C = O$)

Hyperchromic effect :

The effect which causes an increase in the intensity of absorption maximum (ε_{max}) of a compound is called hyperchromic effect. It may be produced by the introduction of an auxochrome. Example: The introduction of a methyl group (an auxochrome) in position 2 of pyridine increase the ε_{max} (λ_{max} 262 nm) from 2750 to 3560 for $\pi \rightarrow \pi^*$ transition in hexane.

Hypochromic effect:

The effect which causes a decrease in the intensity of absorption maximum (ε_{max}) of a compound is called hypochromic effect. The introduction of a methyl group in position 2 of biphenyl decrease the ε_{max} (λ_{max} 250 nm) from 4150 to 3750 for $\pi \rightarrow \pi^*$ transition in ethanol.

5.3 Application of UV spectroscopy

For studying functional groups.

UV spectra is used to detect the presence of functional groups or chromphores.

Identification of functional groups (chromophores)

The position and intensity of bands obtained in the UV spectra are used to identify the functional groups or chromophores.

Determination of Cis-trans isomers (Geometrical isomers)

UV spectroscopy is used to confirm the structure of cis-trans or geometrical isomers.

Examples:

λ_{max} = 280 nm; $\in$ = 13,500 (Z-isomer)

λ_{max} = 295 nm; $\in$ = 27,000 (E-isomer)

UV spectra can be used to distinguish conjugated dienes from non-conjugated dienes.

Examples :

$H_2C = CH - CH = CH - CH_3$
1,3-pentadiene, λ_{max} = 223 nm

$H_2C = CH - CH_2 - CH = CH_2$
1,4-pentadiene, λ_{max} = 182 nm

5.4 Woodward-Fiser rule

Woodward and Fieser derived certain empirical rules for calculating the absorption maximum for α,β - unsaturated carbonyl compounds and conjugated dienes. These are called Woodward-Fieser rules. This rules were latter modified by Scott. The Woodward and Fieser rules are given in Tables I & II

Table 1. Rules for α, β - unsaturated carbonyl compounds

Dienone

Compound	**λ_{max} (nm)**
Base values	
i) Acyclic (or) six membered cyclic	
α, β -unsaturated ketone	215
α, β -unsaturated aldehyde	210
Increments for	
a) Homoannular diene,	+39
b) Double bond extending conjugation	+30
c) Alkyl substitutent or ring residue	
α	+10
β	+12
γ or higher	+18
d) Exocyclic double bond,	+5

Table 2. Rules for diene and triene absorption

Compound	**λ_{max} (nm)**
Base values	
i) Acyclic diene or Heteroannular diene*	214
ii) Homoannular diene	253
Increments for	
a) Double bond extending conjugation	+30
b) Alkyl substituent or ring residue	+5
c) Exocyclic double bond	+5

Examples :

1)

Base value = 215 nm
2 β substituents (2 × 12) = 24 nm
Calculated I_{max} = 239nm

2)

Base value for six membered cyclic
α, β - unsaturated ketones = 215nm
α- substituent (ring residue) = 10 nm

β - substituent (ring residue) = 12 nm

Calculated λ_{max} = 237 nm

3)

Base value = 215 nm
Ring residue β = + 12 nm
Ring residue δ = + 18 nm
Extended conjugation = + 30 nm
Exocyclic double bond = + 5 nm

Calculated λ_{max} = 280 nm

4)

Base value = 210 nm
α - substitutent = + 10 nm
2 β- substitutent = + 24 nm

Calculated λ_{max} = 244 nm

5)

Base value for homoannular diene = 253 nm
3 ring residues = + 15 nm
Exocyclic double bond = + 5 nm

Calculated λ_{max} = 273 nm

6)

Base value for hetero annular diene = 214 nm

3 ring residues = + 15 nm
Exocyclic double bond = + 5 nm
Calculated λ_{max} $= 234$ nm

7)

Base value = 215 nm
Ring residue α = 10 nm
Ring residue δ = 30 nm
Homoannular diene = 39 nm
One exocyclic double bond = 6 nm
Calculated λ_{max} $= 317$ nm

