

**As Per Revised Syllabus of
Swami Ramanand Teerth Marathwada University, Nanded**

A Text Book of
Organic Chemistry
B. Sc. Third Year

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A Text Book of Organic Chemistry

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**DEDICATED TO MY
LATE MOTHER AND FATHER**

PREFACE

I happy to place in the hands of readers, A text book of Organic Chemistry for U.G Students. This book is written according to the revised syllabus [NEP-2020] prepared by Swami Ramanand Teerth Marathwada University, Nanded.

The students of U.G were facing the problems to collect the study material in organic chemistry which include in revised syllabus.

Keeping in the view the needs of the students of U.G

The effort is made to present the topics in simple and lucid language and explained the same with suitable examples, structures and figures.

The newly introduced topics in revised syllabus. Such as **Stereochemistry, Synthetic Drug and Dyes, Molecular rearrangement, Spectroscopy, Reagents and Name reaction.**

I hope that, simple and lucid explanation of the curriculum should be help to understand and will make the students perfect in organic chemistry.

I tried my level best to present a complete text book. I welcome suggestions from teachers and students for further improvement of the book.

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Semester: V

Unit : I

Stereochemistry

Introduction:

A number of compounds are known which possess the same molecular formula but different structures. Such compounds are called isomers. Since isomers have the same molecular formula, differences in their properties must be due to different modes of combination or arrangement of atoms within the molecule.

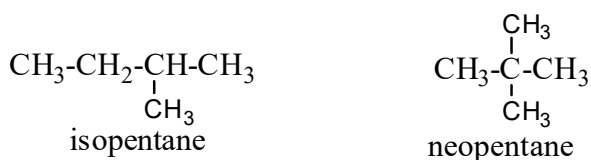
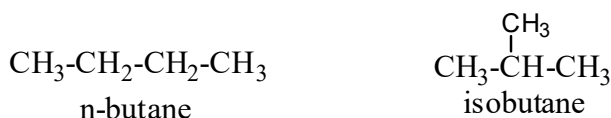
There are main two types of isomerism.

a) Structural isomerism.

b) Stereoisomerism.

a) **Structural isomerism**; when the isomerism due to difference in the arrangement of atoms within the molecule, without any reference to space, the phenomenon is called structural isomerism [structural isomers are compounds that have the same molecular formula but different structural formulas. Structural isomers are five types.

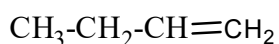
i) **Chain isomerism**; chain isomers have the same molecular formula but differ in the order in which carbon atoms are bonded to each other. For example; n-butane and iso-butane.



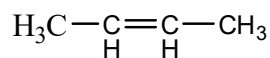
ii) **Position isomerism**; position isomers have the same molecular formula but differ in the position of a functional group on the carbon atom.

For example; 1-propanol and 2-propanol.





1butene



2-butene

- iii) **Functional isomerism**; functional isomers have the same molecular formula but different functional groups.

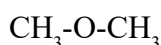
For example; acetic acid and methylformate.



Ethylalcohol

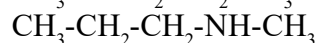
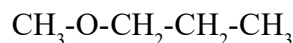
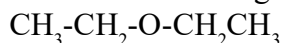


dimethyl ether



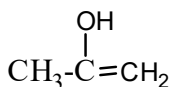
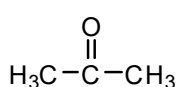
- iv) **Metamerism**; this type of isomerism is due to the unequal distribution of carbon atoms on either side of the functional group.

For example;

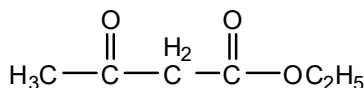


- v) **Tautomerism**: when two structural isomers are mutually interconvertible and exist in dynamic equilibrium, they are called tautomers and the phenomenon is termed tautomerism.

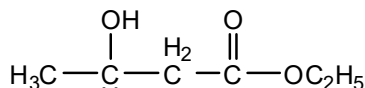
For example:



acetone



keto form



Enol form

b) Stereoisomerism:

When isomerism is caused by the different arrangement of atoms or group in space, the phenomenon is called stereoisomerism. [the stereoisomers have the same structural formula but differ in arrangement of atoms in space] stereoisomerism is of two types;

i) Configurational isomerism.

ii) Conformational isomerism.

i) Configurational isomerism..

The stereoisomers which are non-super imposable and non interconvertible by rotation around the single bonds are known as configurational isomers and the phenomenon is known as configurational isomerism.

The configurational isomerism can be interconvertible only by breaking and making bonds. These isomers may further be two types.

- a) Enantiomers; (optical isomerism): when the two isomerism are the mirror images of each other, these are known as enantiomers. This is also known as inversional isomerism.
 - b) Diastereoisomerism: when the configurational isomers are not mirror images of each other, these are known as diastereoisomers. These also include geometrical isomers.
- ii) Conformational isomerism; the stereoisomers which are non-superimposable but easily interconvertible by rotation about carbon- carbon single bonds are known as conformational isomers, conformational enantiomers. This type of isomerism is found in alkane and cycloalkanes.

Conformation of n-butane; they are rather complicated. All eclipsed conformations are equivalent in case of ethane and propane, but in case of butane, two distinct conformations are possible, one in which a methyl group is eclipsed by methyl group and the other in which the methyl group are eclipsed hydrogen.(fig:1)



Eclipsed Conformation of butane (fig.1)

Of these two eclipsed conformations, the one having larger methyl groups eclipsing(1), will naturally experience more repulsive forces than the one where a methyl group is faced with a hydrogen atom (2). Thus conformation (2) is favoured from stability standpoint.

It will be observed that, for butane two different staggered conformations are possible (fig.2) naturally



(fig.2)

In structure (1), the methyl groups are at angle of 60° to each-other. this is called Gauche conformation.

In structure(2), the methyl groups are at an angle of 180° to each other. This is called anti or trans conformation. The repulsive forces will be greater in (1) than in (2) due to proximity of the methyl groups in the former. Consequently, the conformation(2) is associated with least energy and maximum stability.

6. Optical isomerism:

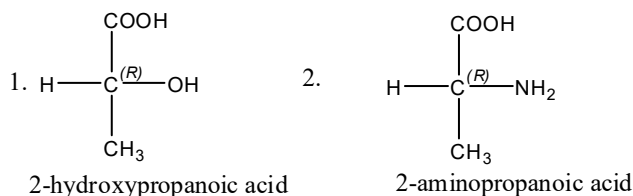
a) Concept of asymmetric carbon atom; [Chiral centre]

a hand can not be superimposed on its mirror images. If you hold your left hand up to a mirror, the mirror looks like a right hand. When we try to superimpose our hands we can not do it. Such an object which can not be super imposed on its mirror image is said to be a chiral. Where as a ball and a cube are achiral objects. Can be super imposed on their mirror images.

We can also say that object having a plane of symmetry [a plane of symmetry divides a molecule in such a way that one half is the mirror image of the other half] are achiral, where as object not having a plane of symmetry are usually chiral.

Chirality in molecule is usually due to presence of on SP^2 carbon atom with four groups attached to it. Such molecules have no plane of symmetry and exist as a pair of enantiomers. A chiral carbon is the one in which all the four substituent's are different. Such carbon atom is also referred to as asymmetric carbon atom.

For example;



Chiral [asymmetric] carbon atom is called as stereogenic centre and is indicated by asterisk.

b. Dextro and Laevo forms, Racemic mixture:-

i) plane polarized light;

According to the physical theory, an ordinary ray of light vibrates in all planes at right angles to plane of the propagation. When this light is passed through a Nicol prism, its vibrations in all planes, except one, are either rejected or absorbed and thus emergent beam vibrates only in one direction. Such type of light whose vibration occurs only in a single plane is known as plane polarized light and the phenomenon is called polarization.

ii) Optical activity and optically active compound:-

When plane polarized light is passed through certain substances or their solution, its plane of polarized light is rotated either towards right (clockwise) or towards left (anticlockwise) by a certain angle. Such substances which rotate the plane polarized light are known as optically active and the phenomenon is referred to as optical activity.

iii) Dextrorotatory:

Those substances which rotate the plane polarized light to right (clockwise) direction are called dextrorotatory, indicated by 'd' or (+).

iv) Laevo rotatory:

Those substances which rotate the plane polarized light to left (anticlockwise) direction are called laevorotatory, indicated by 'l' or (-). The extent or angle of rotation of a plane polarized light or optical activity of substance is measured in an instrument known as polarimeter.

v) Specific rotation:

The measurement of optical activity is reported in terms of specific rotation. Which is constant.

The angle of rotation of the plane of plane polarized light, α , not only depends upon the kinds of molecules, but it also varies considerably with the number of molecules that light encounters to some extent α varies with temperature, wavelength of light and with the solvent.

Quantitative measurement of the optical activity are generally reported as specific rotation ($[\alpha]$).

$$[\alpha]^{t^0} = \frac{\alpha}{l \times C}$$

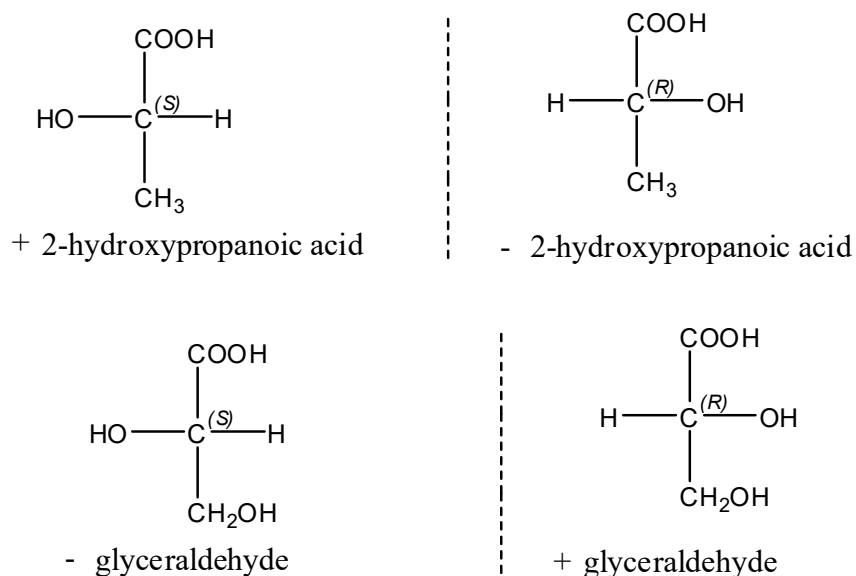
Where, α = observed rotation, t^0 = temperature, λ = wavelength of light and l = length of sample in decimeters.

Thus specific rotation may be defined as, the rotation produced by a solution of length

to centimeter (1 decimeter) and unit concentration (1 g/ml) for given wave length of light at given temperature.

vi) Enantiomerism:-

optical isomers that are mirror images are called enantiomers or enantiomorphs or optical stereoisomers or optical antipodes. For example;- in which structure (A) is mirror images of structure (B).



Enantiomers are stable, isolable compounds that differ from one another in three dimensional spatial rearrangements. Enantiomers cannot be inter-convertible under ordinary condition.

Enantiomers have the same melting point, boiling point, density, solubility, colour and reactivity towards acids and bases. They differ in the direction, in which they rotate the plane of polarized light both rotate the plane polarized light to exactly the same extent (same angle) but one rotate the plane polarized light to the right (clock wise), while other rotate the plane of left (anticlock wise).

An equimolar mixture of two enantiomers is called racemic mixture. Such mixture is optically inactive.

C. Element of symmetry:- [plane, centre and axis]

A symmetry element is a point, line or plane with respect to which one or more symmetry operations are performed. The molecule has any of the three element of symmetry ;(i) a plane of symmetry (ii) a centre of symmetry (iii) an alternating axis of symmetry. This method can be applied to the Fischer's projection formula and tetrahedral formula alike. If there is at least one symmetry element present, the molecule will not show enantiomerism.

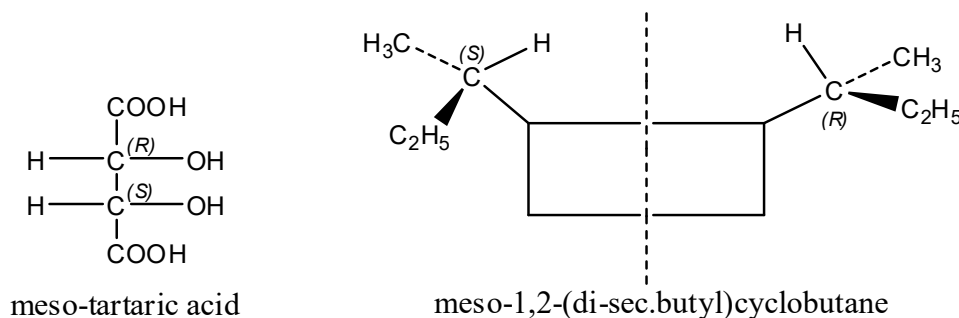
1. plane of symmetry:-

A plane of symmetry is a plane which the molecules (or an object) in to two halves which are mirror images of each other . in other words, a molecule with at least a plane of symmetry can be super imposed on its mirror images and is achiral. A molecule that does not have a plane of symmetry is usually chiral and it cannot be super imposed upon its mirror images for example;

A ball can be divided by a plane into two identical halves, it is a achiral object.

No plane can divide a hand into two identical halves, it has no plane of symmetry, it is chiral.

A plane of symmetry is an imaginary plane, which cuts the molecule into two parts, so that each part is the mirror image of the other. And the molecule possessing such plane are optically inactive and are said to be inactive.



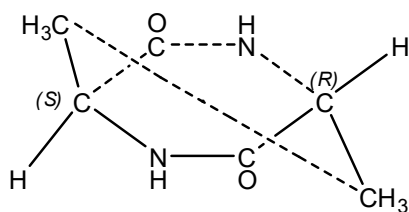
In both the above example, two asymmetric carbon atoms are presents. But they are optically inactive because the mirror plane divides both molecules into two parts, each of which is mirror image of other.

Centre of symmetry :-

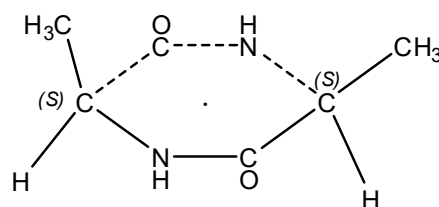
A centre of symmetry is an imaginary point within the molecule such that, if an atom or point is joined to it and the line drawn to an equal distance beyond , it meets an equivalent atom.

In other words, inversion of all atoms in the molecule through the point gives an arrangement indistinguishable from the original molecule.ex; substituted diketopiperazine contains two asymmetric carbon atoms but are still optically inactive because it having a centre of symmetry.

If a line is drawn from methyl group on carbon-1 ,to the centre of symmetry and extended beyond this centre by an equal distance, if it meets the methyl group at carbon-4 and therefore it is optically inactive , while cis-isomer is optically active because it does not contain any centre of symmetry.

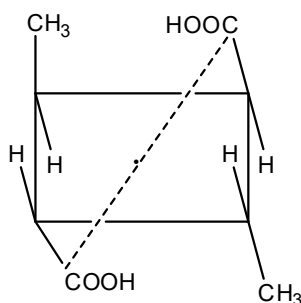


trans-1,4-dimethyl-diketopiperazine



cis-1,4-dimethyl-diketopiperazine

Example(2);-2,4-dimethyl cyclobutane-1,3-dicarboxylic acid has a centre of symmetry [centre of cyclobutane ring] and is therefore optically inactive.

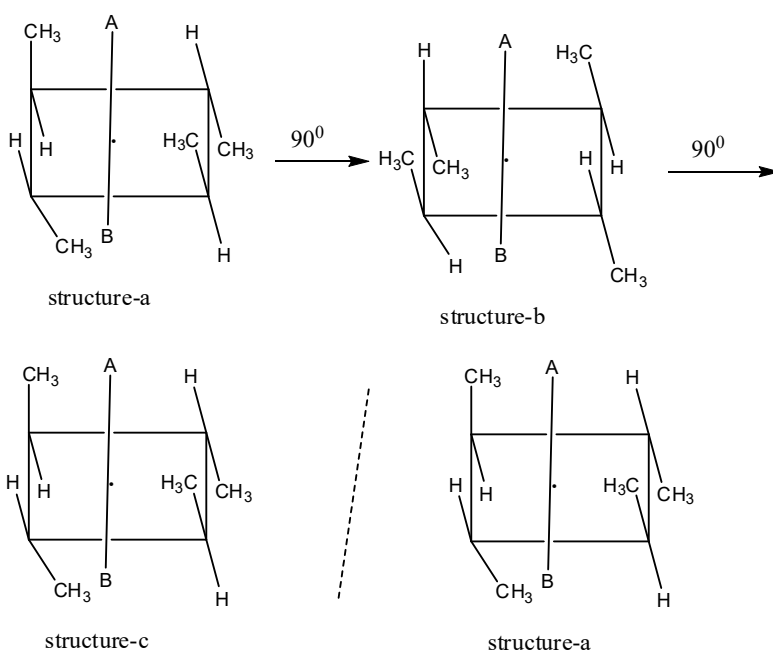


[2,4-dimethylcyclobutane-1,3-dicarboxylic acid

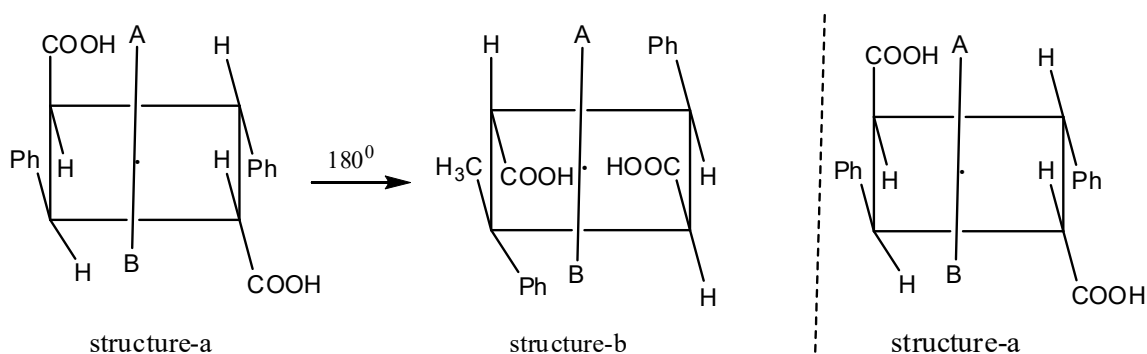
An alternating axis of smetry;

To determine whether an n-fold axis of symmetry is present, the molecule is rotated through an angle of $360^\circ/n$ about this axis followed by reflection in a plane perpendicular to axis. If then we arrive at the original molecule, it is said to have and n-fold axis of symmetry and will be optically inactive. for example : 1,2,3,4-tetramethyl cyclobutane (a) has a four fold axis of symmetry because its rotation by 90° about the axis AB (passing through the centre of the ring perpendicular to its plane) gives (b) the structure (a) is the mirror image of structure (b) by its reflection in the plane parallel to the ring.i.e. perpendicular to the axis AB.

In this case the molecule has two vertical planes of symmetry through the diagonals of the ring.

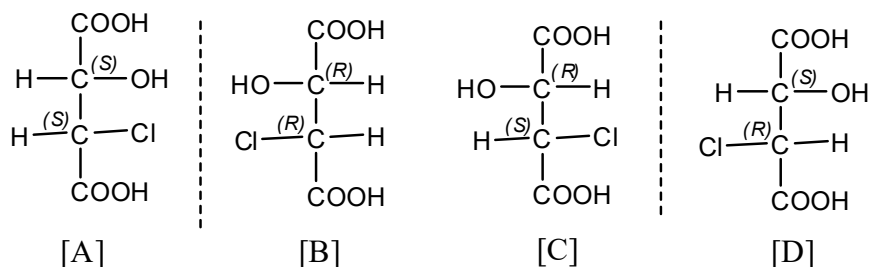


Example (2) [α -truxilic acid]



d. Concept of diastereoisomers;-

Each asymmetric carbon atom in a molecule doubles the number of theoretically possible isomers, Hence molecule with n -asymmetric carbon atom should have 2^n stereoisomers for example: 2-chloro,-3-hydroxy butane dioic acid have two asymmetric carbon atoms and hence exists in four stereoisomeric forms,i.e.as two pairs of enantiomers.



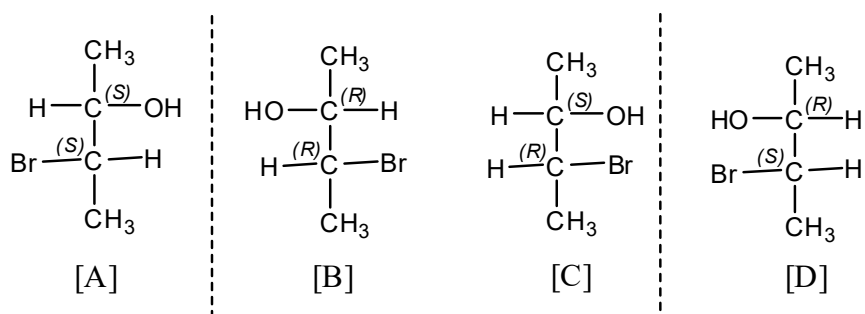
Two enantiomers (A) and (B) are mirror images of each other, and (c) is mirror images of (D).

If (A) and (B) mixed with an equal amount they give rise to racemic modification. i.e. they become optically inactive, similarly structure (C) and (D) mixed with an equal amount they give rise to racemic modification i.e. they become optically inactive.

When structure (A) is compared with structure (C) and (D) or structure (B) is compared with structure (C) and (D) they are optically active but not mirror images such stereoisomers are referred to as diastereoisomers of stereoisomers (C) and (D).

Diastereoisomers have different properties and similar but not identical chemical properties having different boiling points, melting points, Refractive indices, solubilities, densities, molecular shapes and polarity. They can be separated by fractional distillation, fractional crystallization and by chromatography.

Example (2): 3-bromobutan-2-ol

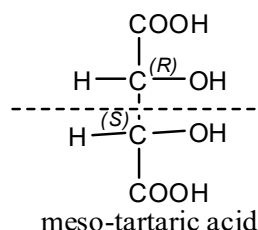
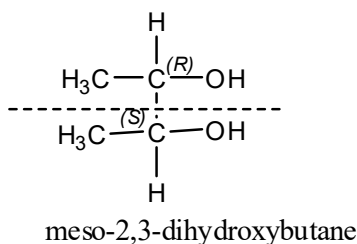


Stereoisomers (A) and (B) are enantiomers, similarly stereoisomers (C) and (D) are enantiomers. But stereoisomer (A) with stereoisomers (C) and (D) are not mirror images but optically active hence they are called diastereoisomers. Similarly stereoisomers (B) with stereoisomers (C) and (D) are not mirror images but optically active hence they are called diastereoisomers.

Properties of meso compounds:-

a compound with two or more asymmetric carbon atoms but also having a plane of symmetry (a mirror plane) is called the meso compound. structure (A) and (B) shows two

meso compounds these molecules have plane of symmetry deviding them at centre between the two asymmetry carbon in each. One-half part molecule is exactly coinside with other part. i.e. both have plane of symmetry and molecules becomes optically inactive, they cannot rotate the plane polarized light.



e) Racemic modification :-[Racemisation]

an equimolar mixture at dextro-rotatory (+) substance and Laevo rotator (-) substance is called racemic mixture.

Conversion of an optically active compound into racemic mixture is called racemisation.

A mixture of equal amount of enantiomers is called a racemic modification. racemic modification will be optically inactive, because the rotation caused by one half of the mixture is exactly cancelled by the opposite rotation displayed by the mixture is denoted by the prefix ($\pm$). For example : ($\pm$) lactic acid, ($\pm$) 2-butanol.

Racemisation can be accomplished by means of heat, light, or by conversion of the isomer into an optically inactive intermediate, which reverts to the racemic mixture.

f) Resolution [Concept]:-

The separation of a racemic mixture into its two optically active components [(+) and (-) isomers] is known as resolution.

Two enantiomers in a racemic mixture have identical chemical and physical properties except towards optically active reagents; they cannot be separated by the usual technique such as fractional distillation, fractional crystallization, chromatography. Therefore, we have to adopt special methods for the separation of the enantiomers in a racemic modification. This process is called resolution some of these methods described below.

(a) Mechanical seperation :-

This is classic method adopted by Pasteur in separating the enantiomers of ammonium tartrate.

A racemic mixture on crystallization may give a two types of crystals, one said being mirror image of the other. Two sets are separated by hand picking with the help of a pair of tweezers and a lens. This method is most painstaking and is there fore and applicable only to those cases, which give well defined crystals that can be of enantiomers .

(b) Biochemical method;

When certain bacteria or moulds are added to a solution of a racemic mixture they brings about the decomposition of one of the optically active forms more rapidly than the other. For ex; penicillium glaucum decomposes (+) tartaric acid more rapidly than the (-) isomer so that the latter can be obtained from the residue after treatment with the mould.

c) Chemical method:

In this method racemic modification is reacted upon with an optically active reagent to give a pair of non- identical derivatives are known as diastereoisomers. since diastereoisomers are not mirror images of each other they will differ in their physical properties and hence it is possible to separate physical means such as fractional distillation, crystallization etc. the pure diastereomers are then decomposed each into the corresponding enantiomers and the originally optically active reagent, which them separated.

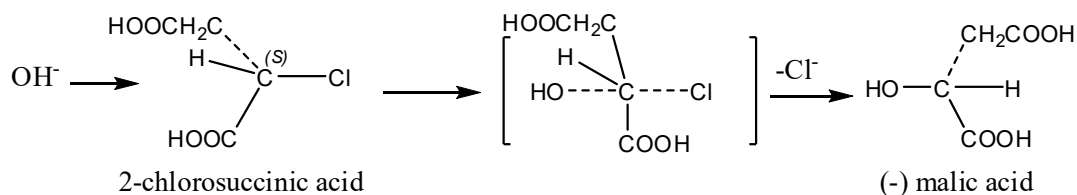
For ex; when ($\pm$) tartaric acid treated with (-) chinchonidine gives a mixture of two diastereomeric salts; (+) tartarate of (-) chinchonidine and (-) tartarate of (-) chinchonidine, which are diastereomers and have widely different solubility. The latter separate out first when a mixture is subjected to fractional crystallization. After separation and purification of two diastereomeric state, each is treated with dilute sulphuric acid, which decomposes the salt into the (+) or (-) tartaric acid.

9. Walden Inversion:-

When a group attached to an asymmetric carbon atom is replaced, the configuration of the new compound may be opposite to that of the original. That is, the product is enantiomers (mirror image) of the expected compounds. This phenomenon is known as Walden inversion.

Mechanism of Walden inversion involves three steps;

- Approach of the attacking group from the side of the molecule opposite to the position of the group which is later replaced.
- formation of an intermediate transition state, in which three groups and the asymmetric carbon lie in one plane.
- separation of group being replaced. This change is analogous to an umbrella being blown inside out. The conversion of (+) chlorosuccinic acid into (-) malic acid is an example of Walden inversion.



h. Relative Configuration and absolute Configuration:-

Specification of Configuration;

The arrangement of atoms or groups that characterizes a particular stereoisomer is called its configuration.