8)

Base value = 215 nm
Ring residue α = 10 nm
Ring residue β = 12 nm
Calculated λ_{max} $= 237$ nm

9)

Base value = 215 nm
Ring residue β = 12 nm
Ring residue higher = 18 nm
Two extended conjugation = 60 nm
Homoannular diene = 39 nm
One exocyclic double bond = 5 nm
Calculated λ_{max} $= 349$ nm

10)

Base value = 214 nm
3 alkyl substituent = 15 nm
(3×5)
Calculated λ_{max} = 229 nm

11) $CH_2 = CH - CH = CH - CH = CH_2$

Base value = 214 nm
Extended conjugation = 30 nm
Calculated λ_{max} = 224 nm

12)

Base value = 215 nm
1 β-ring residue = 12 nm
3 higher ring residues = 54 nm
(3×18)
2 extended conjugation = 60 nm
(2×30)
2 exocyclic double bonds = 10 nm
(2×5)
Calculated λ_{max} = 351 nm

Check Your Progress

Fill in the blanks

1) .... Transition. Require least energy?

2) Wood ward - Fieser rules are applied in ....

3) u.v spectrum mainly give information about ....

5.6 Infrared (IR) spectorscopy

The IR radiation is a part of electromagnetic spectrum between the visible and microwave regions. The various regions of IR spectrum are,

Region	Frequency range
Far IR	700 - 200 cm^{-1}
IR region	4000 - 650 cm^{-1}
Near IR region	14290 - 4000 cm^{-1}

The IR region 4000 - 650 cm^{-1} is extremely useful for the organic chemist.

Characteristic of IR absorption frequencies

Each and every compounds have produced characteristic IR absorption frequencies. Hence we can easily identify any unknown orgainc compound by comparing its IR spectrum with that of known compounds spectrum. In addition, each different functional group such as O-H, C-H or absorb with in a particular narrow range of frequencies. Hence we can easily identify the type of functional group present in a molecule by showing an of an absorption band in a particular position of the IR spectrum.

The absorption frequency of a bond depends on the masses of the atoms forming the bond. The bonds of hydrogen with a heavier atom such as nitrogen, oxygen or carbon absorb radiation at the upper end of the frequency range.

Examples :

Bond type	Frequency range
O-H	3650 - 3600cm^{-1}
C-H	2900 cm^{-1}
N-H	3300 cm^{-1}

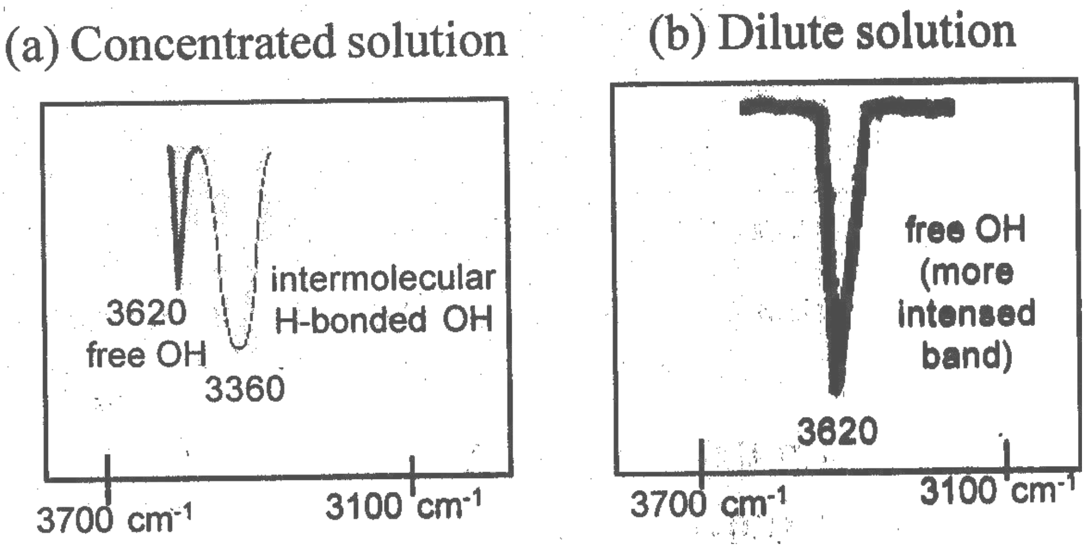
The vibration bonds of two heavier atoms such as C-N, C-O and C-C absorp radiation at the lower end of the frequency range.