Two systems are used to designate the configuration of a molecule.

1. Relative configuration.
2. Absolute configuration.

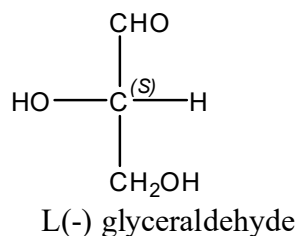
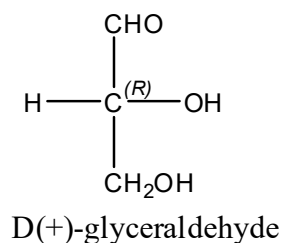
1. Relative configuration: [D, L – Notation]

Before 1951, there was no method for determining the absolute configuration (actual arrangement of atoms in space) of a compound and hence the configuration of all

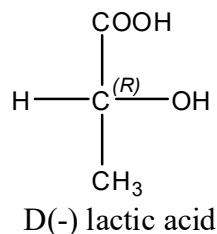
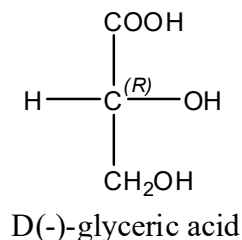
The compounds were studied with respect to glyceraldehydes.

The configuration of a compound with reference to arbitrary assigned configuration of reference substance is known as its relative configuration.

- i) The configuration of which was taken as an arbitrary standard (+) glyceraldehydes, having –OH group on the right and hydrogen atom on the left, the –CHO and CH₂OH groups being at the top and bottom respectively, was arbitrarily given the configurational symbol D. the mirror image compound (-) glyceraldehydes, in which the –OH group is on left and hydrogen atom on the right was given the configuration, L



- ii) For hydroxyl acid, draw the –OH group at the top. (-) glyceric acid and (-) lactic acid have the same absolute configuration.



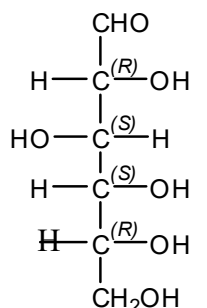
It must clearly understand that in designating an optically active compound, the sign in parentheses refers only to the direction of rotation, while capital letters D and L denote

the configurational relationship.

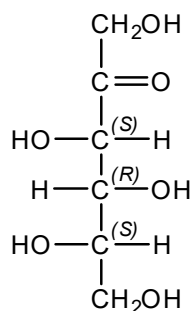
Another point requiring attention is that, an optically active substances having D configuration may yet be laevorotatory, while the substance having L configuration may be dextrorotatory.

For compound containing several chiral carbon atoms, the configuration at one centre is related to glyceraldehydes and the configurations at carbon atoms are determined relative to the first.

For ex: in glucose, this carbon atom is C-5 which is next to the $-\text{CH}_2\text{OH}$ group i.e. the highest numbered chiral carbon atom. Since naturally occurring glucose was assumed to have the $-\text{OH}$ group on this carbon atom projecting at right hand side, it belongs to the D-series. Of compounds and hence designated D-glucose.

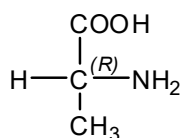


D(+)-glucose

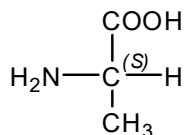


D(-)-fructose

3. Amino acid having configuration with $-\text{NH}_2$ group.



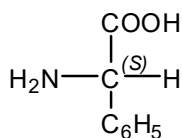
D(-)-alanine



L(+)-alanine

2-aminopropanoic acid

4. phenylalanine ;



L(-)-phenylalanine

2. Absolute Configuration: [R and S system of Nomenclature]

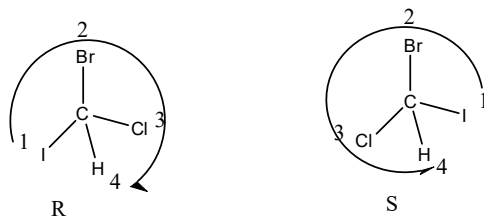
AS D and L system for specification of configuration around a chiral carbon was not found to be suitable for molecules not related to particular glyceraldehydes, another system of nomenclature called the Cahn-Ingold-Prelog system, was developed.

Cahn-Ingold and V. Prelog proposed a scheme of representation of optical isomers on paper by using prefix 'R' derived from Greek 'Rectus' and the prefix 'S' DERIVED FROM Greek 'Sinister'

Two steps are involved as follows;

1. By using sequence rule, priority order is given to the four different atoms attached to chiral carbon atom. Priority order can be depends upon atomic number. An atom with higher atomic number gets higher priority..

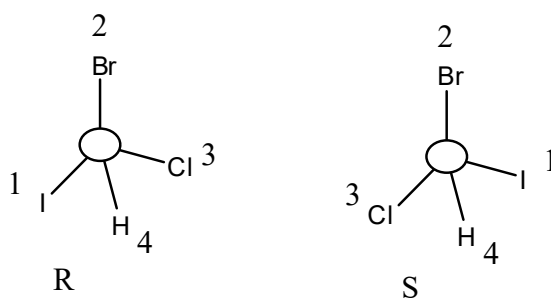
For example; in bromo- chloro-iodomethane.



The sequence priority is; I, Br, Cl and H.

2. The molecule is next visualized in such a that, the group of lowest priority is directed away from us, the arrangement of the remaining group is then observed to give configuration.

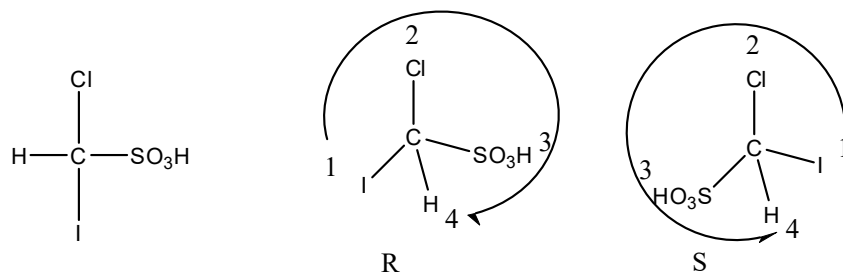
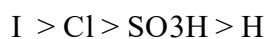
If proceeding from the group of highest priority to priority of second and then to priority to third, then our eye travel in clock-wise direction then configuration 'R'. if in a anticlockwise direction then configuration 'S'.



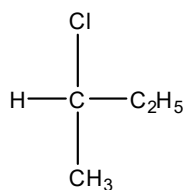
Sequence Rule:-

1. When four different atoms attached to a chiral carbon atom, priority depends upon atomic number. Atom with higher atomic number getting higher priority.

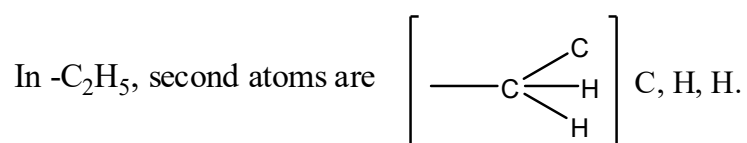
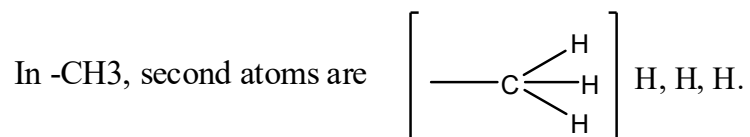
If two atoms are isotopes of same elements, atom of higher mass number has higher priority.
For ex; in chloro, iodo, methanesulphonic acid. Sequence priority order is.



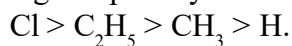
2. If two atoms, attached to chiral carbon atom are same, rule I can not decide the priority.
For ex; 2-chlorobutane.

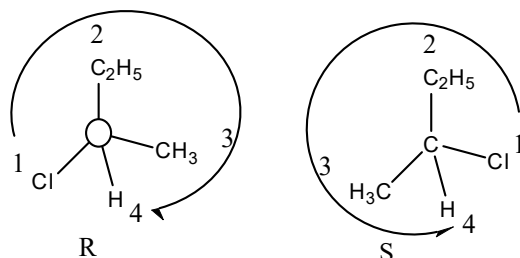


The relative priority of CH_3 and C_2H_5 is decided as.

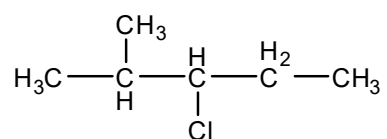


Since, second carbon has highest atomic number than hydrogen, therefore, C_2H_5 has highest priority than $-\text{CH}_3$. Hence, priority order is.



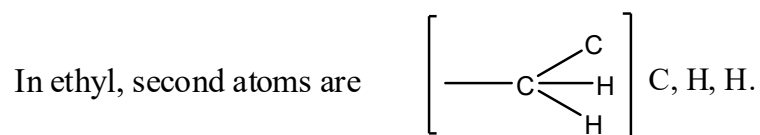
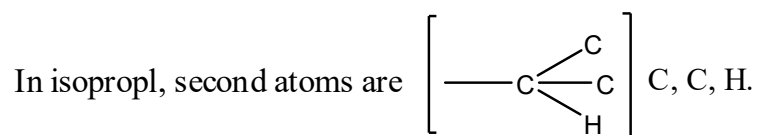


Similarly, in 3-chloro-2-methylpentane.

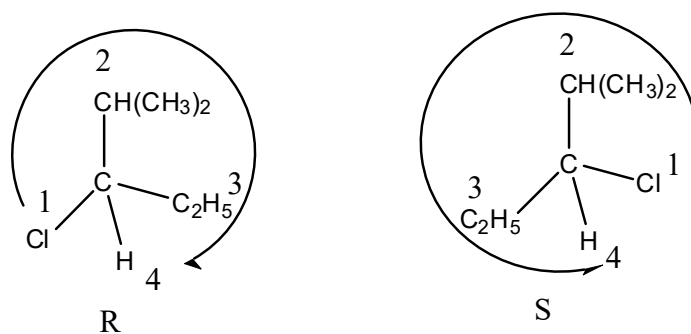


Now, in isopropyl group, second atoms are - C, C, H.

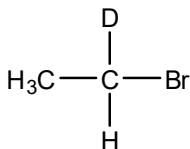
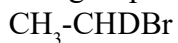
In ethyl group second atoms are - C, H, and H.



In which third carbon atom having higher atomic number than H. therefore, isopropyl group having higher priority than ethyl group.

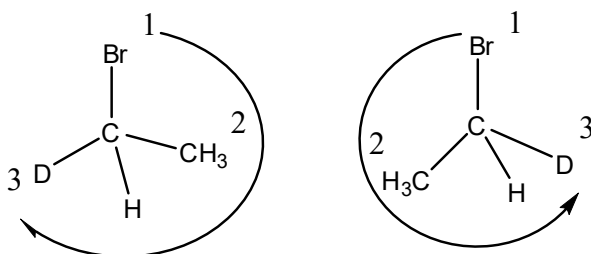


Rule III. If two atoms are isotopes of the same elements. The atom of higher mass number gets the higher priority ex; in á-deuteroethyl bromide.

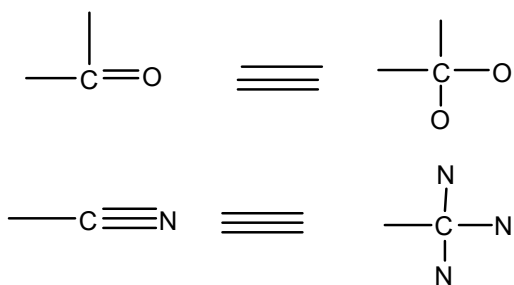


The sequence priority is; $\text{Br} > \text{CH}_3 > \text{D} > \text{H}$.

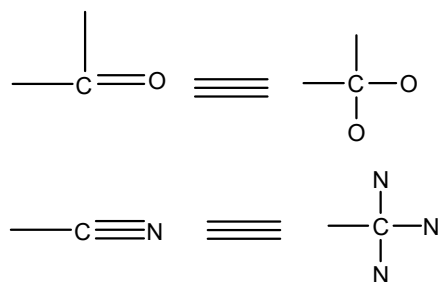
In this example, both H and D having same atomic number but different mass numbers, therefore the atom which having highest mass number gets highest priority. And hence R and S configuration can be represented as.



Rule (iv): if a molecule contains groups with multiple bonds (a double or triple bond) then for the purpose of determining purity, both atoms of that groups are considered to be doubly bonded or triply bonded. Ex;



For example:- in glyceraldehydes:

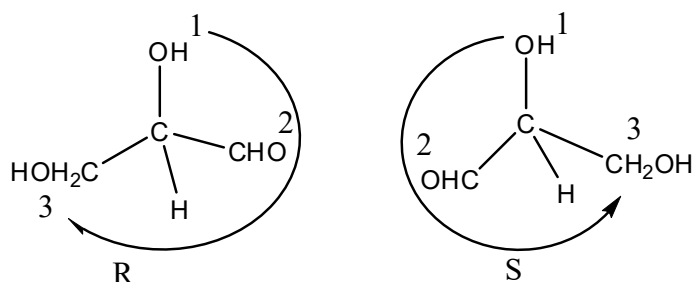


And hence, in -CHO groups second atoms are H, O, and O.

In, $\text{CH}_2\text{-OH}$ group is equivalent to $\begin{array}{c} \text{H} \\ | \\ \text{---C---H} \\ | \\ \text{O} \end{array}$

And hence second atoms are H, H, and O. sequence priority in glyceraldehydes is $\text{OH} > \text{CHO} > \text{CH}_2\text{OH} > \text{H}$.

Hence, R and S configuration of glyceraldehydes can be represented as

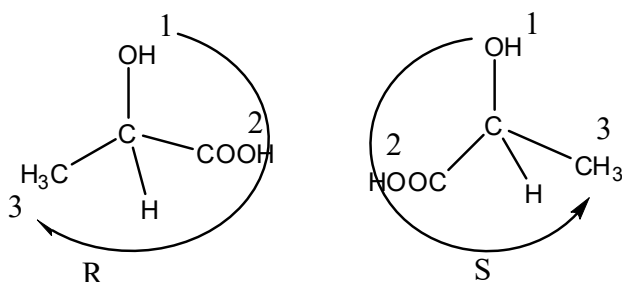


Ex: (2) in Lactic acid. $\text{CH}_3\text{.CH(OH).COOH}$.



i.e. second atom in -COOH groups are O, O, and O and in CH_3 groups H, H, and H. Hence -COOH group gets higher priority than -CH_3 . Sequence priority in lactic acid becomes.

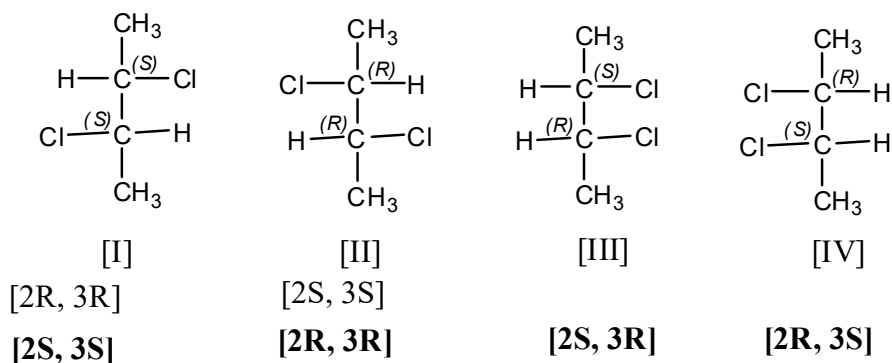
$\text{OH} > \text{COOH} > \text{CH}_3 > \text{H}$.



Optical isomerism exhibited by compounds containing two chiral centers:-

2,3-dichlorobutane contains two chiral centers (carbon-2 and 3). these two chiral centers occupy equivalent position along the carbon chain. Optical stereoisomers exhibited by

2,3-dichlorobutane in the form of two dimensional. Fischer projection formula can be represented as follows.



In optical stereoisomer (I) form, both chiral centre exhibit 2R,3R configuration, while in stereoisomer (D) form, both the chiral centre exhibit 2S,3S.

Both, I and II stereoisomers are mirror images of each other and non-super imposable. Hence, I and II forms are optically active enantiomers.

In III and IV stereoisomers both chiral centers possess opposite configuration. (in III 2S, 3R and in IV 2R,3S)

III form is super imposable with its mirror images IV form, moreover, both III and IV form possess plane of symmetry. Hence, these forms become achiral molecules and they do not exhibit optical activity. I.e. they are optically inactive.

Molecule that has chiral centre but it itself is achiral, is called as mesoform.

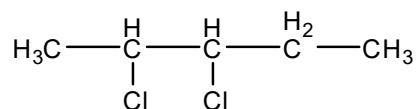
Note: [in Fischer projection formula, when atom or group of lower priority (e.g.) is on the horizontal line, the configuration is opposite to the configuration exhibited by chiral centre is considered.

Ex: in stereoisomer (I), arrows indicated R, R configuration for both chiral centers but they are considered as S, S.

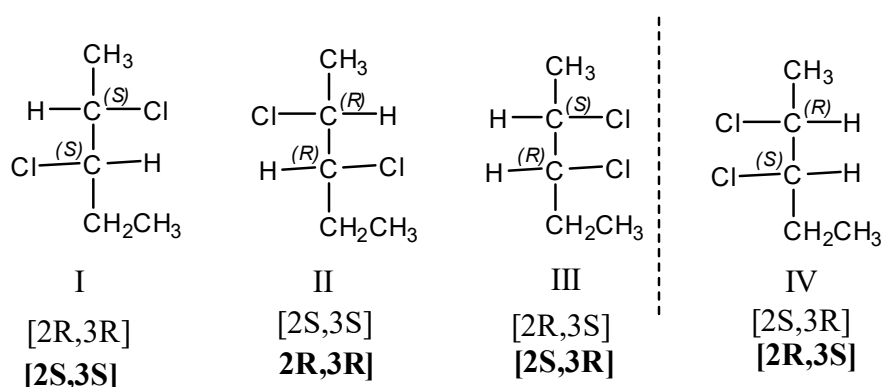
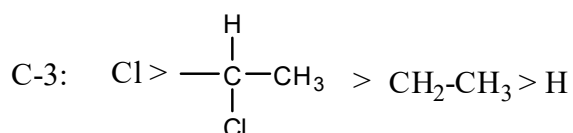
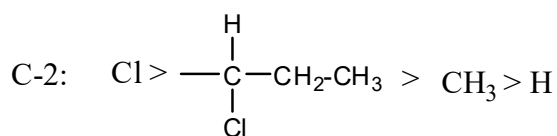
Similarly, in (II) form, both chiral centres represent R, R configurations.

[When atom or group of lowest priority (e.g. H) in Fischer structure is on the vertical line, no change in configuration is made].

Similarly, stereoisomers of 2, 3-dichloropentane.



Sequence priority order is:



Stereoisomer (I) [2S, 3S] and (II) [2R, 3R] are mirror images of each other and non-super imposable, therefore they are enantiomers they don't possess plane of symmetry, Hence they are optically active.

Stereoisomer (III) and (IV) are also mirror images of each other and non-super imposable. Therefore they are enantiomers. Two chiral centers have different groups. They do not possess plane of symmetry. Hence they are optically active are (II) [2S, 3R] and [2R, 3S].

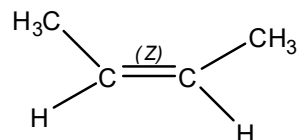
Geometrical Isomerism:-

Geometrical isomerism, also known as cis-trans isomerism, is a consequence of the spatial geometry associated with the double-bond which restricts rotation about it.

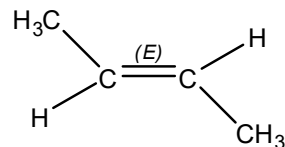
In alkenes, the carbon atoms of the carbon-carbon double bonds are sp^2 hybridized. The carbon-carbon double bond consists of a σ -bond and π -bond. The σ -bond is formed by the overlap of sp^2 hybrid orbital. The π -bond is formed by the overlap p-orbitals. The presence of π -bond locks the molecule in one position. The two carbon atoms of the $\text{C}=\text{C}$ bonds and four atoms that are attached to them lie in one plane and their positions in space are fixed. Rotation around the $\text{C}=\text{C}$ bond is not possible because rotation would break the π -bond.

This restriction of rotation about the carbon-carbon double bond is responsible for the geometrical isomerism in alkenes.

For example; 2-butene exist in two spatial arrangements.



cis-2-butene



trans-2-butene

These two compounds are referred to as geometrical isomers and are distinguished from each other by the terms cis and trans.

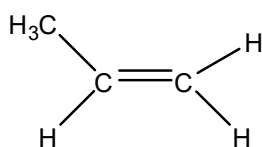
The cis isomer is one in which two similar groups are on the same side of the double bonds.

The trans isomer is that in which two similar groups are on the opposite sides of the double bonds. [Geometrical isomers are stereoisomer's, because they have same structural formula but different spatial arrangements of atoms.]

The conversion of cis-isomer into trans-isomer or vice versa is possible only if either isomer is heated to a high temperature or absorb light. The heat supplies the energy (about 62 kcal / mole) to break the π - bond so that rotation about σ -bond becomes possible. Upon cooling, the reformation of the π -bond can take place. In two ways giving mixture of trans-2-butene and cis-2-butene.

The trans isomers are more stable than cis-isomer. Due to which, in the cis isomer, the bulky groups are on the same side of the double bond. The steric repulsion of the groups make the cis-isomer less stable than trans isomer in which the bulky groups are far appears. The geometrical isomers have different physical and chemical properties.

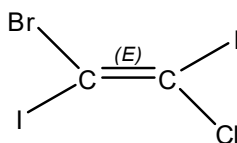
All alkenes donot shows the geometrical isomerism. For ex; propene: because one of the double bonded carbon has two identical groups/atoms (H-atoms).



Propene

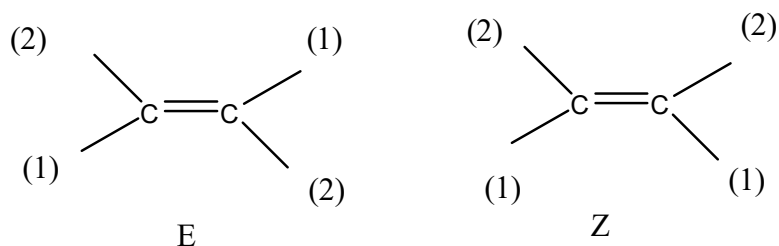
E and Z system of Nomenclature:

It is easy to name the geometrical isomers, if the two groups are identical but when all four groups are different, and then the nomenclature of geometrical isomers becomes difficult. For example; in which the two carbon atoms of a double bond are attached with four different halogens.



It is difficult to name such a compounds either cis or trans isomer. To eliminate this confusion a more general system for designating configuration about a double bond has been adopted. A new system of nomenclature of geometrical isomers called E and Z nomenclature system and this is based on a priority system originally developed by Cahn, Ingold and Prelog for use with optically active substances.

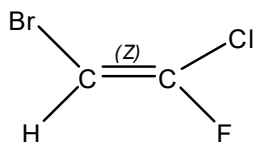
E- Label has been derived from the German word entgegen, meaning opposite, in which the higher priority atoms or groups are on the opposite side of the double bonds. Z-label has been derived from the German word Zusammen, meaning follow together, in which the higher priority atoms or groups are on the same side of the double bond.



In E-Z nomenclature system, configuration is assigned according to the following sequence rule.

Rule;1.

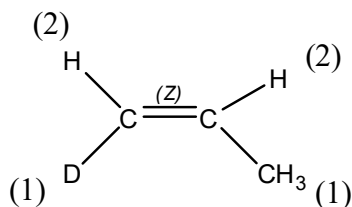
When two different atoms or groups are attached to two double bonded carbon atoms. Then the sequence of priority of atoms or groups at each carbon atom is decided on the basis of atomic numbers for example; 1-bromo-2-chloro-2-fluoroethene.



Sequence priority of atoms at carbon-1 is; Br > H

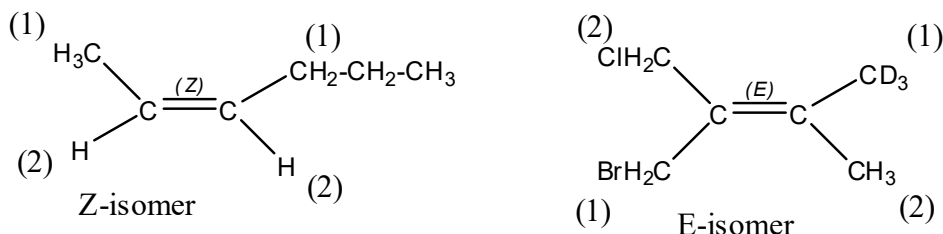
And at carbon-2 is ; Cl > F.

Rule;2. If isotopes of the same elements are attached, the isotopes with higher mass number will have a higher priority.



Sequence priority of atoms at carbon-1 is; D > H

If priority cannot be decided by this rule, it is then determined by comparing the next atoms in the groups, and so on. For example;



$$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}$$
 is considered equivalent to

$$\text{R}-\overset{\text{O}}{\underset{\text{O}}{\mid}}{\text{C}}-\text{R}$$

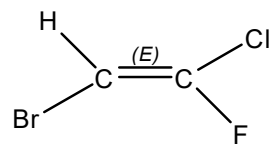
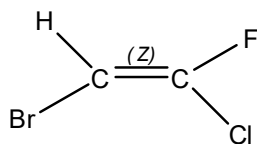
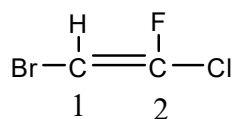
$$\text{R}-\text{C}\equiv\text{N}$$
 is considered equivalent to

$$\text{R}-\overset{\text{N}}{\underset{\text{N}}{\mid}}{\text{C}}-\text{N}$$

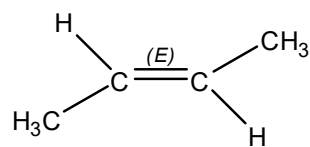
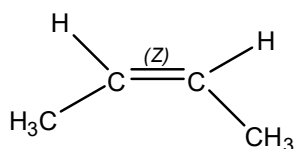
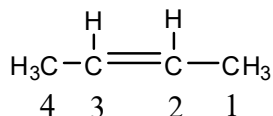
-C. (CH₃)₃, -CH (CH₃)₂ -CH₂.CH₃ -CH₃
-COOCH₃, -COOH, -CONH₂, -COCH₃, -CHO.

The geometrical isomer in which two “a” atoms or groups are on the same side, is designated as “Z” and the geometrical isomer in which two “a” atoms or groups are on the opposite side is designated as “E”.

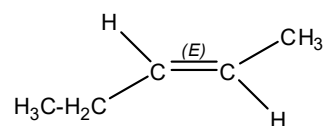
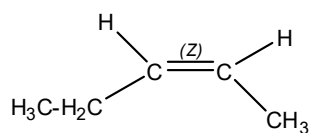
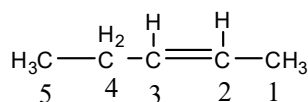
1. 1-bromo-2-chloro-2-fluoroethene.



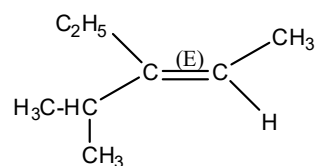
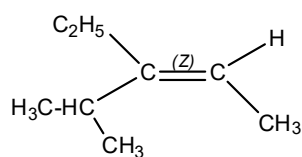
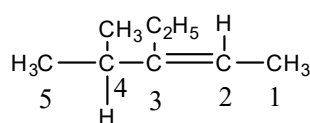
2. 2-butene.



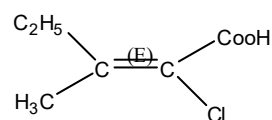
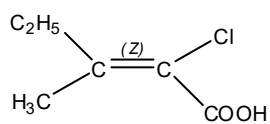
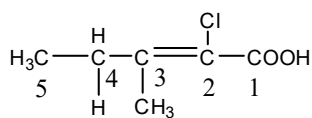
3. 2-pentene;



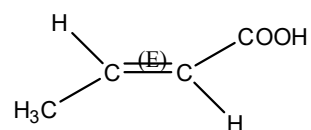
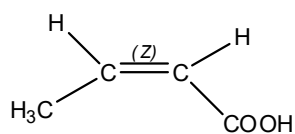
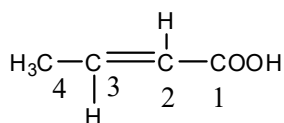
4. 3-ethyl-4-methyl-2-pentene:



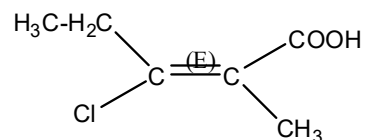
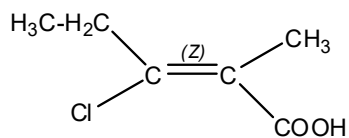
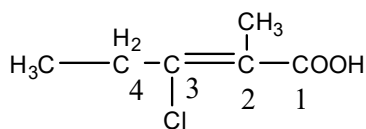
5. 2-chloro-3-methyl-2-pentenoic acid:



6. Crotonic acid:—



7. 3-chloro-2-methyl-2-pentenoic acid:

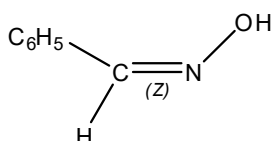
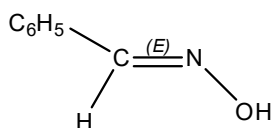


Rule No.4:

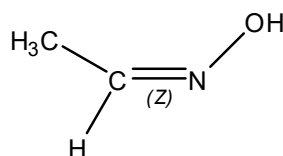
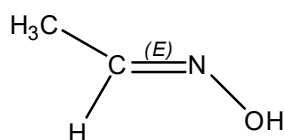
If in a compound, one of the double bonded atom is not having any substituent, then while deciding priority that vacant position is considered to have an atomic number zero.

In benzaldoxime at nitrogen atom, there is only -OH group and another position is vacant, Hence -OH group is designated “a” and vacant position as “b” at double bonded carbon atom, C₆H₅ IS “a” and H is “b”. Therefore, E and Z from benzaldoxime can be represented as,

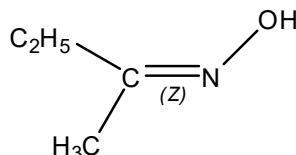
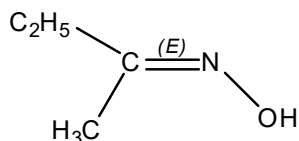
1. Benzaldoxime;



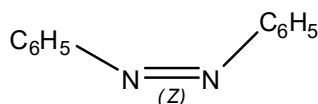
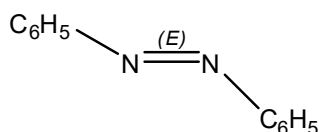
2. Acetaldoxime:



3. ETHYL-METHYLKETOXIME;



4. AZOBENZENE;



In nomenclature, the prefix ‘syn’ and ‘anti’ are adopted instead of “cis and trans”. In the syn-oxime, the hydroxyl group on nitrogen and hydrogen or first named of the two groups on the carbon atom are on the same side, and in the anti- isomer they are on opposite sides.

5. Geometrical Isomerism:-

Geometrical isomerism, also known as cis-trans isomerism, is a consequence of the spatial geometry associated with the double-bond which restricts rotation about it.

In alkenes, the carbon atoms of the carbon-carbon double bonds are SP² hybridized. The carbon-carbon double bond consist of a σ-bond and π-bond. The σ-bond is formed

by the overlap of sp^2 hybrid orbital. The π -bond is formed by the overlap p-orbitals. The presence of π -bond locks the molecule in one position. The two carbon atoms of the $C=C$ bonds and four atoms that are attached to them lie in one plane and their positions in space are fixed. Rotation around the $C=C$ bond is not possible because rotation would break the π -bond.

This restriction of rotation about the carbon-carbon double bond is responsible for the geometrical isomerism in alkenes.

For example; 2-butene exist in two spatial arrangements.

These two compounds are referred to as geometrical isomers and are distinguished from each other by the terms cis and trans.

The cis isomer is one in which two similar groups are on the same side of the double bonds.

The trans isomer is that in which two similar groups are on the opposite sides of the double bonds. [Geometrical isomers are stereoisomer's, because they have same structural formula but different spatial arrangements of atoms.]

The conversion of cis-isomer into trans-isomer or vice versa is possible only if either isomer is heated to a high temperature or absorb light. The heat supplies the energy (about 62 kcal / mole) to break the π - bond so that rotation about σ -bond becomes possible. Upon cooling, the reformation of the π -bond can take place. In two ways giving mixture of trans-2-butene and cis-2-butene.

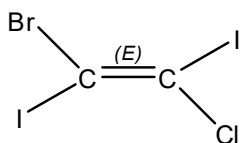
The trans isomers are more stable than cis-isomer. Due to which, in the cis isomer, the bulky groups are on the same side of the double bond. The steric repulsion of the groups make the cis-isomer less stable than trans isomer in which the bulky groups are far appears.

The geometrical isomers have different physical and chemical properties.

All alkenes don't show the geometrical isomerism. For ex; propene: because one of the double bonded carbon has two identical groups/atoms (H-atoms).

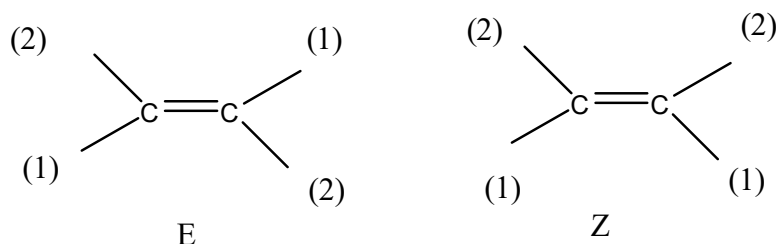
E and Z system of Nomenclature:

It is easy to name the geometrical isomers, if the two groups are identical but when all four groups are different, and then the nomenclature of geometrical isomers becomes difficult. For example; in which the two carbon atoms of a double bond are attached with four different halogens.



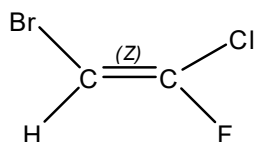
It is difficult to name such a compound either cis or trans isomer. To eliminate this confusion a more general system for designating configuration about a double bond has been adopted. A new system of nomenclature of geometrical isomers called E and Z

E- Label has been derived from the German word entgegen, meaning opposite, in which the higher priority atoms or groups are on the opposite side of the double bonds. Z-label has been derived from the German word Zusammen, meaning follow together, in which the higher priority atoms or groups are on the same side of the double bond.



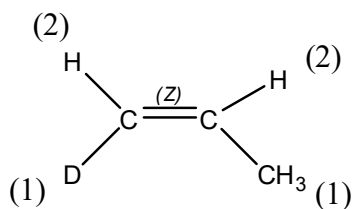
Rule;1.

When two different atoms or groups are attached to two double bonded carbon atoms. Then the sequence of priority of atoms or groups at each carbon atom is decided on the basis of atomic numbers for example; 1-bromo-2-chloro-2-fluoroethene.



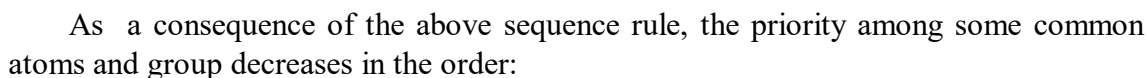
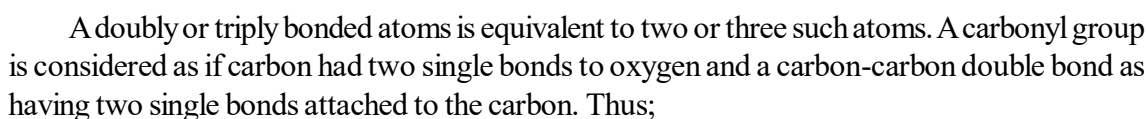
And at carbon-2 is ; $\text{Cl} > \text{F}$.

Rule;2. If isotopes of the same elements are attached, the isotopes with higher mass number will have a higher priority.



And at carbon-2 is ; $\text{CH}_3 > \text{H}$.

If priority cannot be decided by this rule, it is then determined by comparing the next atoms in the groups, and so on. For example;



-C. (CH₃)₃, -CH (CH₃)₂ -CH₂.CH₃ -CH₃
-COOCH₃, -COOH, -CONH₂, -COCH₃, -CHO.

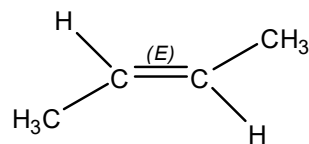
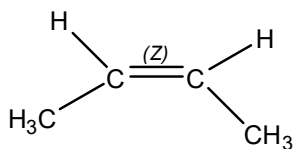
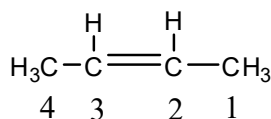
Rule:3: Let us designate atoms or groups with higher atomic number at each double bonded carbon atom as “a” and atoms or groups with lower atomic number at double bonded carbon atom as “b”.

The geometrical isomer in which two “a” atoms or groups are on the same side, is designated as “Z” and the geometrical isomer in which two “a” atoms or groups are on the opposite side is designated as “E”.

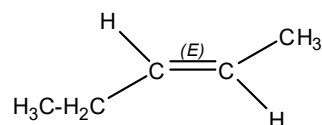
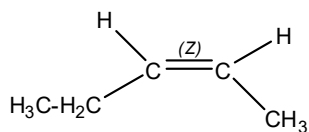
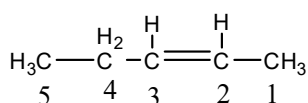
1. 1-bromo-2-chloro-2-fluoroethene.



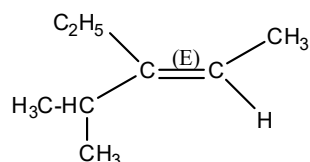
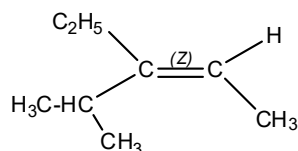
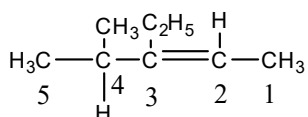
2. 2-butene.



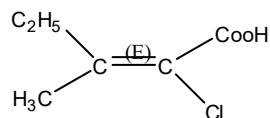
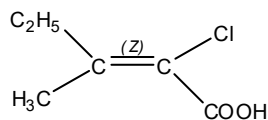
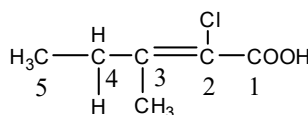
3. 2-pentene;



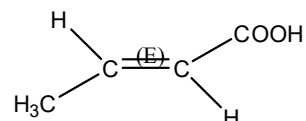
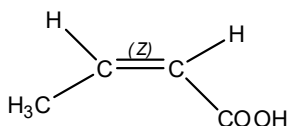
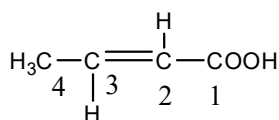
4. 3-ethyl-4-methyl-2-pentene:



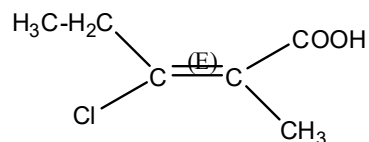
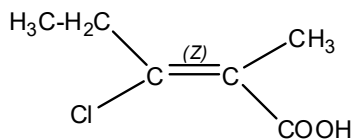
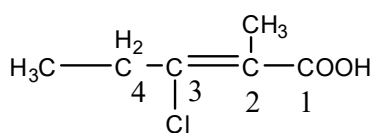
5. 2-chloro-3-methyl-2-pentenoic acid:



6. Crotonic acid:—



7. 3-chloro-2-methyl-2-pentenoic acid:



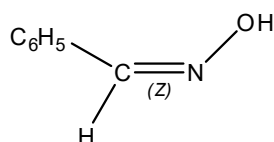
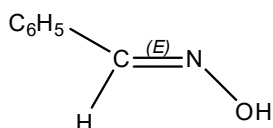
Rule No.4:

If in a compound, one of the double bonded atom is not having any substituent, then while deciding priority that vacant position is considered to have an atomic number zero.

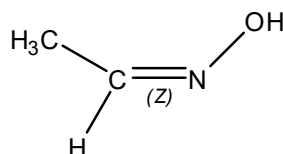
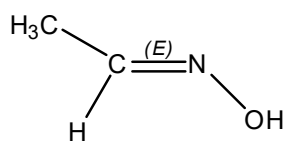
In benzaldoxime at nitrogen atom, there is only -OH group and another position is

vacant, Hence –OH group is designated “a” and vacant position as “b” at double bonded carbon atom, C₆H₅ IS “a” and H is “b”. Therefore, E and Z from benzaldoxime can be represented as,

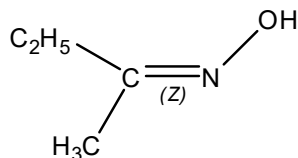
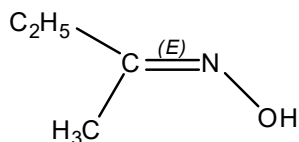
1. Benzaldoxime;



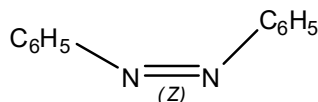
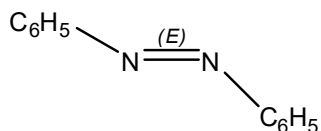
2. Acetaldoxime:



3. ETHYL-METHYLKETOXIME;



4. AZOBENZENE;



In nomenclature, the prefix ‘syn’ and ‘anti’ are adopted instead of “cis and trans”. In the syn-oxime, the hydroxyl group on nitrogen and hydrogen or first named of the two groups on the carbon atom are on the same side, and in the anti- isomer they are on opposite sides.

Question bank;

Q;1. Define the following terms.

- | | |
|-------------------------|-------------------------|
| a) isomerism | b) structural isomerism |
| c) chain isomerism | d) position isomerism |
| e) functional isomerism | f) metamerism |
| g) tautomerism. | |

Q; 2. Explain the following terms;

- a) Configurational isomerism
- b) conformational isomerism.

Q; 3. define the term Geometrical isomerism with suitable example.

Q;4. Give the E and Z nomenclature of the following compounds.

- | | |
|---------------------------------------|-----------------------------------|
| a) 2-butene | b) 1-bromo-2-chloro-2fluoroethene |
| c) 2-pentene | d) 3-ethyl-4-methyl-2-pentene |
| e) 2-chloro-3-methyl-2-pentenoic acid | f) crotonic acid |
| g) 3-chloro-2-methyl-2-pentenoic acid | h) benzaldoxime |
| j) acetaldoxime | k) ethyl methyl ketoxime |
| l) azobenzene. | |

Q;5. Explain the term concept of asymmetric carbon atom.

Q;6. Define the following terms

- | | |
|-------------------------------------|-----------------------|
| a) plane polarized light | b) optical activity |
| c) dextro and laevo rotatory. | d) enantiomerism |
| e) plane of symmetry | f) centre of symmetry |
| g) an alternating axis of symmetry. | |

Q;7. Explain the term Concept of diastereoisomerism, resolution, mesocompounds, racemic modification and Walden inversion with suitable example.

Q;8. Give the R and S nomenclature of the following compounds.

- | | |
|----------------------------------|--------------------------------------|
| a) bromo-chloro-iodomethane | b) chloro-iodomethane sulphonic acid |
| c) 2-chloroutane | d) 3-chloro-2-methylpentane |
| e) α -deuteroethylbromide | f) glyceraldehydes |
| g) lactic acid | h) 2,3-dichlorobutane |
| i) 2,3-dichloropentane | |

A) Functional drugs:

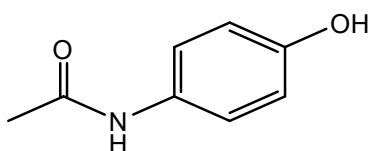
functional drugs are types of drugs which stimulate or depress the various functions of the body to get relief without curing disease.

It includes Antipyretics, Analgesics, Anesthetic, Antifungal, Antidiabetics, Anti inflammatory, Sedatives, Hypnotics and Tranquilizers.

1) **Antipyretics:** Antipyretics are those drugs which are responsible for lowering the temperature of a feverish organism to normal body temperature but it has no effect on normal body temperature. Such drugs are called as Antipyretics.

Antipyretics drugs were also found to have analgesics properties.

For ex. Paracetamol



paracetamol

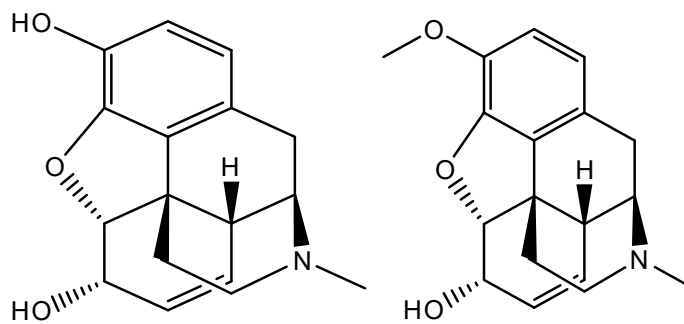
2) **Analgesics:** Analgesics is a type of drug which is used to relieve the pain without loss of consciousness.

Antipyretics are found to have analgesics property because of the analgesics action on CNS there is decrease in the sensation of pain.

On the basis of narcosis analgesic are classifieds two groups.

a) **Narcotics:** they produce analgesia and sleep, because of high dose of narcotics it causes unconsciousness.

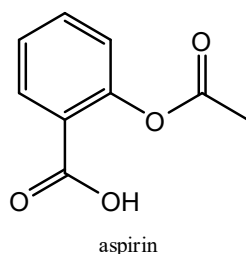
For ex.



Morphine,

Codeine.

b) **Non narcotics:** these are not so potent and not addictive, but they are also antipyretics effect. For ex. Following drugs are used as Antipyretics and Analgesics.



Following drugs are used as Antipyretics and Analgesics.

3) **Anaesthetics**: the term anaesthetic is derived from Greek word anaesthesia and its meaning is insensibility.

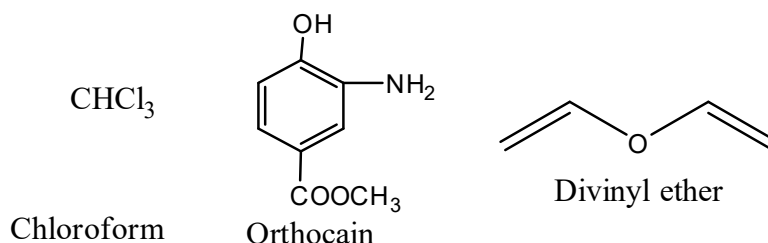
These drugs used to produce insensibility to vital function of all types of cells, especially of the nervous system.

Anaesthetic drugs are in reversible effects, i.e. when the concentration of the drug decreases, then the effect of the organ return to normal position.

On the basis of their applications anaesthetics are divided into two groups.

- a) **General anaesthetics**: it produce unconsciousness all over body.
- b) **Local anaesthetics**: it does not produce unconsciousness to all body, but effect only part of body.

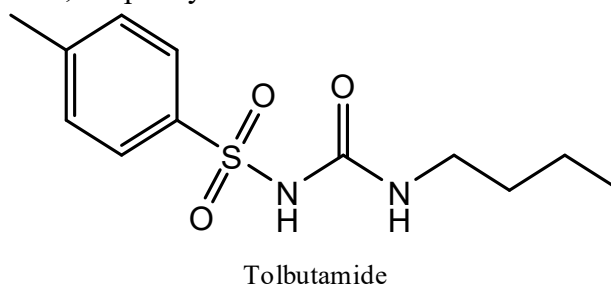
For ex. Nitrous oxide (N₂O), Ether, Divinyl ether, chloroform, orthocaine, benzocaine, procain etc.



4) **Antidiabetics**: Diabetics is disease which is caused by the deficiency of effective insulin insulin is a hormone which is secreted by pancreatic B-cells.

Insulin can control the mechanism of carbohydrates as well as lipid and Proteins. Hence diabetic patient is not able to metabolize glucose at normal rate.

For ex. Tolbutamide, Sulphonyl urease are used secrete the insulin.

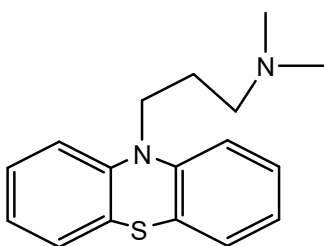


5) **Tranquilizers:** it the drug used for the treatment of mental disorder.

Tranquilizers are responsible to produce a specific improvement in the mood and behavior of the patient which are suffering from mental disorder.

Tranquilizers reduce the mental tension and relieves anxiety [care/tension] without producing sedation and hypnotics.

For ex. Reserpine, chlorpromazine.

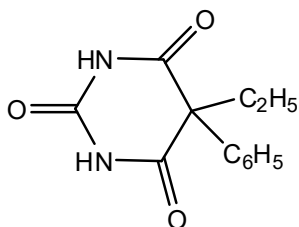


Chlorpromazine

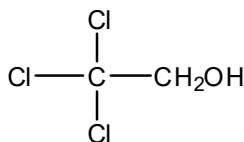
6) **Sedatives and Hypnotics:** both the drugs are CNS depressant that reduce restlessness and emotional tension.

Sedatives: sedatives are the drugs which are CNS depressant and they reduce restlessness and emotional tension without producing sleep.

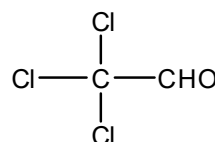
Hypnotics: hypnotics are also CNS depressant that reduces restlessness and emotional tension with producing the sleep. For ex



Phenobarbital



Trichloroethanol



Chloral

If phenobarbital given up to 25-30 mg it acts as milder sedatives but dose is given up to 100 mg it acts as hypnotics and when given large dose produce anesthesia and sometime it become poisonous and even cause death also.

B| Chemotherapeutic agent:

Chemotherapeutic agents are those drugs which are used to attack and destroy the involving microorganism without injuring or destroying the tissue / cells of the infected host.

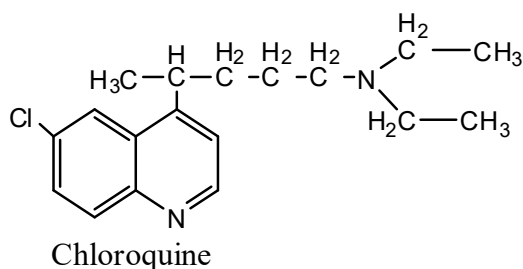
It includes Antimalarials, Antibacterials, Antifungal, Antitubercular, Antibiotics, Disinfectant and Antiviral etc.

1) **Antimalarial:** the drug which is used for the treatment of malaria diseases or to cure the malaria disease is called antimalarial.

The word malaria is derived from Italian word mal=meaning bad and ria= meaning air.

Malaria is caused due to miasma which is coming from the stagnant water. It is characterized by periodic fever, anemia and enlargement spleen and liver.

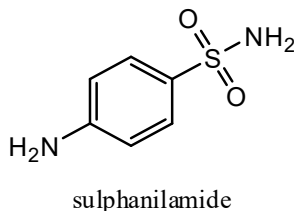
In 1987 Ross Roland discovered the malarial parasite in the wall of stomach of female For ex. Chloroquine, pamaquine, Santoquine, Sulphone derivatives are used.



2) **Antibacterial:** antibacterial are the agents which are used in the treatment of infectious diseases which are caused by bacteria.

Antibacterial drug may be bacteriostatic and bactericidal.

For ex. Sulphadruugs Sulphnilamide.



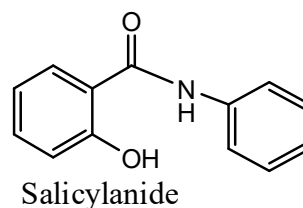
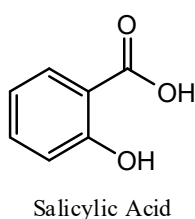
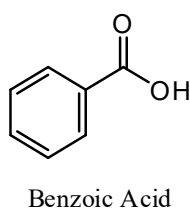
3) **Antifungal:** the agents which are used in the treatment of infectious diseases caused by the fungi are called as fungal drug.

Antifungal may be two types, Fungistatic and Fungicidal

Fungistatic are the agent which inhibit the growth of fungi.

Fungicidal are the agent which kill the fungi.

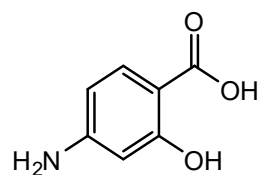
For ex. Propanoic Acid And Its Salts, Benzoic Acid, Salicylic Acid, Salicylanide.



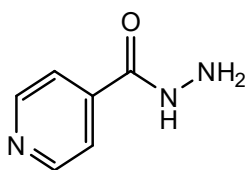
4) **Ant tubercular:** Ant tubercular agents are the drugs which are used for the treatment of tubercular disease which are caused by mycobacterium tuberculosis and mycobacterium bovis. Such drugs are called as antitubercular agent.

Tuberculosis is a systematic infectious disease found in man and animals which is caused by microorganism such as mycobacterium tuberculosis, mycobacterium bovis. Tubercular bacillus is found to be very effective or affective on any organ or tissue in the body but it mostly affect on the lungs due to longer periods of cough.

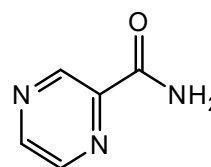
For ex. Para amino salicylic acid, Isoniazid, pyrazinamide.



Para amino salicylic acid



Isoniazid

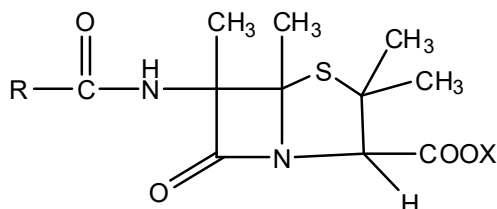


pyrazinamide.

5) **Antibiotics:** the word antibiotic is coming from Antibiosis and meaning is survival to the fittest.

Antibiotic is a chemical substance which is produced by or derived from living cells. Which is capable of inhibiting the life process or destroying the microorganism at a very small concentration?

For ex. Penicillin, streptomycin, cepodoxime, cefixime.



Penicillin

6) **Antiseptic:** Antiseptic is a drug which is directly applied to the skin wounds is known as antiseptic.