Examples :

Bond type	Frequency range
C-C, C-O, C-N	1300 - 800 cm^{-1}
C=C, C=O, C=N, N=O	2260 - 2100 cm^{-1}

5.7 Applications of IR spectroscopy:

IR spectra may be used to distinguish inter and intramolecular hydrogen bonding by studying the effect of dilution. Intermolecular hydrogen bonds are concentration dependent and it increases as the concentration of the solution increases. This appears as an additional broad band at 3500-3200 cm^{-1} along with sharp free OH band at 3650 - 3580 cm^{-1}.



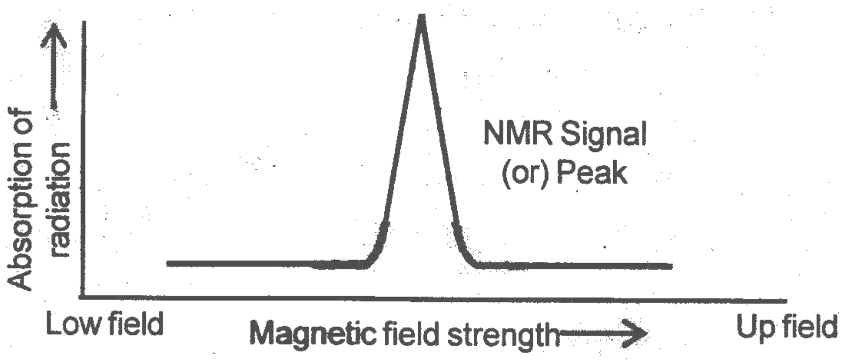
2) Functional group detection
a) Identification of functional groups

Identification of functional group in organic compound is the most important application of IR spectra. The region from 4000-1500cm^{-1} in an IR spectrum is useful for the identification of functional groups.
eg.

Bond	**Group**	**Frequency (cm^{-1})**
C=C	alkene	1680 - 1620
	sym.conjugated dienes	1600
	unsym.conjugated dienes	1650 - 1600

5.8 NMR spectroscopy

The interaction between the nuclei and the radiofrequency radiation is called nuclear magnetic resonance (NMR) spectroscopy.



NMR signal

A plot of magnetic field strength against absorption of radiation gives NMR signal or peak in the spectrum.

Number of NMR signals

The number of signals explain the number of different sets of equivalent protons in a molecule. Each signal corresponds to a set of equivalent protons.

Example

i) 1 nmr signals

ii) 2 nmr signals

iii) 3 nmr signals

iv) 3 nmr signals

v) 4 nmr signals

vi) 1 nmr signals

vii) 2 nmr signals

viii)

From this structure, one can expect two sets of equivalent protons (Two signals). But sterochemical formula shows three sets of protons in it and it gives three NMR signals.

ix) 1,2- dichlorpropane, CH_3 - CH(Cl) - CH_2Cl.

From this structure one can expect three sets of protons (Three signals). But stereochemical formula shows four sets of protons in it and it gives four NMR signals.

Chemical shift (Position of NMR signals)

The separation in the positions of the spectral signals of H- atoms in different chemical environments from that of a standard reference is called chemical shift (δ). Chemical shift is usually reported as,

$$\delta = \frac{H_S - H_{ref}}{H_0} \times 10^6 \text{ and}$$

$$\delta = \frac{v_s - v_{ref}}{v_0} \times 10^6$$

Where H_S and V_S are the resonance field and frequency for the sample, H_{ref} and V_{ref} are the resonance field and frequency for the reference and H_0 and V_0 are the applied field and its frequency.

Generally, the reference compound used is tetramethylsilane (TMS). There are two scale used for measuring chemical shift, namely δ scale and τ scale and they are related by the expression.

$\delta + \tau = 10$ or $\tau = 10 - \delta$

The chemical shift for the TMS proton is taken to be zero in the δ scale.

Reason for TMS used as standard reference :

TMS, tetramethylsilane $(CH_3)_2$ Si is used as reference compound in NMR, because

i) It has 12 equivalent protons and gives a single sharp peak in its NMR spectrum.
ii) It has a low boiling point (27°C) and thus it can be easily recovered after the spectrum is recorded.
iii) It is chemically insert.
iv) It is soluble in most of the organic solvents.
v) Its signal is appeared at the extreme end of the spectrum. i.e. upfield, $\delta = 0$ ppm

Spin-Spin coupling (Spin-spin splitting)

In NMR, the multipicity of the spectral signals are due to spin-spin coupling or spin-spin splitting. The intensity of the peak in the multiplet is given by binomial coefficients of the order n and pascal's striangle.

n	(n + 1)	Relative intensity
0	1 (singlet)	1
1	2 (doublet)	1 : 1
2	3 (Triplet)	1 : 3 : 3 : 1
3	4 (quartet)	1 : 3 : 3 : 1
4	5 (quinet)	1 : 4 : 6 : 4 : 1

Example: Ethanol contains six protons which can be divided into three environments as follows.

CH_3 - CH_2 - OH
a b c

At low resolution NMR, it shows three signals due to three different kinds of protons (Fig.5.6.)

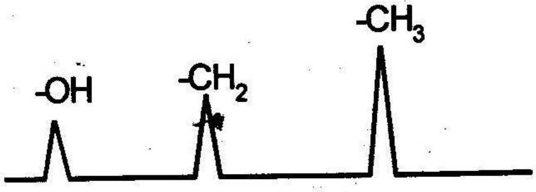


Fig. Low resolution NMR Spectrum Of Ethanol

At high resolution NMR, it gives the spectrum as shown in the Fig.5.7.

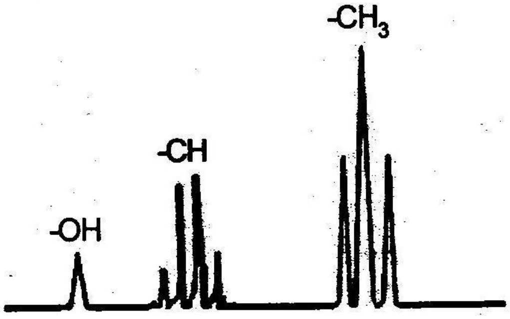


Fig. High resolution NMR Spectrum of ordinary samples of Ethanol

The multiplicity of the signal is due to spin-spin coupling.

For methyl protons; the number of neighbouring protons, n = 2 (from methylene group)
(n + 1) = (2 + 1) = 3 signals (triplet)

The signal for methyl proton splits into three of intensities 1 : 3 : 1.

For methylene protons the number of neighbouring protons, n = 3 (from methyl group) (n + 1) = (3 + 1) = 4 signals (quartet)

The signal for methylene proton splits into four of intensities 1 : 3 : 3 : 1

For hydroxyl proton, no multiplicity of the signal is observed. This is due to no coupling interaction between the neighbouring methylene protons. The reason is the hydroxyl proton undergoes fast chemical exchange with proton in other molecules.

Thus the NMR spectrum of ethanol shows triplet for the methyl protons, quartet for the methylene protons and singlet for the hydroxyl proton.

Interpretation of NMR spectra of simple organic compounds :

The NMR spectra of the following compounds are run in $CDCl_3$ solvent.

1. Acetone

Acetone contains one sets of protons (a). This proton signal is slightly deshielded due to the carbonyl group and produced signal at the upfield. It gives a intense sharp signal at $\delta = 2.15$ in its NMR spectrum due to six equivalent protons.