Antiseptic generally applied to the living tissue, hence it is bacteriostatic.

Antiseptic are milder action, take longer time.

Antiseptic may destroy bacteria, spores, fungi, viruses.

7) **Disinfectant:** disinfectant are bactericidal, because they are used to nonliving cell, Disinfectant having immediate action within shorter time.

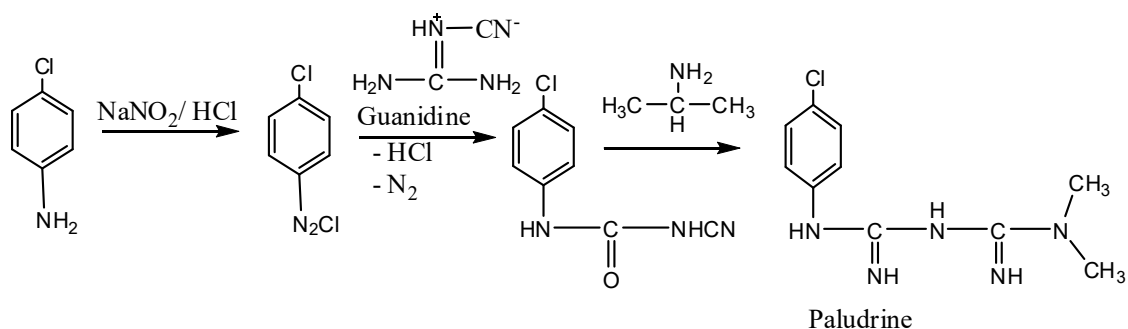
For ex. Alcohol [C_2H_5OH], Aldehyde, [$HCHO$], Phenylsalicylate.



Synthesis and Uses of some drugs:

3] **Paludrine:** [proguanil hydrochloride]:

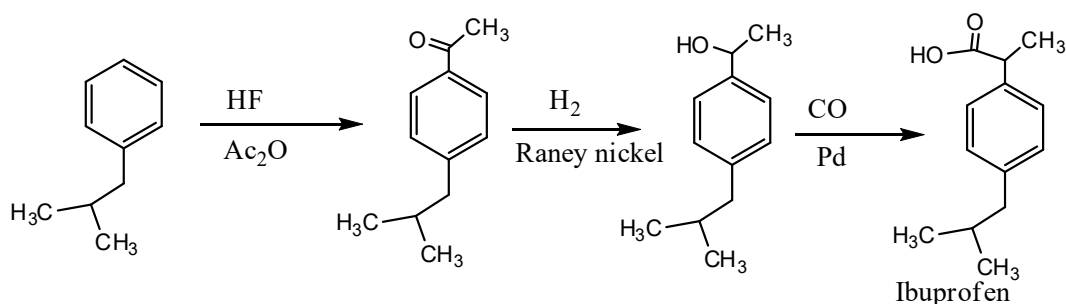
Paludrine is an established prescription-only antimalarial medication. It works stopping the growth of malaria parasite in your blood and liver. Paludrine is primarily prescribed for the prevention and suppression of malaria in travelers visiting endemic region.



Uses: it is used as antimalarial against p-falciparum and p-vivax malaria.

4] **Ibuprofen:** ibuprofen is non-steroidal anti-inflammatory, pain, reduce fever and decrease inflammation.

Synthesis:



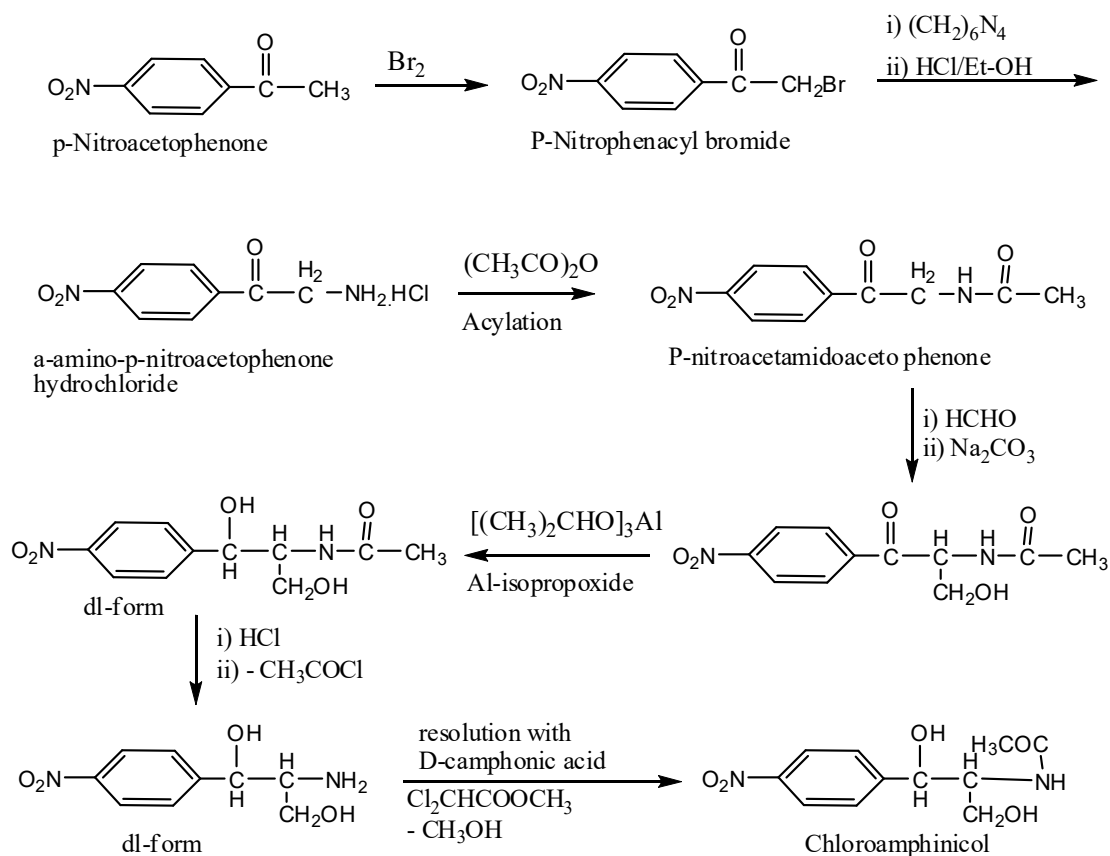
Uses:

it widely used nonsteroidal anti-inflammatory drug [NSAID], That reduces pain, fever, and inflammation.

Pain relief: effective for headache, dental pain, muscle aches, menstrual cramps.

5] **Chloromycetin:** [generic name Chloroamphenicol] chloromycetin is a broad spectrum of antibiotic, originally derived from soil bacterium streptomyces venezuelae. It is reserved for serve bacterial infection such as typhoid fever and meningitis.

Synthesis;



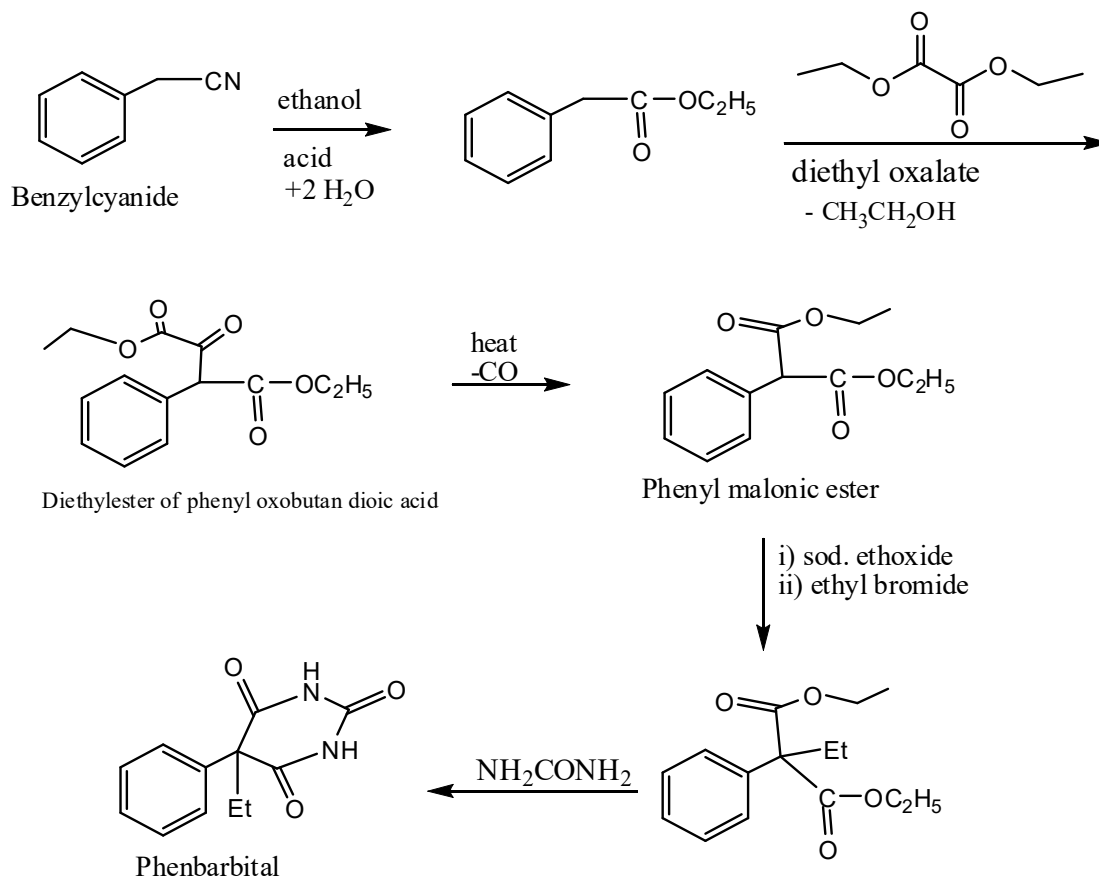
Uses: it is used in

- 1] Typhoid fever
- 2] Hemophilus influenza
- 3] Topical infection of eye and skin
- 4] Eradicate cholera virus and Plague.

6] Phenobarbital: [Phenobarbitone]

It is used as an anticonvulsant to treat various seizure types as sedatives and for alcohol or benzodiazepine.

Synthesis: Phenobarbital is synthesized via condensation reaction, most commonly using diethyl-ethyl-phenylmalonate and urea in the presence of strong base [sodium ethoxide]



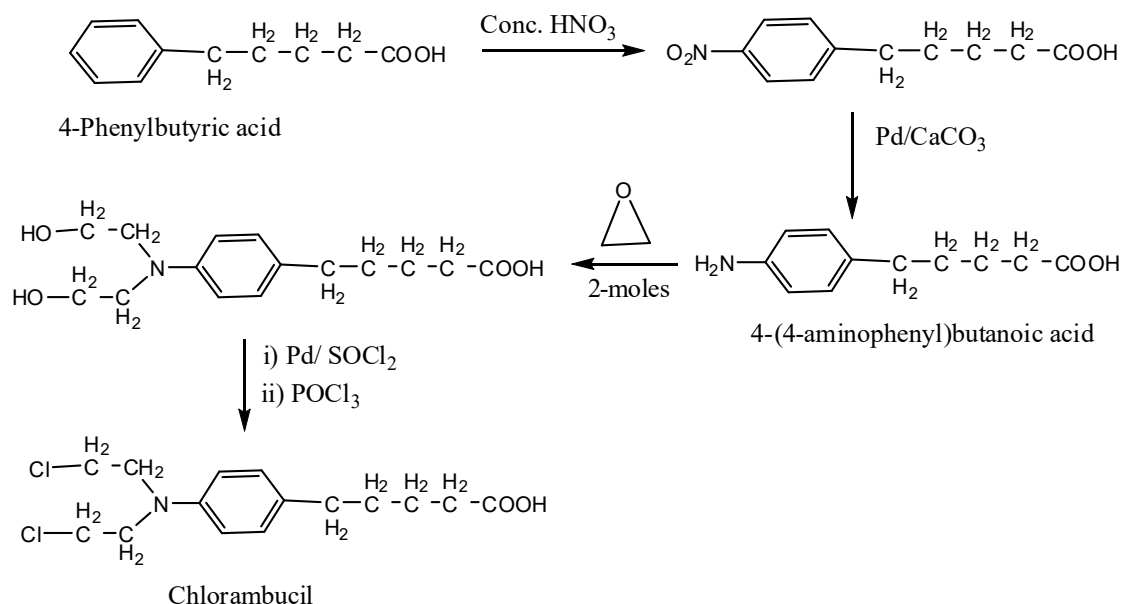
Uses: Phenobarbital is used for

- 1) Treatment of seizures
- 2) For producing sedation during the time of anxiety.

71 Chlorambucil:

Chlorambucil [$\text{C}_{14}\text{H}_{19}\text{Cl}_2\text{NO}_2$] is a bifunctional nitrogen mustard alkylating agent. It is primarily used in chemotherapy to treat chronic lymphocytic leukemia [CLL], Hodgkin lymphoma and Indolent non- Hodgkin lymphomas. It works by covalently crosslinking DNA.

Synthesis:



Uses:

- 1] Chronic lymphocytic leukemia[CLL]primarily used in the treatment of CLL.
- 2] Lymphomas: used to treat Indolent B-cell non Hodgkin Lymphomas and Hodgkin disease.
- 3] Immunosuppression: because of it immunosuppressive properties it is occasionally used off-label or in lower doses to treat severe autoimmune and inflammatory conditions such as rheumatoid, arthritis, uveitis and nephrotic syndrome.
- 4] Veterinary use: to treat various cancers in dogs and cats.

Synthetic Dyes

Introduction:

A dye is a colored substance that chemically bonds to the substrate to which it is being applied.

Dye is generally applied in an aqueous solution, and may require a mordant to improve the fastness of the dye on the fiber.

Types :

Dyes are classified according to application

Acid dye

An acid dye is a dye that is typically applied to a textile at low pH. They are mainly used to dye wool, not cotton fabrics. Some acid dyes are used as food colorants and some can also be

used to stain organelles in the medical field.

Acid dyes are anionic, soluble in water and are essentially applied from acidic bath. These dyes possess acidic groups, such as SO_3H and COOH and are applied on wool, silk and nylon when ionic bond is established between protonated $-\text{NH}_2$ group of fibre and acid group of dye.

Basic dyes

Are water-soluble cationic dyes that are mainly applied to acrylic fibers, but find some use for wool and silk. Usually acetic acid is added to the dye bath to help the uptake of the dye onto the fiber. Basic dyes are also used in the coloration of paper.

Direct or substantive dyeing

Is normally carried out in a neutral or slightly alkaline dye bath, at or near boiling point, with the addition of either sodium chloride (NaCl) or sodium sulfate (Na_2SO_4) or sodium carbonate (Na_2CO_3). Direct dyes are used on cotton, paper, leather, wool, silk and nylon. They are also used as pH indicators and as biological stains.

Vat dyes

Are a class of dyes that are classified as such because of the method by which they are applied. Vat dyeing is a process that refers to dyeing that takes place in a bucket or vat. The original vat dye is indigo, once obtained only from plants but now often produced synthetically.

A mordant or dye fixative

Is a substance used to set (i.e. bind) dyes on fabrics by forming a coordination complex with the dye, which then attaches to the fabric (or tissue). It may be used for dyeing fabrics or for intensifying stains in cell or tissue preparations. Although mordants are still used, especially by small batch dyers, it has been largely displaced in industry by directs.

Azoic dyeing or Developed dyes:

Is a technique in which an insoluble Azo dye is produced directly onto or within the fiber. This is achieved by treating a fiber with both diazoic and coupling components. With suitable adjustment of dyebath conditions the two components react to produce the required insoluble azo dye. This technique of dyeing is unique, in that the final color is controlled by the choice of the diazoic and coupling components. This method of dyeing cotton is declining in importance due to the toxic nature of the chemicals used.

Theories of colour and constitution:

Witt's Theory:

O.N. Witt observed in 1876 that coloured compounds contain certain unsaturated groups which he called chromophores and compound containing a chromophore is called a chromogen. When certain groups called auxochrome are present in the chromogen a dye is obtained. Auxochrome may be either acidic or basic like $-\text{OH}$ or $-\text{NH}_2$.

Some important points of this theory are:

(i) The colour of a substance is mainly due to the presence of unsaturated groups known as chromophores. The important chromophores are:

- C=C-
- C=N-
- C=O-
- N=N-
- NO₂

Quinones.

ii) The compounds possessing chromophores are referred to as chromogens. The higher the number of chromophores in a chromogen higher is the colour bearing capacity. The chromospheric groups are of the following two types:

1. When a single chromophore is sufficient to impart colour to the compound.
Example: NO, NO₂, N=N, =N=N, N=NO, p – quinonoid etc.
2. When more than one chromophores are required to impart the colour.
Example: >C=O, >C< etc.
3. Certain groups, which do not produce colour themselves when present along with a chromophore in an organic substance, intensify the colour. Such colour assisting groups are called auxochromes. They make the colour deep and fast.

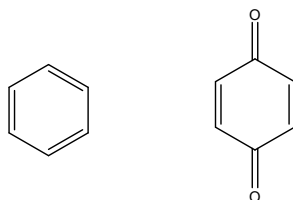
Examples include the hydroxyl group (“OH), the amino group (“NH₂), the aldehyde group (“CHO), and the methyl mercaptan group (“SCH₃).

An auxochrome is a functional group of atoms with one or more lone pairs of electrons when attached to a chromophore, alters both the wavelength and intensity of absorption. An auxochrome can increase the colour of any organic compound. E.g. benzene is a colourless compound, but nitrobenzene is a yellow-coloured compound (nitrobenzene contains a nitro group attached to benzene). Here, the nitro group is a chromophore for benzene molecule. When a hydroxyl group gets attached to the para position of nitrobenzene, it appears in a dark yellow colour (the intensity of nitrobenzene is increased due to the auxochrome group).

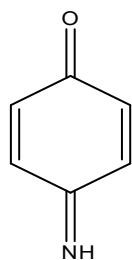
Armstrong Theory (Quinonoid theory):

Armstrong (1885) suggested that all colouring matters may be represented by § quinonoid structures (p or o), and thus believed that if a particular compound can be formulated in a quinonoid form, it is coloured, otherwise it is colourless. Some of the important compounds, the colouring properties of which can be explained on the basis of this theory are given below:-

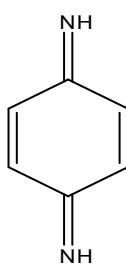
On the basis of this theory we can see that benzene is colourless, where as benzoquinones are coloured. Benzene Benzoquinones



But the quinonoid theory is not sufficient to account for the colouring characteristics of all the compounds. For example, iminoquinone and di iminoquinone, both possess a quinoid structure even then they are colourless.



Iminoquinone

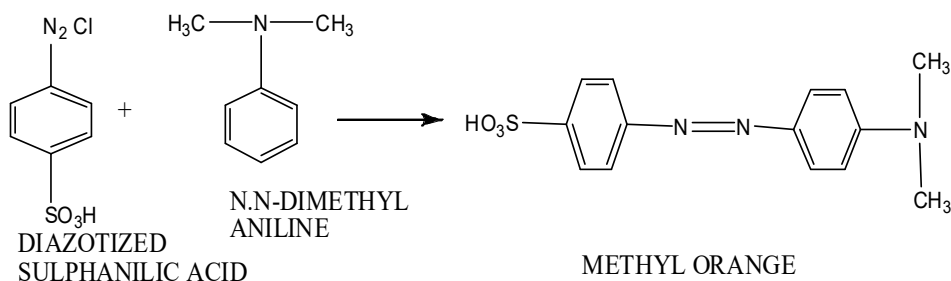


Di-iminoquinone

SYNTHESIS AND USES OF DYES:

1. Methyl Orange:

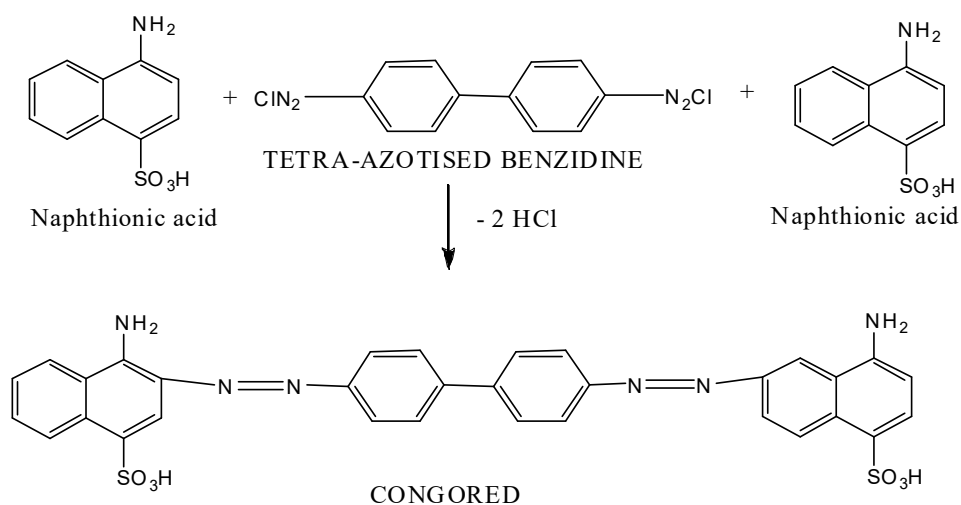
It can be prepared by the coupling reaction of diazotized sulphanilic acid with N,N-dimethylaniline.



- Uses:**
- 1) It is used as good acid-base indicator.
 - 2) It is not used as dye because it is not stable to soap and light

2. CONGO RED:

It is the member of diazo dyes. It is synthesized by the coupling reaction of one mole of tetra-azotised benzidine with two mole of naphthionic acid.

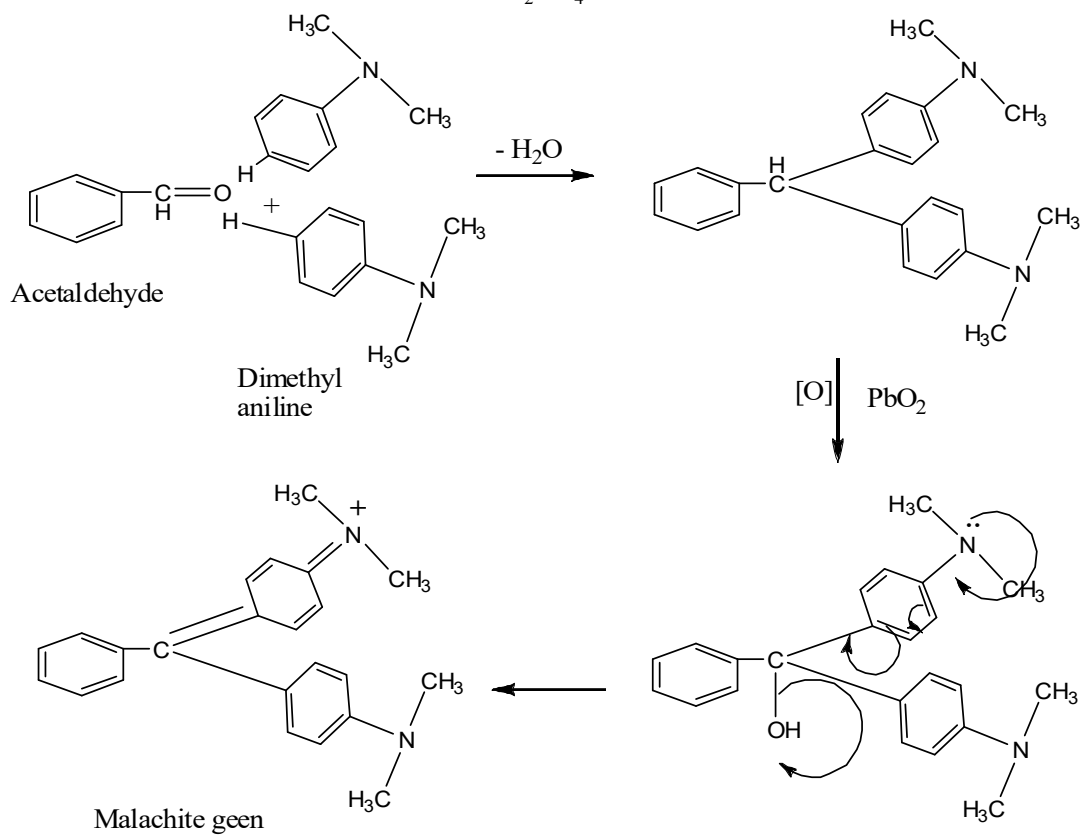


Uses:

- 1) It is first synthetic dye used for cotton. 2) Its salt of dye dyes cotton perfectly.

3. MALACHITE GREEN :

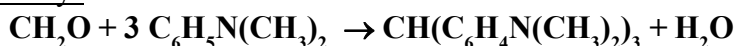
It is prepared by the reaction of one mole of benzaldehyde with two mole of *n,n*-dimethyl aniline in the presence of conc. H_2SO_4 at 373°K . followed by oxidation using PbO_2 .



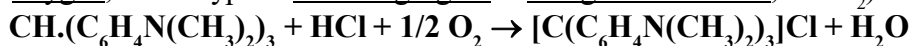
4. Crystal violet or gentian violet:

Also known as methyl violet 10B or hexamethyl pararosaniline chloride, is a triarylmethane dye used as a histological stain and in Gram's method of classifying bacteria. Crystal violet has antibacterial, antifungal, and anthelmintic (vermicide) properties and was formerly important as a topical antiseptic. The medical use of the dye has been largely superseded by more modern drugs, although it is still listed by the World Health Organization.

Crystal violet prepared by the condensation of formaldehyde and dimethylaniline to give a leuco dye:



Second, this colourless compound is oxidized to the coloured cationic form (hereafter with oxygen, but a typical oxidizing agent is manganese dioxide, MnO_2):



Uses:

Non Medical:

Crystal violet is used as a textile and paper dye, and is a component of navy blue and black inks for printing, ball-point pens, and inkjet printers.

It is sometimes used to colourize diverse products such as fertilizer, antifreeze, detergent, and leather.

The dye is used as a histological stain, particularly in Gram staining for classifying bacteria.

When conducting DNA gel electrophoresis, crystal violet can be used as a nontoxic DNA stain as an alternative to fluorescent,

Medical:

Gentian violet has antibacterial, antifungal, antihelminthic, antitrypanosomal, antiangiogenic, and antitumor properties. It is used medically for these properties, in particular for dentistry, and is also known as “pyoctanin” (or “pyoctanine”).

It is commonly used for Marking the skin for surgery preparation and allergy testing;

5. Phenolphthalein:

It is synthesized by the heating one mole of phthalic anhydride and two mole of phenol in the presence of conc. H_2SO_4 .

Uses:**Biochemical use:**

Fluorescein can also be conjugated to nucleoside triphosphates and incorporated into a probe enzymatically for in situ hybridisation. The use of fluorescein amidite, shown below right, allows one to synthesize labeled oligonucleotides for the same purpose.

Medicinal Use:

Fluorescein sodium, the sodium salt of fluorescein, is used extensively as a diagnostic tool in the field of ophthalmology and optometry, where topical fluorescein is used in the diagnosis of corneal abrasions, corneal ulcers and herpetic corneal infections.

It is also used in rigid gas permeable contact lens

Uses:

- 1) It is used as dye
- 2) It is used as dye to wool

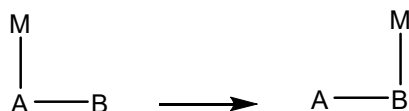
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Unit: III

Molecular Rearrangements

Many organic reactions involve change at functional groups while the molecular skeleton of the reactants remains unchanged. We have, however, encountered some examples in which groups migrate within molecule and carbon skeleton are modified such transformation are known as molecular rearrangements.

The most common kinds of rearrangement involve migration of group from one atom to the next within the molecule, that is they are 1,2-rearrangements.



Molecular rearrangements are usually not considered as a separate class of organic reactions. They normally involve intramolecular substitutions with mechanistic features similar to those of their intramolecular counterparts.

Molecular rearrangements are two types.

1. Intramolecular rearrangements:

If rearrangement occurs within the same molecule they are said to be intramolecular. In these rearrangements the migrating group does not get detached completely from the system in which rearrangement is taking place.

2. Intermolecular rearrangements:

If rearrangement involve the migration of groups between two molecules. They are said to be intermolecular. In these rearrangements the migrating group is first detached and reattached at another site.

Types of molecular rearrangements:

The molecular rearrangement can be conveniently classified into following types.

a) Nucleophilic rearrangement:

These are the rearrangement reaction in which the migrating group (nucleophile) gets migrated to electron deficient centre. For ex. Pinacol-Pinacolone rearrangement reaction.

b) Electrophilic Rearrangement:

These are the rearrangement reaction in which the migrating group (electrophile) gets migrated to electron rich centre.

c) Free-radical Rearrangement:

These are the rearrangement reaction in which the migrating group moves to a free radical centre.

d) Aromatic Rearrangement:

These are the rearrangement reaction in which the migrating group moves to aromatic nucleus.

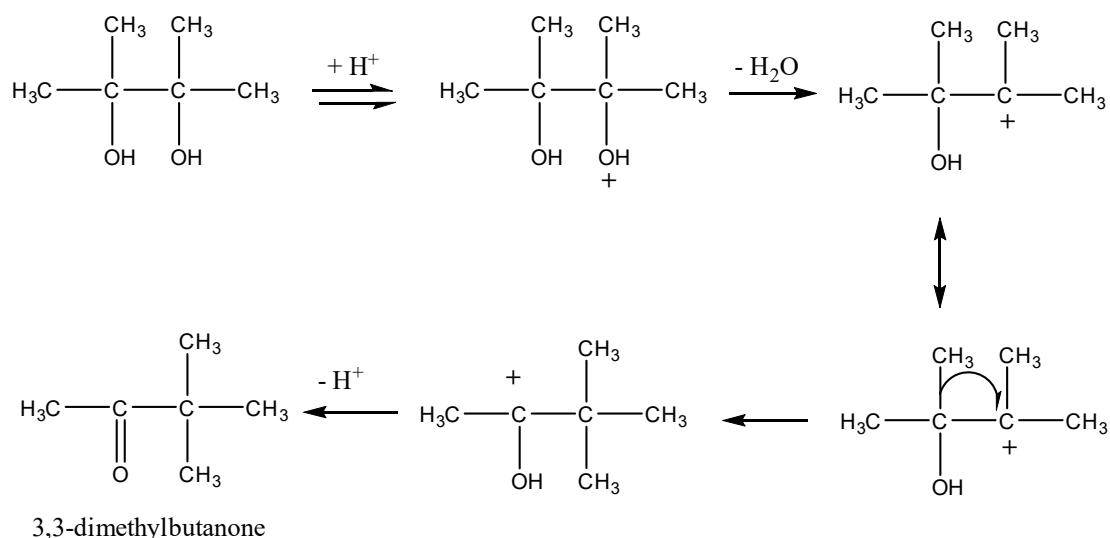
The first three types of molecular rearrangements are intra-molecular, while the fourth type of molecular rearrangement may be intra-molecular, intermolecular or both.

Study of following rearrangements with Mechanism:

1) Electrophilic Rearrangement:

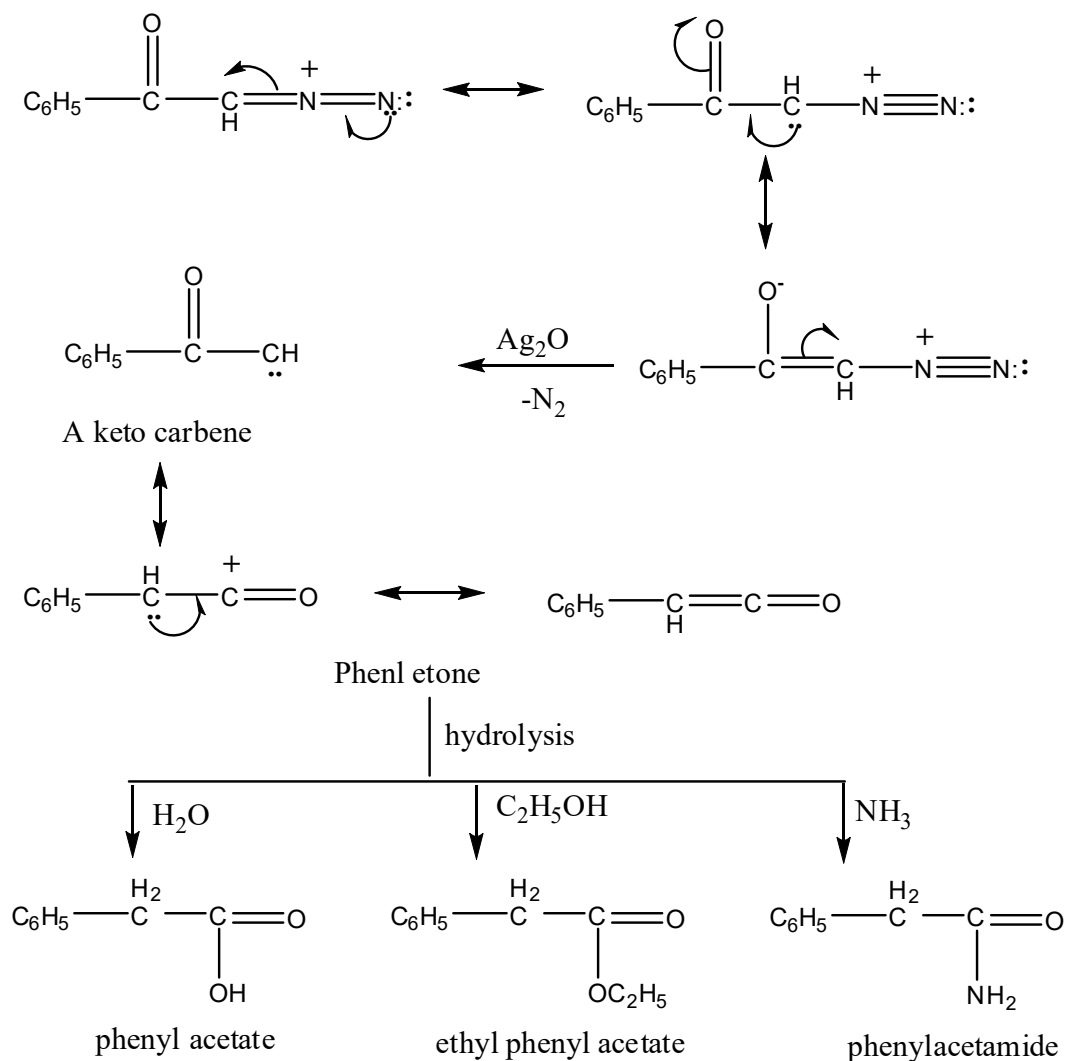
i) Pinacol-Pinacolone Reaction:

Conversion of 2, 3-dimethylbutanediol to 3, 3-dimethyl-2-butanone



ii) Wolff rearrangement:

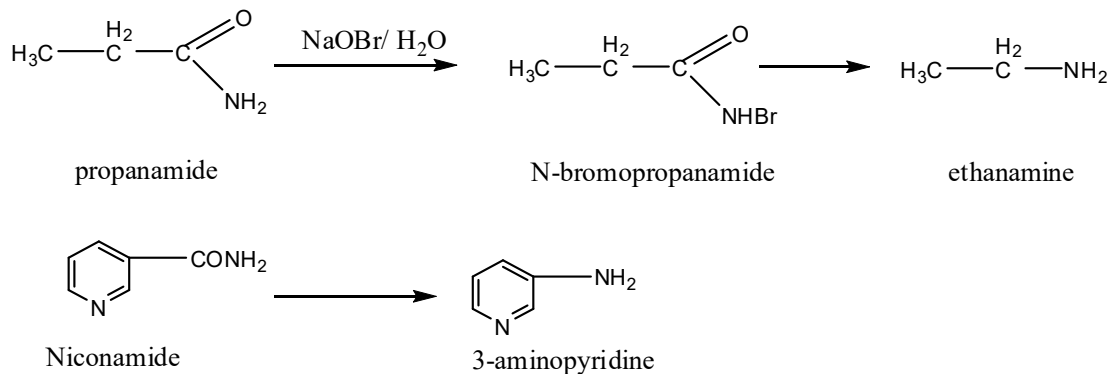
In the Wolff rearrangement an α -diazoketone loses nitrogen by the action of silver oxide or irradiation with light to produce an intermediate carbene. Rearrangement of an adjacent group to that carbon atom leads to a ketene. Which rapidly reacts with the reactant solvent? When the solvent is water, alcohol, or an amine, the final product is a carboxylic acid, an ester, or an amide, respectively.



2] Nucleophilic Rearrangement:

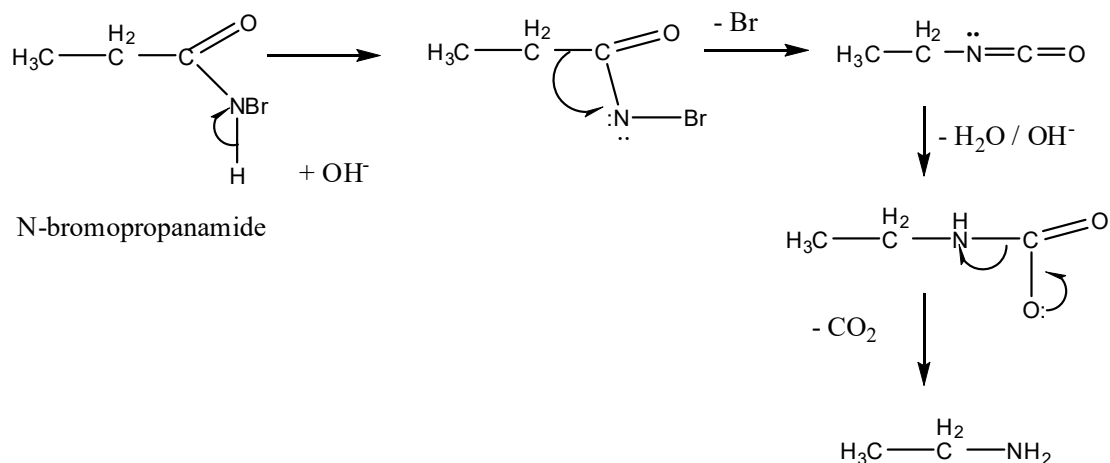
i] Hofmann Rearrangement:

This rearrangement involves migration of an electron deficient nitrogen atom. Hofmann rearrangement of N-haloamides is the most common rearrangement of the family, and it has been extensively studied since its discovery by Hofmann in 1882. Possessing one less carbon atom.



Mechanism:

The Hofmann rearrangement proceeds through formation of an N-haloamides anion that rearranges, with loss of bromide, to an isocyanate. Water adds to isocyanate to produce carbamic acid, which readily loses carbon dioxide to give the amine.

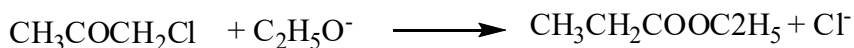


ii) THE FAVORSKII REARRANGEMENT

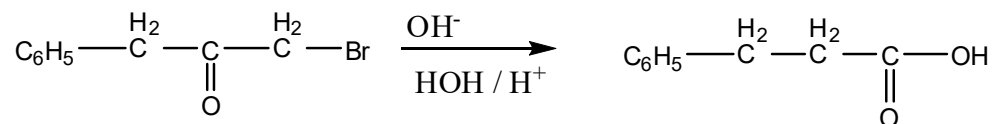
The reaction of α -haloketones with alkoxide ion to give rearranged ester is called Favorskii rearrangement.

Cyclic α -haloketones leads to ring contraction.

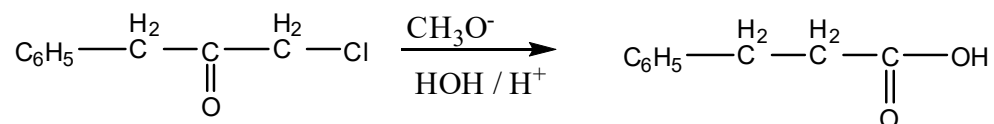
For ex:1



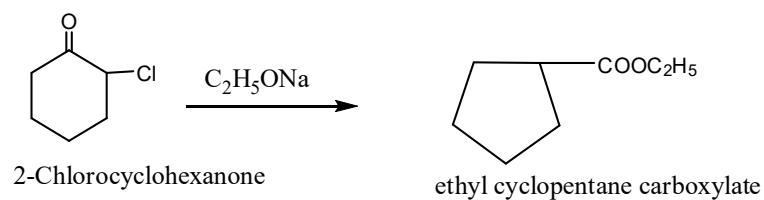
For ex: 2



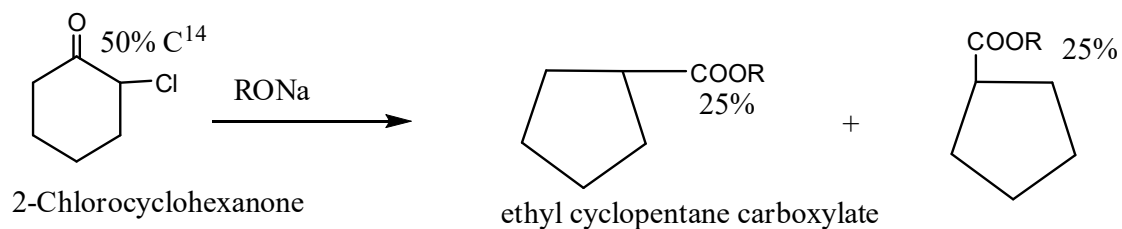
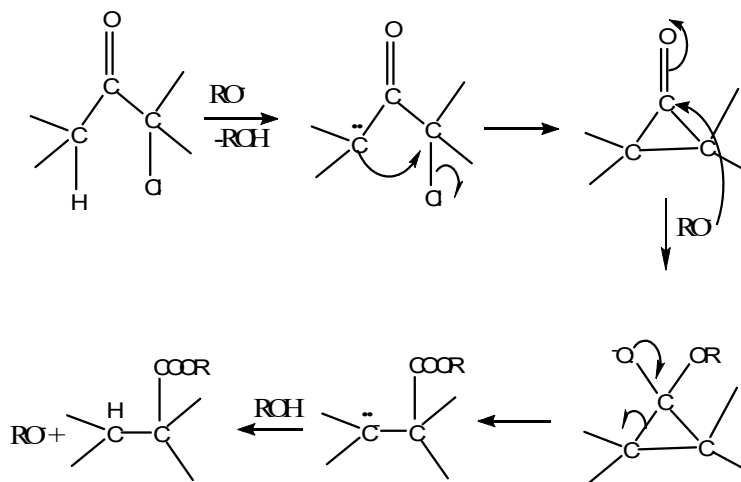
For ex:3

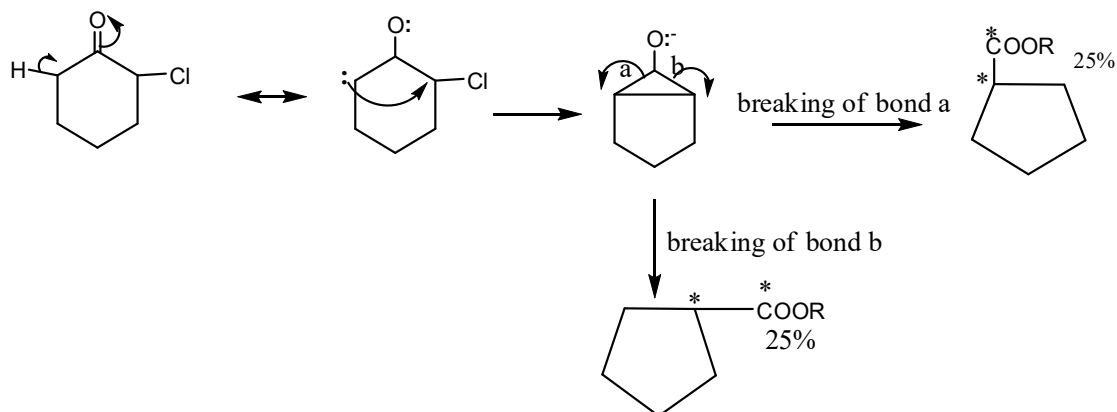


For ex:4



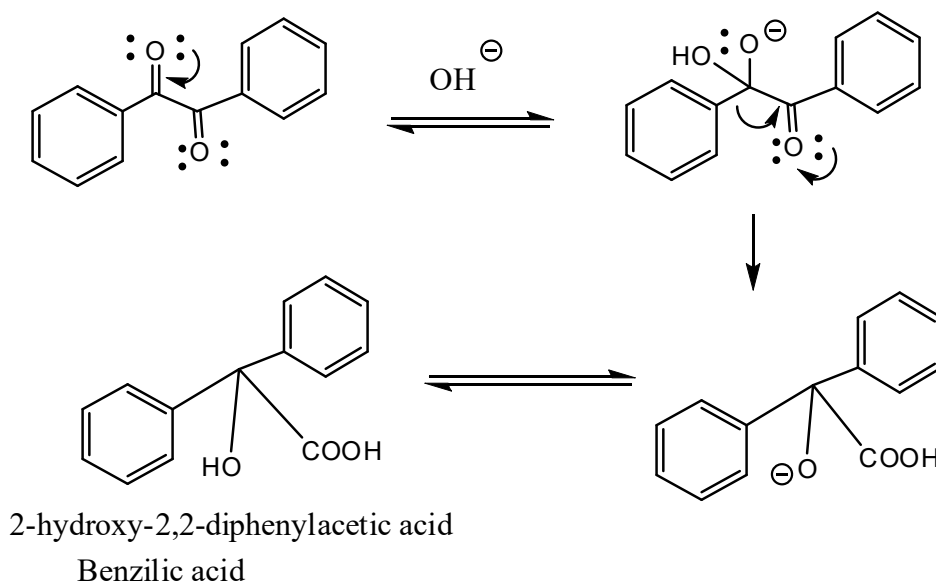
Mechanism:





iii] Benzilic Acid:

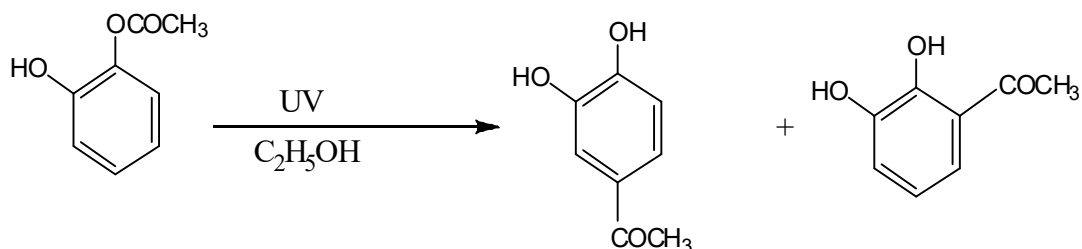
Benzilic acid rearrangement is the base catalyzed. Conversion of 1,2-diketone into α -hydroxycarboxylic acids. The classic example is the transformation of benzyl into benzilic acid using potassium hydroxide.



3] [FREE-RADICAL REARRANGEMENT] PHOTO FRIES REARRANGEMENT:

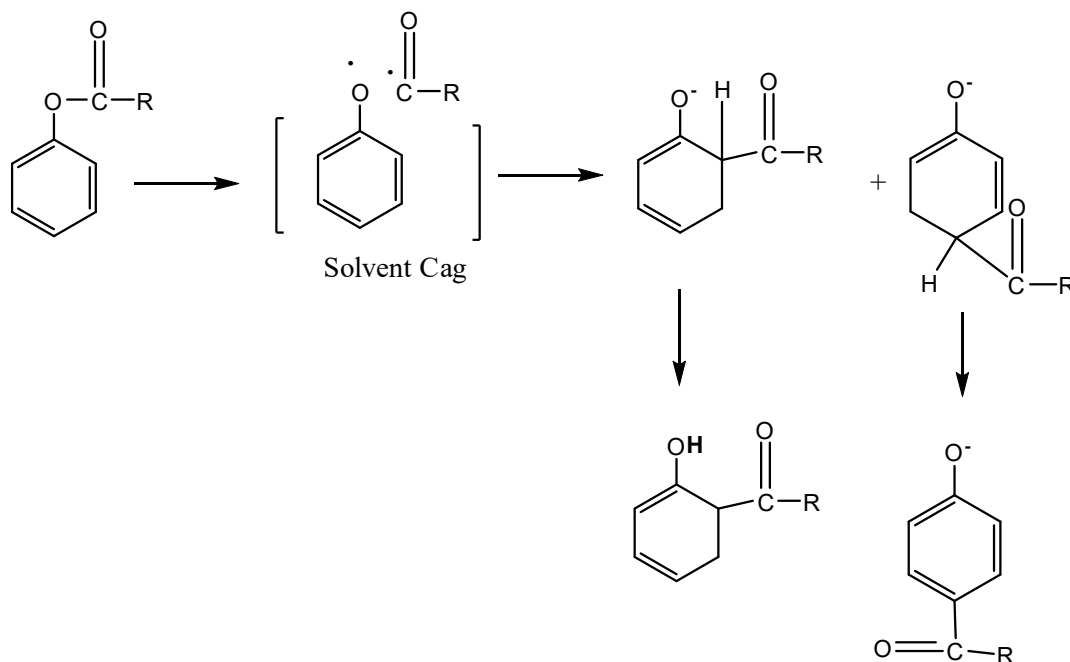
These are the rearrangement reaction in which the migrating group moves to a free radical centre.

Photo-Fries reaction can also be carried out in the presence of UV light for ex: When a solution of o-hydroxyacetophenone was irradiated with phenol, 2-hydroxyacetophenone (cross product) was not obtained indicating the intramolecular nature of the reaction.



MECHANISM:

The ester molecule absorb a photon and gets dissociated into radicals within a solvent cage. Recombination of the radical takes place before diffusion from the solvent cage to form the rearranged product.

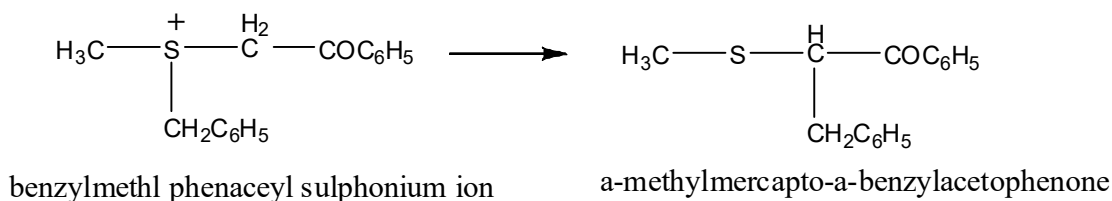
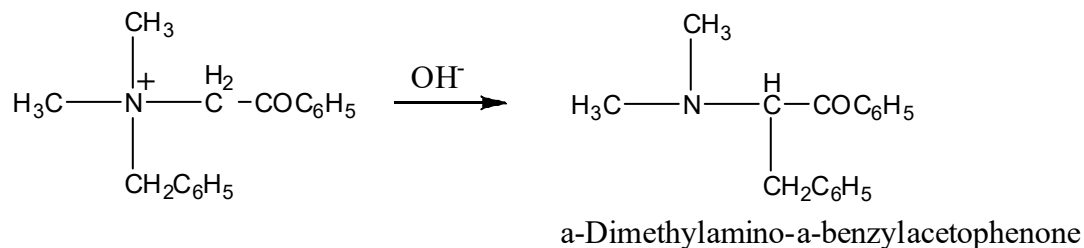


4] Aromatic Rearrangement:

Stevens Rearrangements:

Stevens's rearrangement involves the rearrangement of keto quaternary ammonium or sulphonium salts to amino ketones under the influence of a strong base such as NaOR

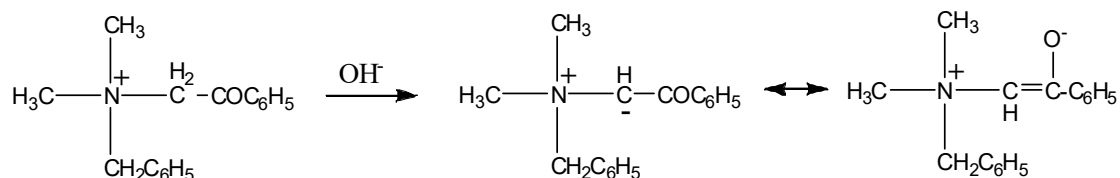
or NaNH_2 .



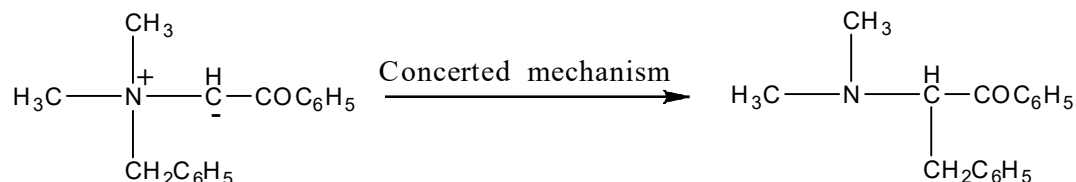
Mechanism: Rearrangement is intramolecular.