Benzaldehyde :

Benzaldehyde contains three sets of protons (a, b and c) and gives three signals in its NMR as shown in the following figure.

a) Singlet, δ 9.9, 1H (-CHO protons)

b) Multiplet, δ 7.7, 2H (Two protons ortho to -CHO)

c) Triplet, δ 7.4, 3H (Three remaining protons of the ring)

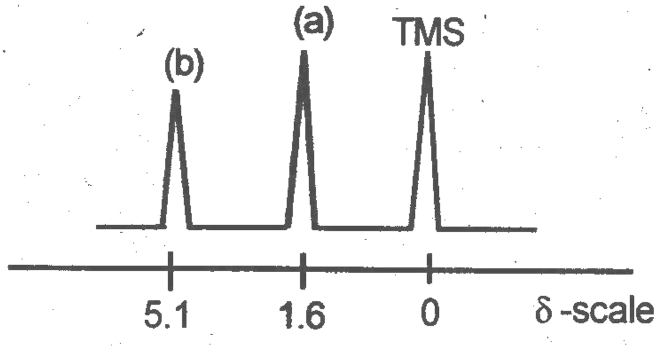
Explanation :

i) The signal of δ = 9.9 (for down field) is due to the aldehydic proton. It does not show any coupling with the neighbouring protons and gives singlet.
ii) The signal at d = 7.7 is due to the two protons ortho to the aldehydic group (b). It splits into a multiplet by the neighbouring three protons of H_c and one H_a protons. They appear at downfield due to deshielding by anistropic effect of the carbonyl group.
iii) The signal at δ = 7.4 is due to the remaining three ring protons (c). It splits into a triplet by the neighbouring two ortho Hb protons.

Mesitylene:

Mesitylene contains two sets of protons (a & b). It gives two signals in its NMR spectrum. They are,

a) Singlet, δ = 1.6, 9 protons (-3CH_3)
b) Singlet, δ = 5.1, 3 protons (benzenoid ring)



Explanation:

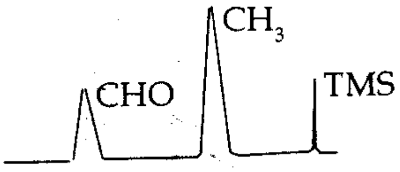
i) The signal at δ = 1.6 is due to the nine protons of the three -CH_3 groups (a).
ii) The signal at δ = 5.1 is due to the three protons of the benzenoid ring. It appears at the downfield.

Acetaldehyde

Acetaldehyde displays NMR spectrum with two peaks.

$$\underset{a}{CH_3} - \underset{b}{CHO}$$

Two peak
CH_3 (δ = 2.7 ppm)
CHO (δ = 9.5 ppm)



Check Your Progress

Fill in the blanks

1) IR spectroscopy is highly useful in detecting ....

2) NMR spectroscopy gives information about ....

3) The reference compound in NMR spectra is ....

5.9 Let us Sum up :

Spectroscopy is a technique in which the energy difference between the states are measured by determining the frequency of the electromagnetic radiation absorbed. Applications of u.v, I.R and NMR spectra are clearly explained.

5.10 Key words

U.V → Ultra Violet - electronic excitation within the molecule
I.R → Infra red - vibration of bonds and rotation of the molecule.
NMR → Nuclear magnetic resonance - change in nuclear spin orientations.

5.11 Questions for Discussion

1) Explain the different types of electronic transition.
2) Explain the following
    a) Red shift
    b) Blue shift
    c) Hyperchromic shift
    d) Hypochromic shift
3) Write a short note on chemical shift
4) Draw and explain the NMR spectrum of ethyl alcohol
5) Draw and explain the NMR spectra of the following
    a) Acetaldehyde
    b) Acetone
    c) Meritylene
    d) Benzaldehyde.

Check Your Progress : Model Answers

CYP I

1) n → π^* transition

2) u.v. spectroscopy

3) conjugation

CYP II

1) Functional Group

2) Carbon skeleton

3) TMS (Tetramethyl silane)

5.12 Suggested readings.

[1] Y.R. Sharma O.P.Vig. Elementary Organic absorption spectroscopy.