STEP:I;

Removal of an α -hydrogen atom by the base to give an ylid. [proton removal is facilitated by the positive charge in cationic substrate and by virtue of the delocalization energy of the enolate ion]



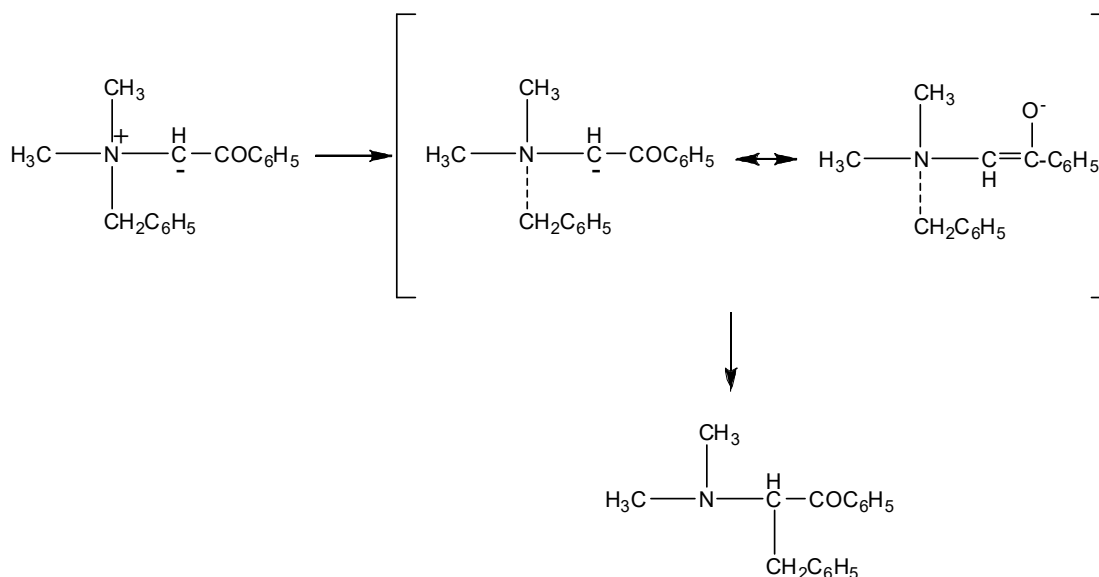
STEP:II;



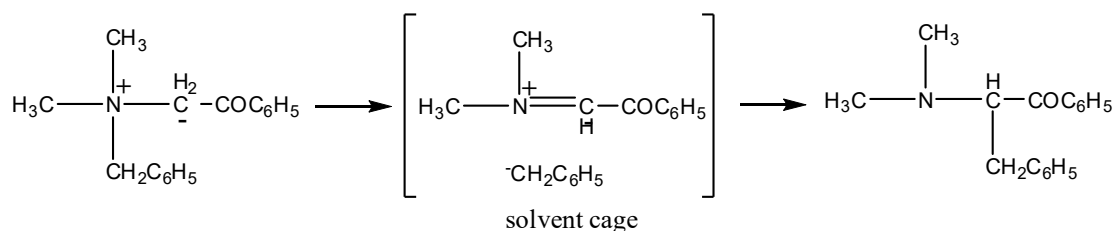
The ylid then rearranged to amino ketones via a concerted 1,2-shift, radical pair mechanism and ion pair mechanism is a solvent cage.

Radical pair mechanism:

The ylid formed above changes to product via the formation of radical pair. The two radicals do not drift apart because they are held together by solvent cage. Radical then recombine rapidly to form the final product.

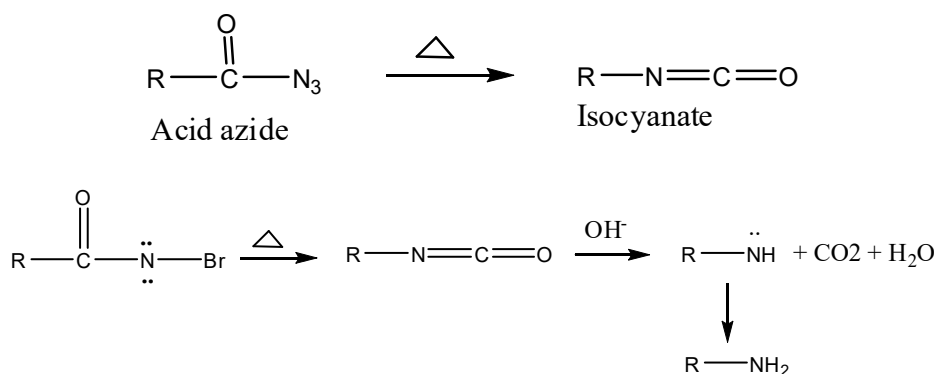


Ion pair mechanism: this is similar to radical pair mechanism here ion pair is formed in a solvent cage.

**SELF LEARNING:-****1) CURTIUS REARRANGEMENT:**

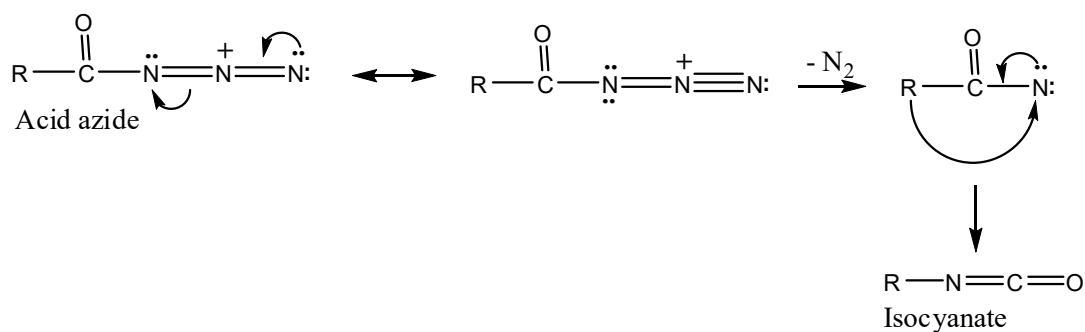
The thermal or photo chemical rearrangement of acyl azides to isocyanate was discovered by Curtius rearrangement.

Acyl azides are normally prepared either by reaction of sodium azide with a reactive acylating agent or by diazotization of an acyl hydroazide.



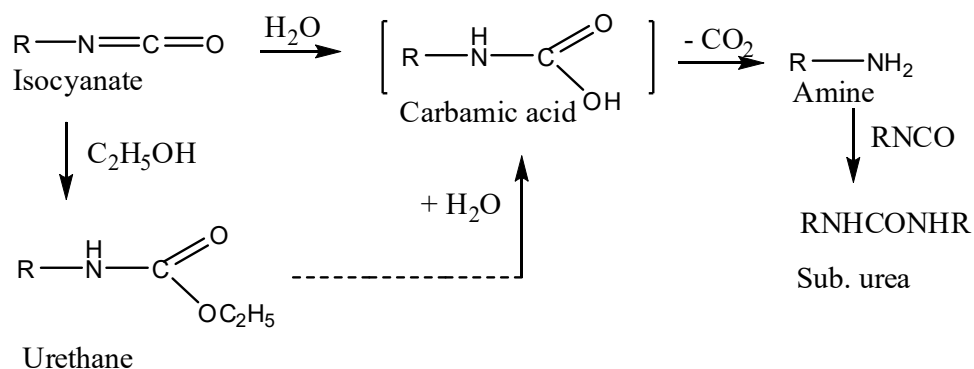
Mechanism:

The mechanism of Curtius reaction is quite similar to Hoffmann reaction as represented as.



The isocyanate may be isolated by carrying out by the reaction in an aprotic solvent such as chloroform.

While in aq. And alcoholic solvents it forms amines, urea and urathan.[carbaminates] respectively.



Semester : VI

Unit: I

Spectroscopy

INTRODUCTION

The word spectroscopy is derived from spectro (related to spectrum) + scopy (study or observation). Thus spectroscopy is the production, measurement, and analysis of electromagnetic spectra produced as a result of the emission or absorption of energy by various substances.

The electromagnetic spectrum is the range of all possible frequencies of electromagnetic radiation. The “electromagnetic spectrum” of an object is the characteristic distribution of electromagnetic radiation emitted or absorbed by that particular object.

The molecular spectroscopy is the study of the interaction of electromagnetic waves and matter. The scattering of sun's rays by raindrops to produce a rainbow and appearance of a colorful spectrum when a narrow beam of sunlight is passed through a triangular glass prism are the simple examples where white light is separated into the visible spectrum of primary colors. This visible light is merely a part of the whole spectrum of electromagnetic radiation, extending from the radio waves to cosmic rays. All these apparently different forms of electromagnetic radiations travel at the same velocity but characteristically differ from each other in terms of frequencies and wavelength.

ELECTROMAGNETIC RADIATIONS

Electromagnetic radiation (sometimes abbreviated EMR) is a ubiquitous (everywhere) phenomenon that takes the form of self-propagating waves in a vacuum or in matter. It consists of electric and magnetic field, components that oscillate in phase perpendicular to each other and perpendicular to the direction of energy propagation. The propagation of these radiations involves both electric and magnetic forces which give rise to their common class name electromagnetic radiation. In spectroscopy, only the effects associated with electric component of electromagnetic wave are important. Therefore, the light wave traveling through space is represented by a sinusoidal trace (figure 1). In this diagram λ is the wavelength and distance A is known as the maximum amplitude of the wave. Although a wave is frequently characterized in terms of its wavelength λ , often the terms such as wavenumber (ν), frequency (ν), cycles per second (cps) or hertz (Hz) are also used.

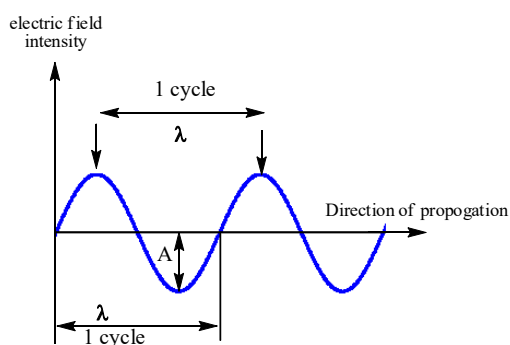


Figure 1 : Wave like propagation of light (λ = wavelength and A = amplitude)

Electromagnetic radiation is classified into several types according to the frequency of its wave. These types include (in order of increasing frequency and decreasing wavelength): radio waves, microwaves, infrared radiation, visible light, ultraviolet radiation, X-rays and gamma rays. EM radiation carries energy and momentum that may be imparted to matter with which it interacts.

The electromagnetic spectrum

Radiation type	Wave length λ , (Å)	Frequency ν , (Hz)	Applications
Radio	10^{14}	3×10^4	
Nuclear magnetic resonance	10^{12}	3×10^6	
Television	10^{10}	3×10^8	Spin orientation
Radar	10^8	3×10^{10}	
Microwave	10^7	3×10^{11}	
Far infrared	10^6	3×10^{12}	Rotational
Near infrared	10^4	3×10^{14}	Vibrational
Visible	$8 \times 10^3 - 4 \times 10^3$	$3.7 \times 10^{14} - 7.5 \times 10^{14}$	
Ultra violet	3×10^3	1×10^{15}	Electronic
X-rays	1	3×10^{18}	
Gamma rays	10^{-2}	3×10^{20}	Nuclear transitions
Cosmic rays	10^{-4}	3×10^{22}	

UNITS USED IN SPECTROSCOPY (A) WAVELENGTH (B) WAVENUMBER (C) FREQUENCY:

1. Wave length :(λ)

It is the distance between the two adjacent crests(c-c) or trough (T-T) in a particular waves. It is denoted by the letter (λ).

The unit commonly used to describe the wavelength is centimeters (cm), the different units are used to express the wavelengths in different parts of the electromagnetic spectrum. For example, in the ultraviolet and visible region, the units use is angstrom (E) and nanometer (nm). Ultraviolet light can be detected by photoelectric cell and infrared light can be detected by photographically. In some techniques like ultraviolet and infrared spectroscopy. The common unit is wavelength.

2. Wave number: (ν):

It is the reciprocal of wavelength and it is expressed in per centimeter. In other words, it is defined as the total number of waves which can pass through a space of one cm. it is denoted by (ν). It is frequently used in Infrared technique.

3. Frequency:

It is defined as the number of waves which can pass through a point in one second. It is expressed as (ν).

4. The velocity(c):

The distance traveled by the waves in one second is called the velocity of the waves. It is expressed in cm per second.

In the infrared region, the commonly used unit is wavenumber (ν), which gives the number of waves per centimeter. Thus

$$1 \text{ cm} = 10^7 \text{ nm} = 10^8 \text{ E}$$

$$1 \text{ E} = 10^{-1} \text{ nm} = 10^{-8} \text{ cm}$$

The four quantities wavelength, wavenumber, frequency and velocity can be related to each other by following relationships

$$\text{Wavelength } (\lambda) = c/\nu$$

$$\text{Wave-number } (\nu) = 1/\lambda = \nu/c$$

$$\text{Frequency } (\nu) = c/\lambda = c \nu$$

$$\text{Velocity } (c) = \nu\lambda = \nu/\nu$$

Absorption of Different Electromagnetic radiations by Organic Molecules

In absorption spectroscopy, though the mechanism of absorption of energy is different in the ultraviolet, infrared and nuclear magnetic resonance regions, the fundamental process is the absorption of a discrete amount of energy. The energy required for the transition from a state of lower energy (E_1) to state of higher energy (E_2) is exactly equivalent to the energy of electromagnetic radiation that causes transition.

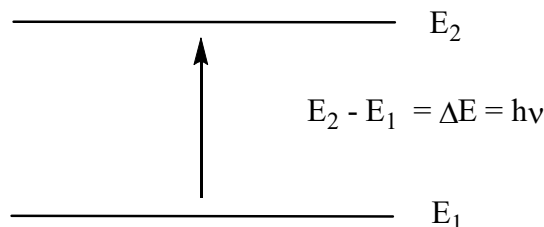


Figure 2: Energy transition for the absorption of any electromagnetic radiation

$$E_2 - E_1 = \Delta E = h\nu = hc / \lambda,$$

Where ΔE is energy of electromagnetic radiation being absorbed, h is the universal Planck's constant, 6.624×10^{-27} erg sec and ν is the frequency of incident light in cycles per second (cps or hertz, Hz), c is velocity of light 2.998×10^{10} cm s⁻¹ and λ = wavelength (cm). Therefore, higher is the frequency, higher would be the energy and longer is the wavelength, lower would be the energy. As we move from cosmic radiations to ultraviolet region to infrared region and then radio frequencies, we are gradually moving to regions of lower energies.

A molecule can only absorb a particular frequency, if there exists within the molecule an energy transition of magnitude $E = h\nu$. Although almost all parts of electromagnetic spectrum are used for understanding the matter, in organic chemistry we are mainly concerned with energy absorption from only ultraviolet and visible, infrared, microwave and radiofrequency regions.

Ultraviolet – visible spectroscopy (200 - 800 nm) studies the changes in electronic energy levels within the molecule arising due to transfer of electrons from p- or non-bonding orbitals. It commonly provides the knowledge about p-electron systems, conjugated unsaturations, aromatic compounds and conjugated non-bonding electron systems etc.

Infrared spectroscopy (400-4000 cm) studies the changes in the vibrational and rotation -1 movements of the molecules. It is commonly used to show the presence or absence of functional groups which have specific vibration frequencies viz. C=O, NH, OH, CH, C-O etc.

Nuclear magnetic resonance (radiofrequency 60-600 MHz) provides the information about changes in magnetic properties of certain atomic nuclei. ¹H and ¹³C are the most commonly studied nuclei for their different environments and provide different signals for magnetically non-equivalent nuclei of the same atom present in the same molecule.

ULTRAVIOLET SPECTROSCOPY

1. Introduction:

The absorption of radiant energy in U.V and Visible region causes electronic excitation of the molecule such an excitation are known as U.V –Visible spectrum and it is also

called as electronic spectra. The U. V region of electronic spectrum extend from 4 to 400 nm (40 to 4000 Å) the U.V region is obtained into two region.

- a) Near U.V region 200 to 400 nm.
- b) Far U.V region 4 to 200 nm.

Organic chemist interest to work in the U.V region 200 to 400 nm in wave length. U.V radiations provide energy for promoting electrons of a molecule from ground state to excited state.

When U.V electromagnetic radiation passed through a molecule containing double or triple bonds, a part of incident radiation gets absorbed by a molecule. these absorption radiation energy causes promotion of electrons in σ (sigma), π (pi), and n (nonbonding) non bonding molecular orbital i.e. ground state molecular orbit to higher energy level antibonding molecular orbitals and amount of UV radiations absorbed can be depends upon structure of compounds and wavelength of radiations and it is measured with the help of U.V spectrophotometer.

Principles of Absorption Spectroscopy:

Beer's and Lambert's Law

The greater the number of molecules that absorb light of a given wavelength, the greater the extent of light absorption and higher the peak intensity in absorption spectrum. If there are only a few molecules that absorb radiation, the total absorption of energy is less and consequently lower intensity peak is observed. This makes the basis of Beer-Lambert Law.

Which states that the fraction of incident radiation absorbed is proportional to the number of absorbing molecules in its path.

When the radiation passes through a solution, the amount of light absorbed or transmitted is an exponential function of the molecular concentration of the solute and also a function of length of the path of radiation through the sample. Therefore,
 $\text{Log } I_0 / I = \epsilon c l$

Where I_0 = Intensity of the incident light (or the light intensity passing through a reference cell)

I = Intensity of light transmitted through the sample solution

c = concentration of the solute in mol^{-1}

l = path length of the sample in cm

ϵ = molar absorptivity or the molar extinction coefficient of the substance whose light absorption is under investigation. It is a constant and is a characteristic of a given absorbing species (molecule or ion) in a particular solvent at a particular wavelength. ϵ is numerically equal to the absorbance of a solution of unit molar concentration ($c = 1$) in a cell of unit length ($l = 1$) and its units are $\text{liters. moles}^{-1} \cdot \text{cm}^{-1}$. However, it is customary practice among organic chemists to omit the units.

The ratio I / I_0 is known as transmittance T and the logarithm of the inverse ratio I_0 / I is known as the absorbance A .

Therefore

$$\begin{aligned} -\text{Log } I / I_0 &= -\log T = \epsilon c l \\ \text{and } \text{Log } I_0 / I &= A = \epsilon c l \\ \text{or } A &= \epsilon c l \end{aligned}$$

For presenting the absorption characteristics of a spectrum, the positions as λ_{max} (in nm) values and the absorptivity is expressed in parenthesis.

Types of electronic transitions

The total energy of a molecule is the sum of its electronic, its vibrational energy and its rotational energy. Energy absorbed in the UV region produces changes in the electronic energy of the molecule. As a molecule absorbs energy, an electron is promoted from an occupied molecular orbital (usually a non-bonding n or bonding π orbital) to an unoccupied molecular orbital (an antibonding π^* or σ^* orbital) of greater potential energy (figure 3). For most molecules, the lowest-energy occupied molecular orbitals are σ orbitals, which correspond to σ bonds. The π orbitals lie at relatively higher energy levels than σ orbitals and the non-bonding orbitals that hold unshared pairs of electrons lie even at higher energies. The antibonding orbitals (π^* and σ^*) are orbitals of highest energy. The relative potential energies of these orbitals and various possible transitions have been depicted in figure 3. The saturated aliphatic hydrocarbons (alkanes) exhibit only $\sigma \rightarrow \sigma^*$ transitions but depending on the functional groups the organic molecules may undergo several possible transitions which can be placed in the increasing order of their energies viz. $n \rightarrow \pi^* < n \rightarrow \sigma^* < \pi \rightarrow \pi^* < \sigma \rightarrow \pi^* < \sigma \rightarrow \sigma^*$. Since all these transitions require fixed amount of energy (quantized), an ultraviolet or visible spectrum of a compound would consist of one or more well defined peaks, each corresponding to the transfer of an electron from one electronic level to another. If the differences between electronic energy levels of two electronic states are well defined i.e. if the nuclei of the two atoms of a diatomic molecule are held in fixed position, the peaks accordingly should be sharp. However, vibrations and rotations of nuclei occur constantly and as a result each electronic state in a molecule is associated with a large number of vibrational and rotational states.

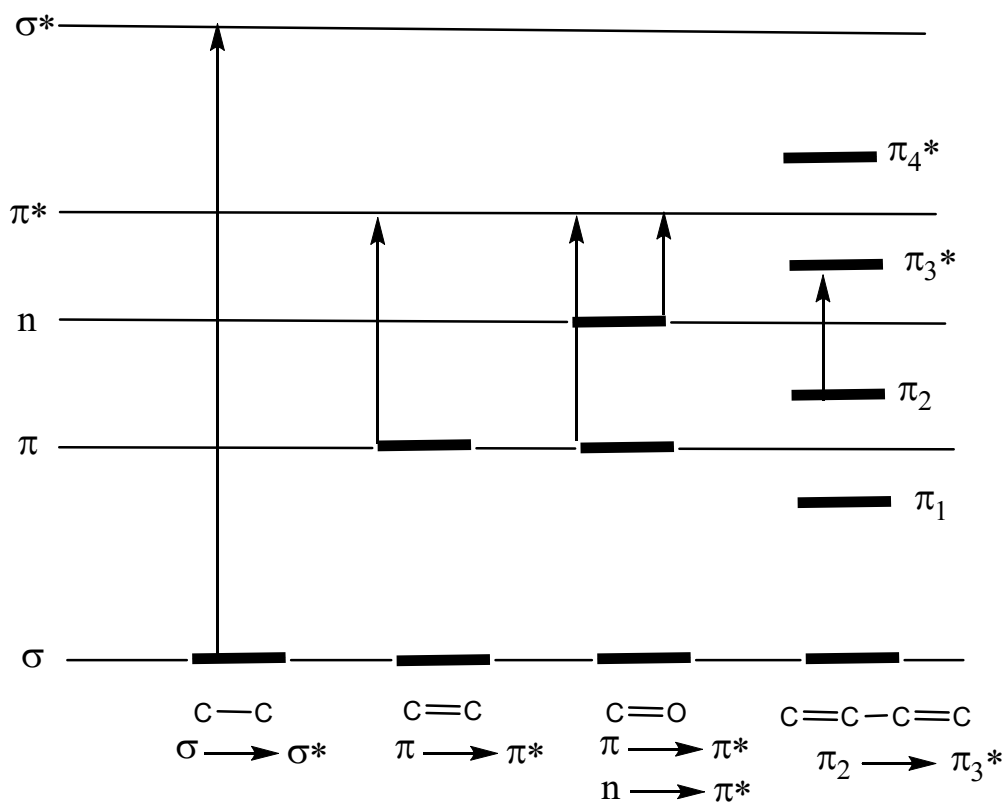


Figure 3 : Relative energies of orbitals most commonly involved in electronic spectroscopy of organic molecules

1. $\sigma \rightarrow \sigma^*$ transition:

A transition in which a bonding σ electron is excited into an antibonding orbital is referred to as a $\sigma \rightarrow \sigma^*$ transition.

σ -bonds are very strong hence high energy is required for this electronic transition this electronic transition occurs at wave length shorter than 165 nm. For ex. In saturated hydrocarbons, like CH_4 this transition takes place due to absorption of radiation of 150 nm in wavelength.

2. $n \rightarrow \sigma^*$ transition:

A transition in which the transition of one electron of lone pair (i.e. non bonding pair of electron) to an antibonding σ orbital.

$n \rightarrow \sigma^*$ transition are of low energy than $\sigma \rightarrow \sigma^*$ transition it associated with energy less than 150 kcal/mole and occurs at wave length around greater than 175 nm. Alcohols, aldehydes, ketones, ethers, halides, amines etc. Undergo this type of transition.

$\text{CH}_3\text{-OH}$ absorb AT 174 nm due to $n \rightarrow \sigma^*$ transition.

3. $\pi \rightarrow \pi^*$ transition:

A transition in which transition of a bonding π electron to an antibonding π^* .

This transition occurs in aromatic compounds, compounds containing double or triple bonds for ex. Carbonyl compounds, cyanides etc. shows $\pi \rightarrow \pi^*$ transition.

This transition require less energy than that of $n \rightarrow \sigma^*$ transition.

4. $n \rightarrow \pi^*$ transition:

It represents the transition of one electron of a lone pair to an antibonding π^* orbital.

This transition require still less energy than $\pi \rightarrow \pi^*$ transition and hence absorption occurs at longer wave length. For ex. Saturated aldehydes shows two transitions.

- i) $n \rightarrow \sigma^*$ transition at 290 nm (less intense R-band) and
- ii) $\pi \rightarrow \pi^*$ transition at 180 nm (more intense k-band)

$n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions are most useful to organic chemists for establishing the structure of a molecule.

Terms used in U.V spectroscopy / Concept of chromophore and auxochrome, Bathochromic, Hypsochromic, Hyperchromic, Hypochromic shift.

Chromophore:

The energy of radiation being absorbed during excitation of electrons from ground state to excited state primarily depends on the nuclei that hold the electrons together in a bond. **The group of atoms containing electrons responsible for the absorption is called chromophore.** Most of the simple un-conjugated chromophores give rise to high energy transitions of little use. Some of these transitions have been listed below.

Absorption maxima of simple un-conjugated chromophores

Chromophore	Transition	ϵ_{max}	λ_{max} (nm)
<i>σ – bonded electrons</i>			
(C-C, C-H etc.)	$\sigma \rightarrow \sigma^*$		~ 150
<i>Lone pair electrons</i>			
-O-, -N-, -S-	$n \rightarrow \sigma^*$	100-1000	~ 190
C=O, C=N	$n \rightarrow \pi^*$	15	~300
	$\pi \rightarrow \pi^*$	500	~190
R-C $\equiv$ N	$n \rightarrow \pi^*$	5	~ 170
R-COOH, RCONH ₂ , RCOOR	$n \rightarrow \pi^*$	50	~ 210
<i>π- bonded electrons</i>			
C=C	$\pi \rightarrow \pi^*$	14000	~ 190
C $\equiv$ C	$\pi \rightarrow \pi^*$	2000	~ 195
C=O	$\pi \rightarrow \pi^*$	500	~ 180

For example, alkanes contain only single bonds with only possible $\sigma \rightarrow \sigma^*$ type electronic transitions. These transitions absorb radiations shorter than wavelengths that are experimentally accessible in usually available spectrophotometers. In saturated molecules with heteroatom bearing non-bonding pairs of electrons, $n \rightarrow \sigma^*$ transitions become available. These are also high energy transitions. In unsaturated compounds, $\pi \rightarrow \pi^*$ transitions become possible. Alkenes and alkynes absorb ~ 170 nm but the presence of substituents significantly affects their position. The carbonyl compounds and imines can also undergo $n \rightarrow \pi^*$ transitions in addition to $\pi \rightarrow \pi^*$. Amongst these, the most studied transitions are $n \rightarrow \pi^*$ as these absorb at relatively longer wavelength 280-300 nm. These are low intensity (ϵ 10-100) transitions.

(ii) Auxochrome:

An auxochrome is a functional group of atoms with non bonded electrons which, when attached to a chromophore, alters both the wavelength and intensity of absorption.

If these groups are in direct conjugation with the pi-system of the chromophore, they may increase the wavelength at which the light is absorbed and as a result intensify the absorption. **A feature of these auxochromes is the presence of at least one lone pair of electrons which can be viewed as extending the conjugated system by resonance.**

For example,

- i) benzene does not display color as it does not have a chromophore; but nitrobenzene is pale yellow color because of the presence of a nitro group ($-\text{NO}_2$).
- ii) Para-hydroxynitrobenzene exhibits a deep yellow color. Here an auxochrome ($-\text{OH}$) is conjugated with the chromophore $-\text{NO}_2$.
- iii) Similar behavior is seen in azobenzene which has a red color, but para-hydroxy azobenzene is dark red in color.

The substituents like methyl, hydroxyl, alkoxy, halogen, amino group etc. are some examples of auxochromes.

- (a) Bathochromic Shift or Red shift:** A shift of an absorption maximum towards longer wavelength or lower energy.
- (b) Hypsochromic Shift or Blue Shift:** A shift of an absorption maximum towards shorter wavelength or higher energy.
- (c) Hypochromic Effect:** An effect that results in decreased absorption intensity.
- (d) Hyperchromic Effect:** An effect that results in increased absorption intensity.

Effect of conjugation on position of U.V and visible bonds.

The wave length of absorption is shifted to higher values (Bathochromic shift), if two or more chromophore group are present in a molecule.

For ex. Ethylene (one double bond) absorb at 170 mu ($\pi \rightarrow \pi^*$ transitions), while butadiene (two double bonds in conjugation) absorb at 217 mu.

The bathochromic shift is more pronounced if the double bonds are in conjugation as compared to the isolated double bonds in which there is a little interaction between them.

The absorption maxima is usually shifted 15-45 mu towards higher wave length in conjugated system. The value of extinction coefficient also increases.

In conjugated dienes $\pi \rightarrow \pi^*$ transitions results in the formation of a band, called **k-band**.

Brief Information Regarding U.V spectroscopy:

A spectrophotometer is a device which detects the percentage transmittance of light

radiation. When light of certain intensity and frequency range is passed through the sample, thus the instruments compare the intensity of the transmitted light with that of the incident light.

U. V spectrophotometer is made up of three basic components.

- i) A source of radiation
 - ii) A monochromator
 - i) A detector and measuring assembly.
- I] now days, visible- ultraviolet spectrophotometer are built together, containing two different sources of radiation. (a) Tungsten lamp for scanning in the visible region (400-800) and (b) deuterium discharge lamp for scanning in the near UV region(200-400)
- II] These radiation passed through a monochromator which automatically select the required wavelengths.

The monochromatic beam is split up into two parallel beams (i) one of which is passes through a cell containing very dilute solution of organic compound it is called as sample beam.

(ii) the another beam is passed through a cell containing solvents only. It is termed as reference beam.

III] The spectrophotometer electronically subtract the absorption of solution in the sample beam.

“A plot of absorbance against wavelength is auto record through detector in the form of UV spectrum.”

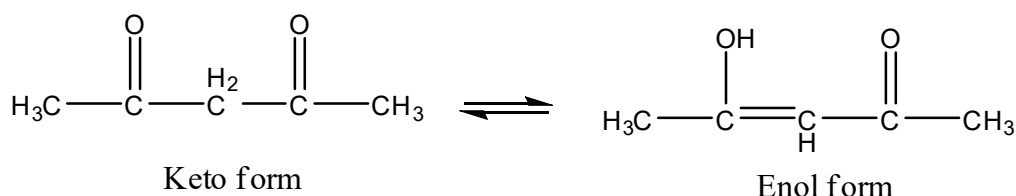
Application of U.V spectrophotometer:

1. For determining the structure of a compound:-

U.V spectroscopy is useful in determining the presence or absence of chromophores. Characteristic UV absorptions for some of the chromophores are as in table no.1

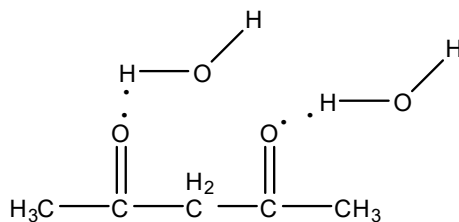
2. Tautomerism:

We can determine the presence of tautomerism in a molecule by Scanning UV spectra in different solvents. Ex. Acetylacetone can under go tautomeric changes.



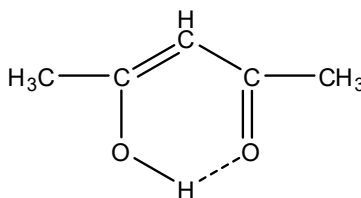
In aqueous polar solvent, keto form this compound predominates due to stability by means, of intermolecular hydrogen bonding with polar solvent. It shows absorption band at λ_{max} 274 nm

(ϵ_{max} = 2050)



Keto form

On the other hand in non-polar solvents, such as iso-octane, intermolecular hydrogen bonding is not possible. In this situation, the enol form can gain stability by means of intramolecular hydrogen bonding. Thus in nonpolar solvent iso-octane, a strong absorption band at λ_{max} 272 nm ($\epsilon_{\text{max}} = 12000$) indicates the predominance of the enol form.



Since the band intensities in the UV spectra are the function of the concentration of the keto and enol forms by the UV spectroscopy and also calculate the equilibrium constants.

III] Conjugated System:

If two or more chromophore groups are presents in a molecule and they are separated by two or more single bonds, there is less effects on the spectrum ex. $\text{CH}_2=\text{CH}_2$ absorb at λ_{max} 165 nm

($\epsilon_{\text{max}} = 15000$). While 1,4-pentadiene $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}_2$ absorb at nearly the same position as the single ethylinic chromophore i.e. at λ_{max} 175 nm. ($\epsilon_{\text{max}} = 15000$). However, if two chromophore groups are separated by only one single bond (a conjugated system),

A large effects on the absorption band results because Π electros get delocalised over four carbon atoms. Absorption band is generally shifted to 15-45 nm to longer wavelength with respect to the simple conjugated chromophore with high intensity ex. Ethylene shows absorption band at

λ_{max} 165 nm. ($\epsilon_{\text{max}} = 15000$).while 1,3- butadiene $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ shows absorption band at λ_{max} 217 nm. ($\epsilon_{\text{max}} = 21000$).

UV spectroscopy is especially applicable for determining the presence of conjugation system in an unknown compound.

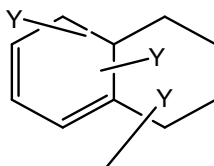
Table no. 1: Characteristic UV absorption for some of the chromophores.

Chromophore group	Example	λ_{max}	E max	Transition
$\begin{array}{c} \text{---C=C---} \\ \quad \end{array}$	ethylene	165	15000	Pi-Pi*
$\text{---C}\equiv\text{C---}$	Acetylene	190	8000	Pi-Pi*
$\begin{array}{c} \text{---C=O} \\ \end{array}$	Acetone	190	900	n- σ^*
		270	30	n- Pi*
$\begin{array}{c} \text{HC=O} \\ \end{array}$	Aldehyde	210	1200	Pi-Pi*
		290	16	n- Pi*
benzenoid ring	Benzene	180	60000	Pi- Pi* E ₁ -band
		200	8000	Pi- Pi* E ₂ -band
		255	215	Pi- Pi* B-band
Aromatic hydroxy compounds	Phenol	210	6200	Pi- Pi* E ₂ -band
		270	1450	Pi- Pi* B-band
	methoxy benzene	217	600	
		269		
	Aceto-phenone	245.5	9800	

Woodward Fieser Rules for predicting λ_{max} can be summarised as follows.

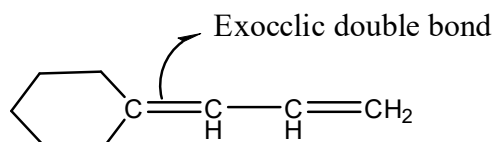
- 1, 3-butadiene system is considered as the parent chain and alicyclic dienes. Its base value is considered as 214 nm. (217 nm)
- Each alkyl group or ring residue, attached to the parent 1, 3-butadiene system, shift the absorption 5 nm towards the longer wavelength region.

A part of the carbocyclic ring directly linked to the diene moiety is called ring residue and is denoted by “Y” ex.

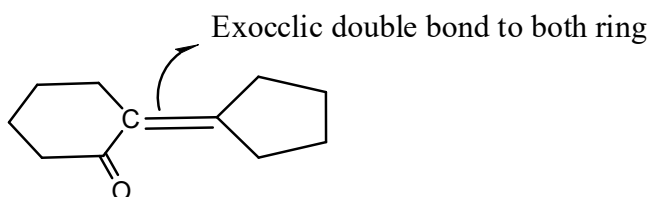


This compound contains 3 ring residues, hence, increment of three ring residues $5 \times 3 = 15$ nm is added to base value.

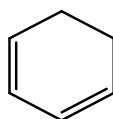
3. Increments for extended conjugation of parent diene system is calculated as 30 nm, which is then added to base value of parent diene.
4. When one carbon atom of the double bonded carbon atom is in the ring with the double bond extending outside of the ring. It is said to be an exocyclic double bond. Each exocyclic double bond causes an additional 5 nm increment to the base value of parent diene.



If the double bond is exocyclic to two rings, additional becomes 10nm.

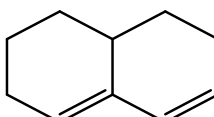


5. When both of the conjugated double bonds are present in same ring, the system is known as homo-annular diene.



Its base value is considered as 253 nm.

6. When both of the conjugated double bonds are not present in same ring, the system is known as hetero-annular diene.



Its base value is considered as 214 nm.

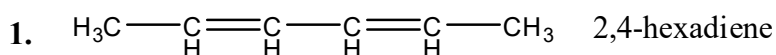
7. Increments are also considered for substituents like OAc, OR, Cl, Br, SR, NR₂, etc. On parent diene system.

The base value for conjugated diene system and increments for substituent's and ring residues, as per Woodward Fieser rules, are given in the following table no. 2.

Table no. 2

Base value for butadiene system	214 nm
Parent open chain or hetero-annular diene	214 nm
Homo-annular diene	253 nm
Increments for	
(a) Each alkyl substituent or ring residue	5 nm
(b) Double bond extending conjugation	30 nm
(c) Exocyclic double bond	5 nm
(d) Lone pair conjugation	
(i) O-C(=O)-R	0 nm
(ii) O-alkyl	6 nm
(iii) S-alkyl	30 nm
(iv) -Cl, -Br	5 nm
(v) NR ₂	60 nm

Applications of Woodward Fieser rules to calculate λ_{max} of the following compounds:

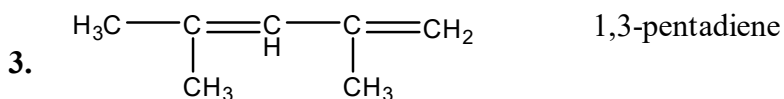


Basic unit in this compound is butadiene and two -CH₃ groups are substituent's.

Base value for 1,3-butadiene 214 nm

Increments for two alkyl groups (2x5=10) + 10

$$\lambda_{\text{max}} = \underline{\underline{224 \text{ nm}}}$$



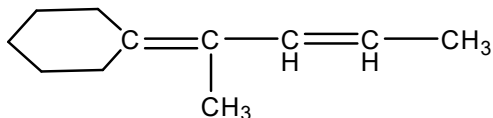
Basic unit in this compound is butadiene and two -CH₃ groups are substituent's.

Base value for 1,3-butadiene 214 nm

Increments for three alkyl groups (3x5=10) + 15

$$\lambda_{\text{max}} = \underline{\underline{229 \text{ nm}}}$$

4.



Basic unit in this compound is butadiene and two $-\text{CH}_3$ groups are substituent's.

Base value for 1,3-butadiene 214 nm

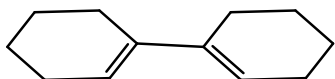
Increments for two alkyl groups ($2 \times 5 = 10$) + 10

Increments for two ring residue ($2 \times 5 = 10$) + 10

One exocyclic double bond + 05

$$\Lambda_{\text{max}} = 239 \text{ nm}$$

5.



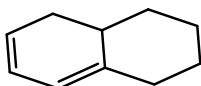
It is heteroannular diene having four ring residues.

Base value for heteroannula diene 214 nm

Increments for four ring residue ($4 \times 5 = 20$) + 20

$$\Lambda_{\text{max}} = 234 \text{ nm}$$

6.



It is homoannular diene having three ring residues.

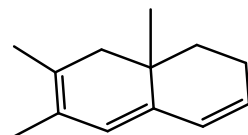
Base value for heteroannula diene 253 nm

Increments for three ring residue ($3 \times 5 = 15$) + 15

One exocyclic double bond + 05

$$\Lambda_{\text{max}} = 273 \text{ nm}$$

7.



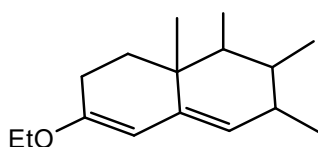
It is homoannular diene having five ring residues, one exocyclic double bond and one

extended double bond.

Base value for homoannular diene	253 nm
Increments for five ring residue (5x5=25)	+ 25
One exocyclic double bond	+ 05
One extended double bond	+ 30

$$\lambda_{\text{max}} = 313 \text{ nm}$$

8.



It is hetero-annular diene having three ring residues, one exocyclic double bond and one alkoxy group.

Base value for heteroannular diene	214 nm
Increments for three ring residue (3x5=15)	+ 15
One exocyclic double bond	+ 05
One alkoxy group substituted	+ 06

$$\lambda_{\text{max}} = 240 \text{ nm}$$

Woodward Fieser rules for calculating absorption maxima in α, β -unsaturated ketones and aldehydes .

Woodward and Fieser framed certain empirical rules for estimating the absorption maxima for α, β -unsaturated ketones and aldehydes. The rules were later modified by Scott and are as follows.

a) The basic value of α, β -unsaturated ketones is taken as 215 mu. The α, β -unsaturated ketones may be cyclic or six membered.

For compound, $=\text{CH}-\text{COX}$, basic value is 215 mu, if x is an alkyl group.

If $x=\text{H}$, basic value becomes 207 mu. If $x=\text{OH}$ or OR basic value becomes 193 mu.

b) If the double bond and the carbonyl group are in a five member ring (cyclopentenone), then for such α, β -unsaturated ketones, the basic value becomes 200 mu. The ϵ_{max} for such compounds is generally above 10,000.

The structural increments for estimating λ_{max} for a given α, β -unsaturated carbonyl compounds are as follows.

- | | |
|--|-------|
| i) For each exocyclic double bond | +5 mu |
| ii) For each double bond endocyclic in five or seven | +5 mu |

iii)	For each alkyl substituent or ring residue at the α , - position	+10 mu
	β - Position	+12 mu
	γ or δ or higher position	+18 mu
iv)	For each double bond extending conjugation	+ 30mu
v)	For a homoannular conjugated diene	039 mu

Parent acyclic ketone or six-membered	215 nm
Parent α , β -unsaturated pentenone	202 nm
Parent α , β -unsaturated aldehyde	207 nm

(a) A double bond extending conjugation	30 nm
(b) Each alkyl group or ring residue α	10 nm
β	12 nm
or higher	18 nm

(i) -OH	α	35 nm
	β	30 nm
	δ	50 nm

(iii) $-\text{OCH}_3$	α	35 nm
	β	30 nm
	γ	17 nm
	δ	31 nm

(v) -Br	α	25 nm
	β	30 nm

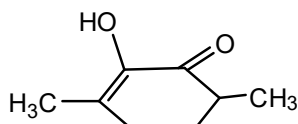
(e) Homocyclic diene	30 nm
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$$\text{H}_3\text{C}-\underset{\text{CH}_3}{\text{C}}=\underset{\text{H}}{\text{C}}-\underset{\text{CH}_3}{\text{C}}=\text{O}$$

The basic value for a cyclic α, β -unsaturated ketone is 213 mu.
 Two β -alkyl substituent. (2x 12= 24) + 24 mu

$$\lambda_{\text{max}} = 239 \text{ mu}$$

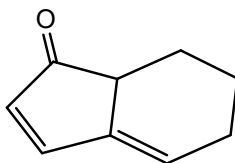
1. Calculate the λ_{max} for given structure.



Basic value for α, β -unsaturated ketone is 215 mu.
 One $-\text{OH}$ group substituent at α , + 35
 One α -alkyl substituent and + 12 mu
 one ring residue at α -position. + 12 mu

$$\lambda_{\text{max}} = 274 \text{ mu}$$

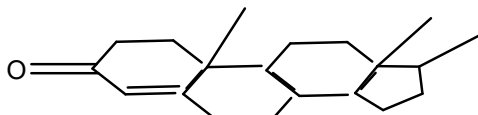
2. Calculate the λ_{max} for given structure.



Basic value for α, β -unsaturated ketone is 215 mu.
 One α -alkyl substituent and + 12 mu
 One α and one β ring residue (18 + 18) + 36 mu
 One exocyclic double bond + 05 mu
 One double bond extending conjugation + 30 mu

$$\lambda_{\text{max}} = 274 \text{ mu}$$

3. Calculate the λ_{max} for given structure.



Basic value for α, β -unsaturated ketone is 215 mu.
 Two α -ring residues + 24 mu.
 exocyclic double bond + 05 mu

$$\lambda_{\text{max}} = 274 \text{ mu}$$

Question Bank

Q1. Define the following terms

- i) Wavelength
- ii) Wavenumber
- iii) Frequency
- iv) Velocity

Q2. Explain Lamberts and Beers law

Q3. Explain the following terms

- i) $\sigma \rightarrow \sigma^*$ transition
- ii) $n \rightarrow \sigma^*$ transition
- iii) $\pi \rightarrow \pi^*$ transition
- iv) $n \rightarrow \pi^*$ transition

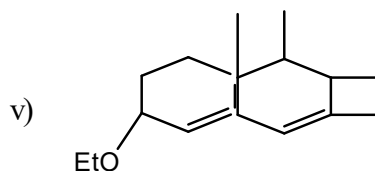
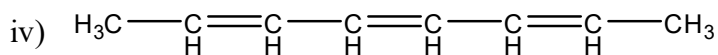
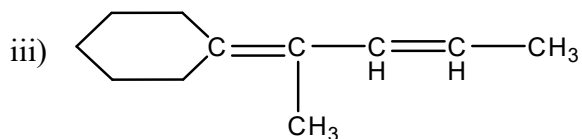
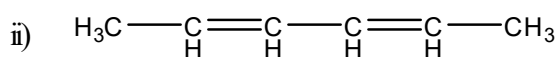
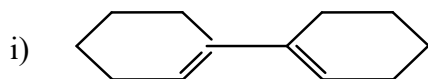
Q4. Define the following terms with suitable examples

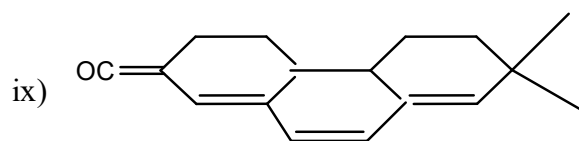
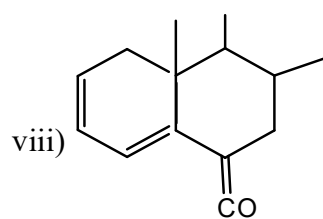
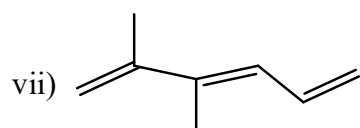
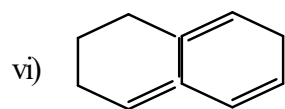
- i) Chromophore
- ii) Auxochrome
- iii) Bathochromic shift
- iv) Hypsochromic shift
- v) Hyperchromic effect
- vi) Hypochromic effect

Q5. Give the brief information regarding U. V. spectrophotometer.

Q6. Give the applications of U. V. spectrophotometer.

Q7. Calculate the $\lambda_{\max}$ of following compounds





...

Unit : II

Infrared Absorption Spectroscopy

Introduction:

At ordinary temperatures, organic molecules are in a constant state of vibrations, each bond having its characteristic stretching and bending frequencies. When infrared light radiations between $4000\text{--}400\text{ cm}^{-1}$ (the region most concerned to an organic chemist) are passed through a sample of an organic compound, some of these radiations are absorbed by the sample and are converted into energy of molecular vibrations. The other radiations which do not interact with the sample are transmitted through the sample without being absorbed. The plot of % transmittance against frequency is called the infrared spectrum of the sample or compound.

This study of vibrations of bonds between different atoms and varied multiplicities which depending on the electronegativity, masses of the atom and their geometry vibrate at different but specified frequencies; is called infrared spectroscopy.

The presence of such characteristic vibrational bands in an infrared spectrum indicates the presence of these bonds in the sample under investigation. The infrared radiation expressed in terms of wavelength (λ) or wave number (ν).

This is one of the most widely used Spectroscopic techniques for the detection of Functional group in pure unknown compounds.

The region from $0.5\text{ }\mu$ to $2.5\text{ }\mu$ of IR radiation is called near IR.

The region from $2.5\text{ }\mu$ to $15\text{ }\mu$ of IR radiation is called middle IR.

The region from $15\text{ }\mu$ to $200\text{ }\mu$ of IR radiation is called far IR ($1\text{ }\mu = 10^{-4}\text{ cm}$) the most important region for organic chemist is $2.5\text{ }\mu$ to $15\text{ }\mu$ (4000 to 667 cm^{-1}) in which molecular vibrations can be detected and measured in IR spectrum.

Bond intensity is either expressed in terms of absorbance (A) or transmittance (T)

$$A = \log_{10} 1/T$$

Fundamental modes and types of vibrations: Hooks law;

When Irradiations passed through organic compounds vibrational and rotational energies of the molecule get increases. A non-linear molecule can undergo two kinds of fundamental vibrations.

- 1] Stretching Vibrations
- 2] Bending Vibrations

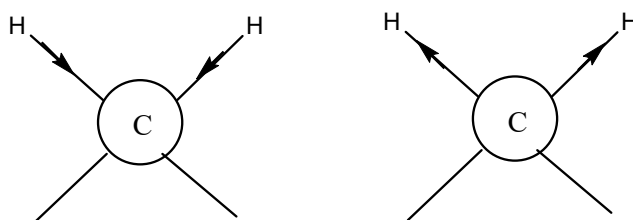
1] Stretching Vibrations:

In this type of vibrations the distance between two atoms increases or decreases but atoms remains in the same bond axis

The two atoms joined together by a chemical bond (may be single, double or triple bond), macroscopically can be composed as two balls joined by a spring. The application of a force like.

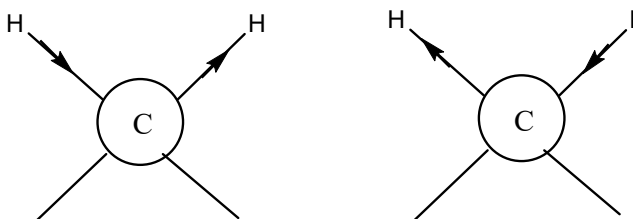
a) Symmetric stretching:

Stretching of both the balls (atoms) away from each other or closer to each other i.e. both atoms expand or compress in the same direction along same bond axis



b) Asymmetric stretching:

Out of two one atom is expanded while the other atom is compressed, so it is asymmetric stretching.



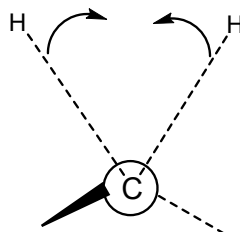
2] Bending vibrations: in this type vibrations the distance between two atoms increases or decreases but the position of atoms changes with respect to the original bond axis.

Bending vibrations are also called as “deformation”

They are as follows

a) Scissoring: [In the plane deformation]

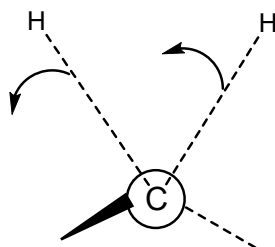
In these type two atoms approaches to each other i.e. bond angle changes.



Scissoring
(δ_s CH₂)
 $\sim 1465\text{ cm}^{-1}$

b) Rocking: [In the plane deformation]

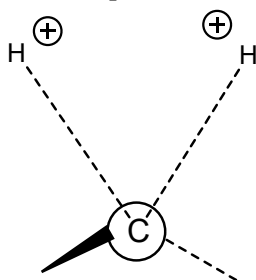
In this type both atoms in the same direction i.e. bond angle remains constant.



rocking
(ρ CH₂)
 $\sim 720\text{ cm}^{-1}$

c) Wagging : [out of plane deformation]

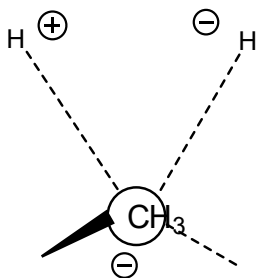
In this type both atoms move up and down (below) in the plane with respect to the centre atom. [bond angle remains constant]



wagging
(τ CH₂)
 $\sim 1350\text{-}1150\text{ cm}^{-1}$

d) Twisting: [out of plane deformation]

In this type one of atom moves up of the plane while other atom moves down in the plane with respect to centre atom. [bond angle changes]



twisting
(ω CH₂)
 $\sim 1350\text{-}1150\text{ cm}^{-1}$

[$\oplus$ and $\ominus$ indicate movement above and below the plane of page]

i) Modes of molecular vibrations

ii) Molecules with large number of atoms possess a large number of vibrational frequencies.

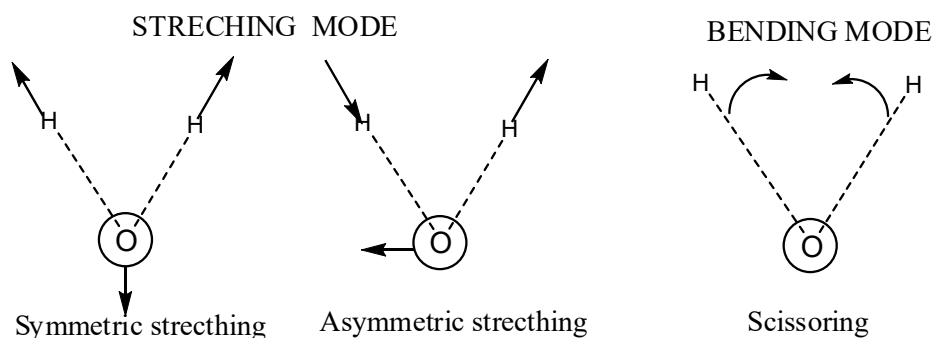


Figure 1 : Vibrational modes for water molecule

Hooke's law and Absorption of radiations

The band positions in the IR spectrum are presented in wave number ($\bar{\nu}$) whose unit is the reciprocal centimeter (cm^{-1}). $\bar{\nu}$ is proportional to the energy of vibration.

$$E = h \bar{\nu} = hc / \lambda = hc \bar{\nu}$$

Therefore, in principle, each of absorption of radiation in the infrared region is quantized and should appear as sharp line. However, each vibrational transition within the molecule is associated with number of rotational energy changes and thus appears as combination of vibrational-rotational bands.

The analogy of a chemical bond with two atoms linked through a spring can be used to rationalize several features of the infrared spectroscopy.

The approximation to vibration frequency of a bond can be made by the application of Hooke's law.

Hooke's law:

In Hooke's law, two atoms and their connecting bond are treated as a simple harmonic oscillator composed of two masses joined by a spring and frequency of vibration is stated as

$$\bar{\nu} \propto \frac{\text{bond strength}}{\text{mass}}$$
$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{K}{m_1 m_2 / (m_1 + m_2)}} \quad \text{----- equation (1)}$$

Where, $\bar{\nu}$ = the vibrational frequency (cm^{-1})

c = velocity of light (cm/s)

K = force constant of the bond (dyne/cm)

m_1 and m_2 = masses of the two atoms

The quantity $(m_1 \times m_2) / (m_1 + m_2)$ is often expressed as μ , the reduced mass of the system.

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu}} \quad \text{----- equation (2)}$$

Since according to equation (2) ———

$$\bar{\nu} \propto \sqrt{k}$$

Therefore, the vibrational frequency of a bond would increase with the increase in bond strength. Consequently, we can expect that C=C and C=O stretching will have higher frequencies than C-C and C-O stretching, respectively. Also,

$$\bar{\nu} \propto \sqrt{\frac{1}{\mu}}$$

Therefore, the vibrational frequency of a bond would increase with the decrease in reduced mass of the system. It implies that C-H and O-H stretching absorptions should appear at higher frequencies than C-C and C-O stretching frequencies. Similarly, O-H stretching should appear at higher frequency than O-D stretching. Further, the stretching of the spring requires more energy than to bend it, the stretching absorption of a band always appear at higher energy than the bending absorption of the same band.

Brief information regarding IR Spectroscopy:

IR Spectrophotometer consists of following components.

1. A source of radiations
2. A monochromator
3. Recording assembly.

1. A source of radiations:

IR Spectrophotometer is a globular rod or Nernst filaments.

Globular rod: is a rod of silicon carbide, and Nernst filament is a mixture of the oxides of Zr, Y, Ce, and Th. These are electrically heated at 1500°C.

2. A Monochromator:

- a) The output from the source can be divided and focused by the two mirrors to produce two beams. Reference beam and sample beam.
- b) Sample beam passes through NaCl cell containing sample and the reference beam passes through reference cell containing only solvent.
- c) These two beams pass through rotating segmented mirror, it alternately allows

light from each of the two beams to enter the monochromator.

- d) A monochromator is made up of crystals of NaCl, CaF_2 OR LiF i.e glass or quartz as they strongly absorb IR RADIATIONS.

3. Recording assembly:

- a) These two beams alternatively passes through electronic amplifier and fall on the detector, which scan the range of IR frequencies.
b) Moving a pen along the corresponding frequencies on the x-axis of chart paper.
c) Higher frequencies (shorter wavelength) appear towards left of paper. Detector signal is proportional to the difference in the intensity of light in sample and reference beam. Detector signal controls movement of pen along y-axis with 100 % transmittance (no absorption) at the top of the paper and 0 % transmittance (absorption of all the light) at the bottom.

Sampling method:

IR Spectra of gaseous and liquid sample can be directly obtained. The spectrum of a solid sample is often best determined as an alkali halide pellet.

About 1-3 mg of the substance and 100-200 mg KBr are ground together, dried to remove moisture and passes at room temperature. Under high pressure into a small disk. Since KBr does not absorb infrared radiation in the region 4000 cm^{-1} - 667 cm^{-1} (2.5 μ to 15 μ) a complete spectrum of sample is obtained.

The spectrum of a solid is also determined in a mull. The most commonly used mulling agent is Nujol. It is a mixture of high molecular weight liquid paraffin. In this method 2.5 mg of sample is ground together with Nujol. In IR spectrum Nujol gives absorption band at 2920 cm^{-1} - 2860 cm^{-1} due to C-H stretching and at 1460 cm^{-1} and 1380 cm^{-1} due to C-H bending. Hence, when Nujol is used as mulling agent no information can be derived about absorption of the sample in this region.

Another mulling agent is hexachloro-butadiene which does not contain any C-H bond. And hence in IR spectrum of the sample, hexachloro-butadiene does not exhibit any absorption bands due to C-H bond.

Conditions for IR absorption: Let us consider how the radiations are being absorbed. At normal temperature, molecules are in constant state of vibrations. The change in dipole moment during vibration of the molecule produces a stationary alternating electric field. When the frequency of incident electromagnetic radiations is equal to the alternating electric field produced by changes in the dipole moment, the radiation is absorbed and vibrational levels of the molecule are excited. Once in the vibrational levels are excited state, the molecules can loose the extra energy by rotational, collision or translational processes etc. and come back to ground state.

Therefore, only those vibrations which result in a rhythmical change in the dipole moment of the molecule absorb infrared radiations and are defined as IR active. The others

which do not undergo change in dipole moment of the molecule are IR inactive e.g. the stretching of a symmetrically substituted bond, viz. C $\equiv$ C in acetylene and symmetrical stretching in carbon dioxide (figure-2) – a linear molecule, produce no change in the dipole moment of the system and these vibrations cannot interact with infrared light and are IR inactive. In general, the functional groups that have a strong dipole give rise to strong absorption bands in the IR.

IR Spectrum: Functional group region and Finger print region:

An infrared spectrum of an organic compound comprises many bands and assigning each band to a particular mode of vibration is practically impossible but two non-identical molecules generally have different IR spectra. An IR spectrum, therefore, is a fingerprint of the molecule.

Fingerprint region:

The region most useful for the purpose of “fingerprinting” of the compound is 650-1350 cm^{-1} . This region comprises a large number of bands due to skeletal vibrations and when the spectrum we are studying coincides exactly with the spectrum of a known compound, it can be safely assumed that the two compounds are identical.

Functional group region:

The region above 1350 cm^{-1} to 4000 cm^{-1} often provides easily recognizable bands of various functional groups and thus known as functional group region.

Functional region is related with vibrationnal changes in the functional groups in the molecule by observing absorption in this range, we can draw some conclusions regarding the functional groups present in the molecule. Hence this region is called the functional group region.

The region from 1400 to 1430 cm^{-1} to the left in an IR spectrum is useful for identification of functional groups.

Fundamental bands:

When molecule absorb IR radiant energy which is equal to the difference between two vibrational energy levels (ΔE_{vib}). Vibrational transition in a molecule takes place. Transition from vibrational ground state to the first excited state give rise to intense bands, called as Fundamental bands.

Overtone: Transition from the ground state to the second excited state with the absorption of infrared radiation gives rise to weak bands, called overtones.

Sr. no.	Functional group	compound	Wave number cm^{-1}
1	O-H	Alcohol, Carboxylic acids	3600-3200
2	$\begin{array}{c} \text{—NH} \\ \end{array}$	Amines and amides	3600-3200
3	$\equiv\text{CH}$	Acetylene	3600-3200
4	$\begin{array}{c} =\text{CH} \\ \end{array}$	Alkenes	3100-3000
5	Ar-H	Aromatic	3100-3000
6	$\begin{array}{c} \\ \text{—CH} \\ \end{array}$	Saturated alkanes	3000-2800
7	C-H band -CHO	Aldehyde	2900-2700
8	—S-H	Thioles	2950-2550
9	$\text{—C}\equiv\text{C—}$	Alkynes	2200-2100
10	$\text{—C}\equiv\text{N}$	Nitriles	2280-2240
11	$\begin{array}{c} \text{—C=O} \\ \end{array}$	Aldehydes, Ketones. Acids, Esters & Amides	1870-1650
12	$\begin{array}{c} \text{—C=C—} \\ \quad \end{array}$	Alkenes	1680-1620
13	$\begin{array}{c} \text{—C}\cdots\text{C—} \\ \quad \end{array}$	Aromatic ring	1600-1400 (4-bands)
14	—NO_2	Nitro compounds	1560-1575 1355-1345
15	$\begin{array}{c} \quad \\ \text{—C—O—C—} \\ \quad \end{array}$	Ethers	1270-1050
16	$\begin{array}{c} \\ \text{—C—X} \\ / \end{array}$	Halo alkanes	750-500

Interpretation of IR Spectra of following organic compounds:

Following points are to be observed while interpreting IR spectrum.

1. Always start interpreting from high frequency and of the spectrum (shorter wavelength 4000 cm^{-1}) use the finger print region 1400 cm^{-1} - 667 cm^{-1} . only for confirmation.
2. Absorption bands due to main functional groups give much information about the structure of the molecule. Total interpretation of IR spectrum is not required.

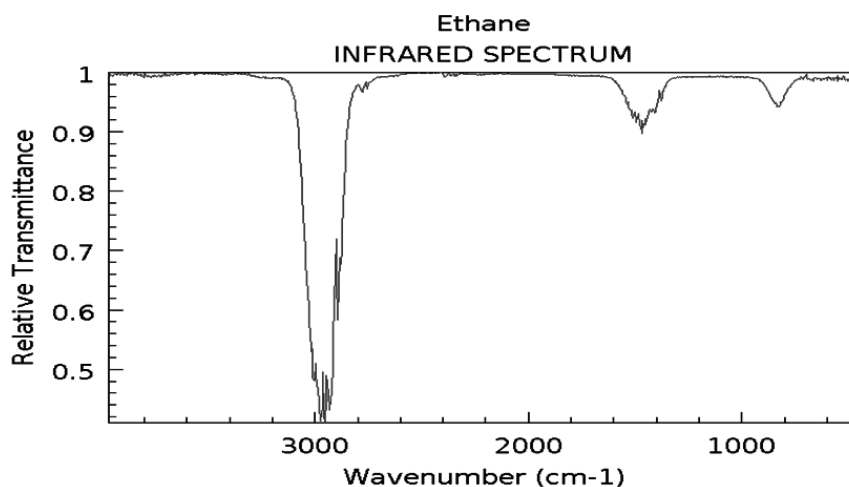
- Always take into consideration negative evidence. Absence of an absorption band due to certain functional groups indicates that molecule does not contain that functional group. Ex. If spectrum does not show absorption band in 1870 cm^{-1} - 1650 cm^{-1} region. The sample does not contain carbonyl group.
- A strong broad band in 3600 cm^{-1} - 3200 cm^{-1} region indicates the presence of -OH group.
- Aromatic compounds show characteristic band due to Ar-H stretching at 3030 cm^{-1} , due to $\text{C}=\text{C}$ STRETCHING IN 1600 cm^{-1} - 1400 cm^{-1} region. and due to C-H bending in 710 cm^{-1} - 690 cm^{-1} region.
Absence of these bands in IR spectrum indicates that compound is aliphatic.

Examples:

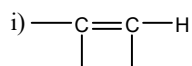
1. Alkanes (ethane) :

Ethane gives two strong absorption bands in high frequency region.

- One band at 2940 cm^{-1} due to -C-H asymmetric stretching.
- Another band at 2880 cm^{-1} symmetric stretching.
- Asymmetric -C-H bending vibrations appears at 1465 cm^{-1} . while
- Symmetric -C-H bending vibrations appears at 1380 cm^{-1} .

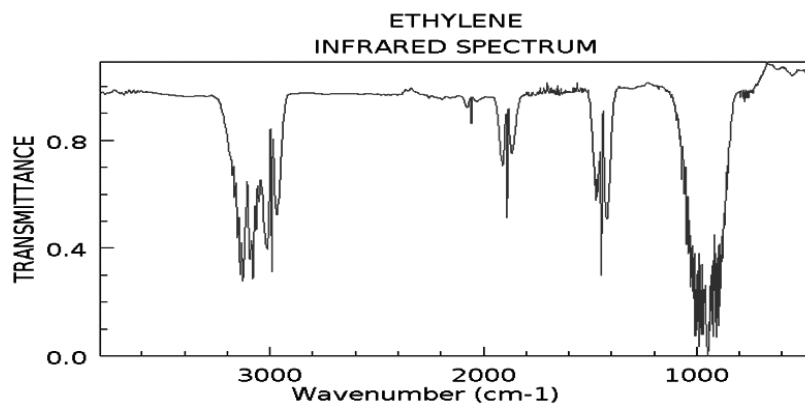


2. Alkene [ethylene]



Stretching strong absorption band appears in the region 3100 cm^{-1} - 3000 cm^{-1}

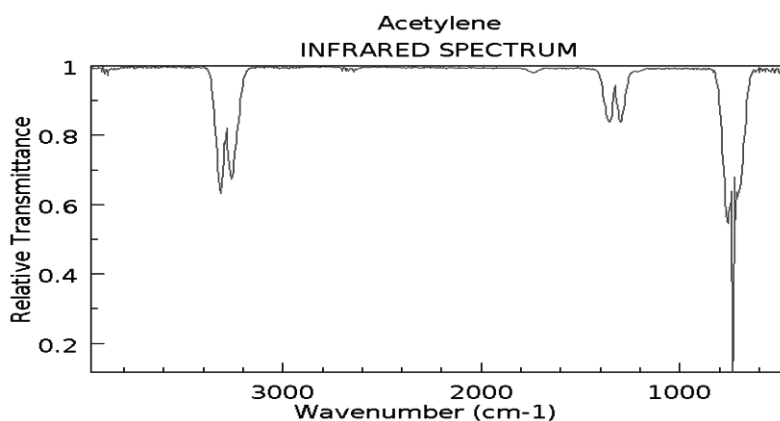
- $\text{C}=\text{C}$ Stretching band appears in the region 1680 cm^{-1} - 1620 cm^{-1} .



3. Alkynes [Ethyne]:

In acetylene, a strong band for $\text{—C}\equiv\text{CH}$ stretching appears at about 3400 cm^{-1} - 3300 cm^{-1} .

And $\text{—C}\equiv\text{C—}$ stretching occurs at 2200 cm^{-1} - 2100 cm^{-1} .



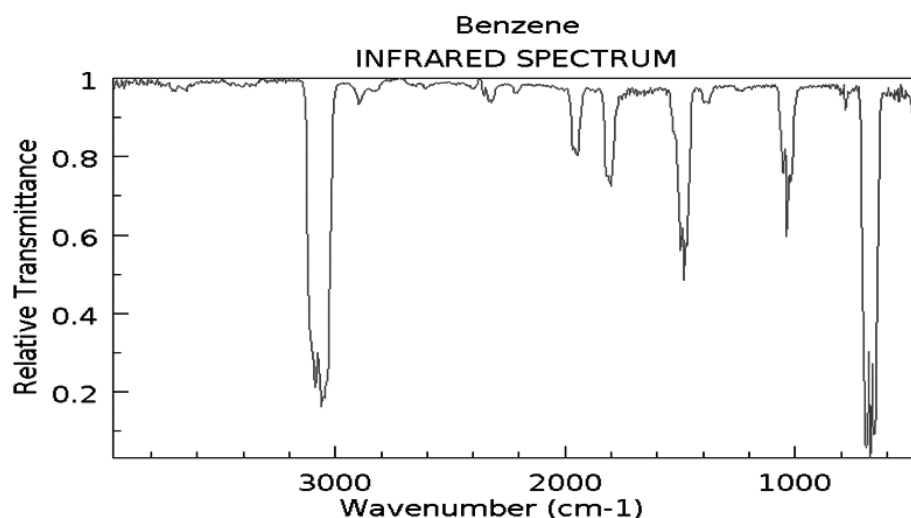
4. Benzene:

In IR Spectrum of benzene, aromatic C-H stretching band occurs in 3100 cm^{-1} region. Absorption bands due to STRETCHING occurs

at 1600 cm^{-1} , 1580 cm^{-1} , 1500 cm^{-1} , 1450 cm^{-1}

In plane C-H bending absorption bands appears in 1300 cm^{-1} - 1000 cm^{-1} region and out of plane.

A C-H bending absorption band appears in 900 cm^{-1} - 675 cm^{-1} region.



5. Alcohols:

The characteristic bands observed in the IR spectra of alcohol result from O-H and C-O stretching.

These vibrations are sensitive to hydrogen bonding. OH group of alcohol is not involved in hydrogen bonding gives sharp band at 3640 cm⁻¹ - 3610 cm⁻¹ region.

A strong broad band appears in 3600 cm⁻¹ - 3200 cm⁻¹ region due to -OH stretching involved in hydrogen bonding.

A primary alcohol shows characteristic strong broad band at 1050 cm⁻¹.

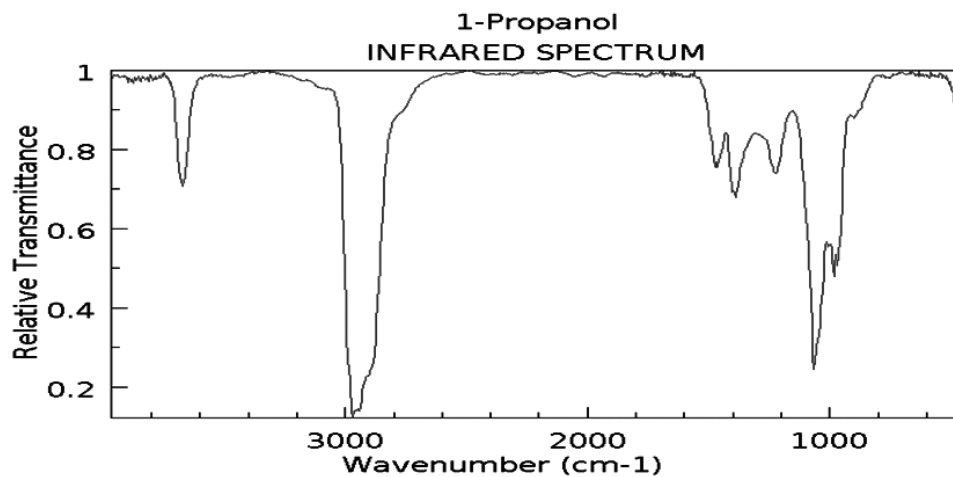
Secondary alcohols shows characteristic strong broad band at 1100 cm⁻¹.

Tertiary alcohols shows characteristic strong broad band at 1150 cm⁻¹. due to C-O stretching.

On the basis of these bands, primary, secondary and tertiary alcohols can be distinguished.

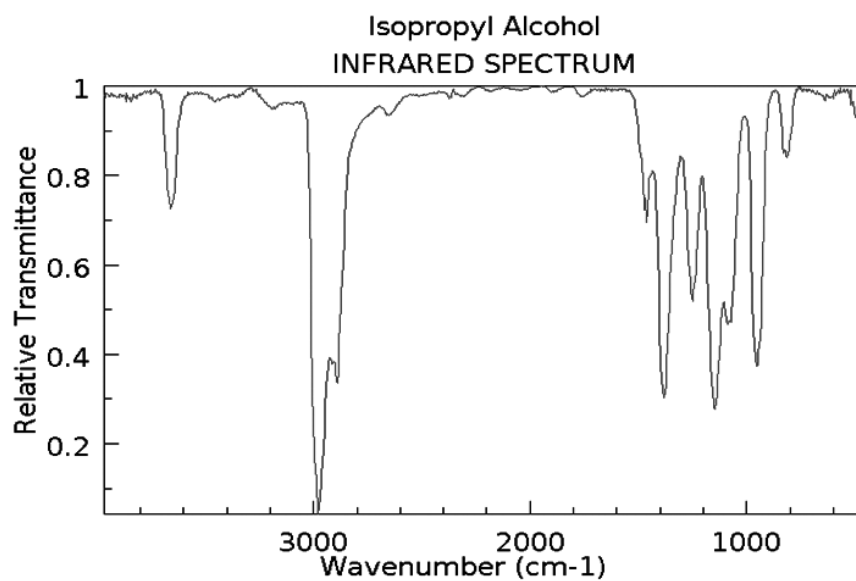
1-Propanol:

A strong broad band appears in 3640 cm^{-1} - 3610 cm^{-1} region due to -OH stretching.
Characteristic strong broad band at 1050 cm^{-1} due to C-O stretching.



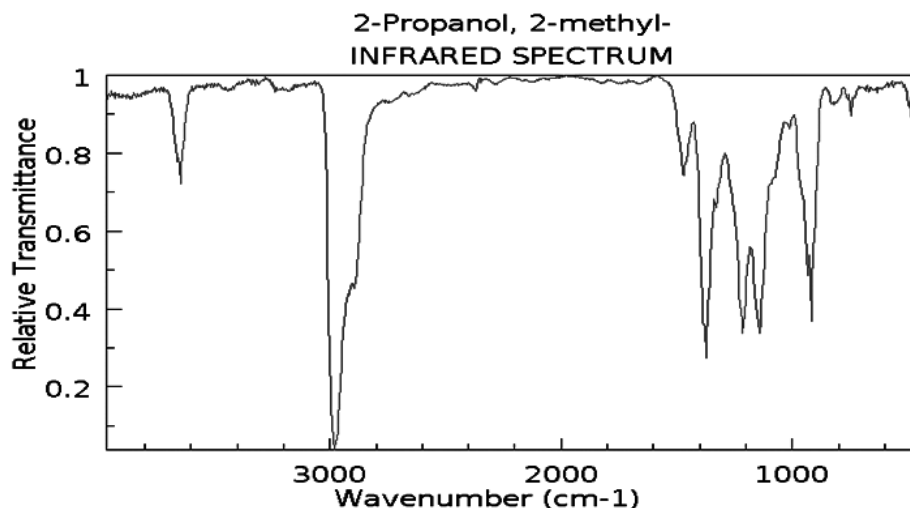
2-Propanol:

A strong broad band appears in 3640 cm^{-1} - 3610 cm^{-1} region due to -OH stretching.
Characteristic strong broad band at 1050 cm^{-1} due to C-O stretching.



2-methyl-2-propanol:

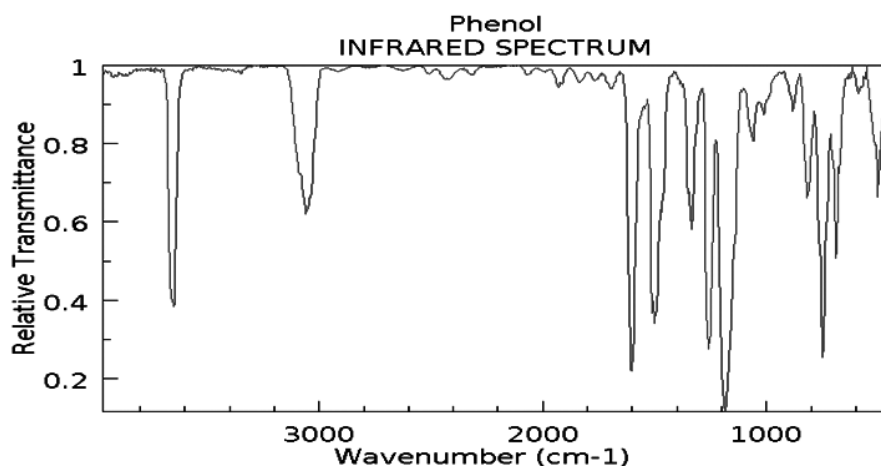
A strong broad band appears in 3640 cm^{-1} - 3610 cm^{-1} region due to -OH stretching.
Characteristic strong broad band at 1150 cm^{-1} due to C-O stretching.



6. Phenol:

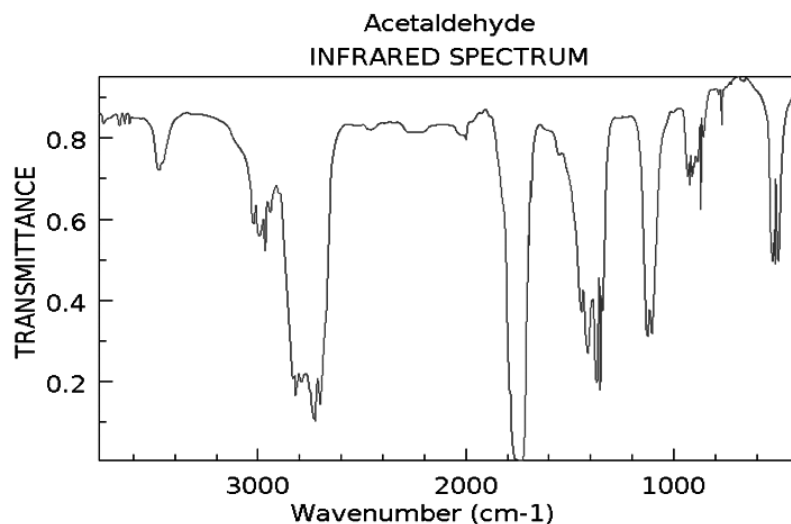
In IR spectrum of phenol,

- i) Aromatic C-H stretching bands occurs in 3100 cm^{-1} - 3000 cm^{-1} region.
- ii) Absorption bands due to STRETCHING occurs
at 1600 cm^{-1} ,
 1580 cm^{-1} ,
 1500 cm^{-1} ,
 1450 cm^{-1}
- iii) A strong broad band appears in 3640 cm^{-1} - 3610 cm^{-1} region due to -OH stretching.
- iv) Out of plane C-H bending absorption bands appears in 900 cm^{-1} - 675 cm^{-1} region.



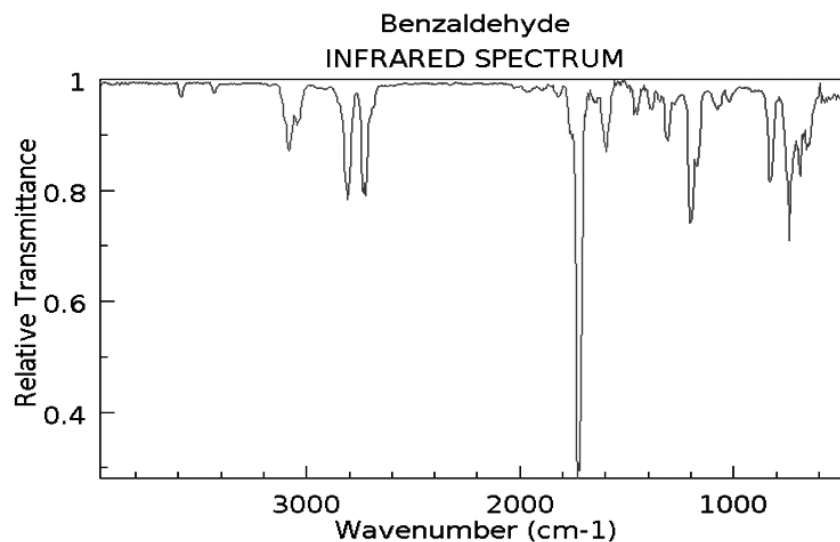
7. Acetaldehyde :

- i) The C=O stretching absorption for acetaldehyde 1745 cm^{-1}
- ii) C-H stretching in methyl group at 2850 cm^{-1} - 2950 cm^{-1} .



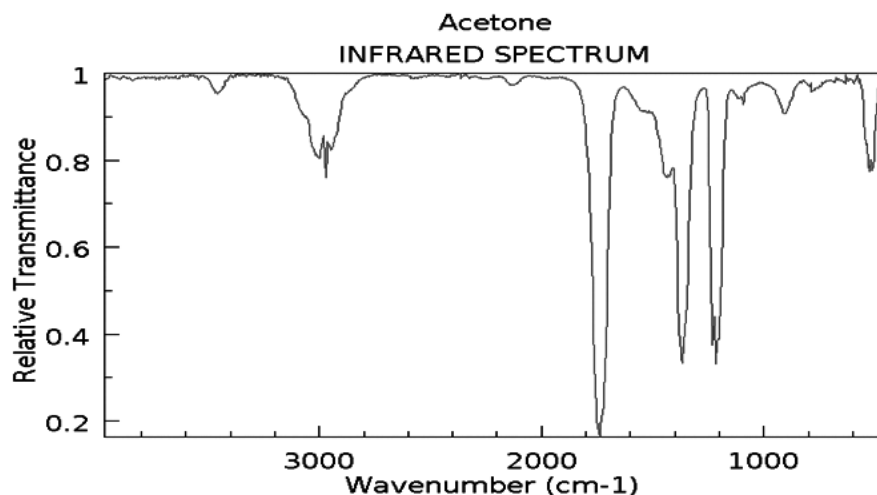
8. Benzaldehyde:

- i) the C=O stretching absorption for benzaldehyde 1700 cm^{-1} .
- ii) Aromatic C-H stretching at 3080 cm^{-1} .
- iii) STRETCHING of aromatic ring 1595 cm^{-1} .
- iv) Characteristic bands of aromatic substitution 745 cm^{-1} .
- v) C-H stretching in aldehyde at 2860 cm^{-1} - 2775 cm^{-1} .



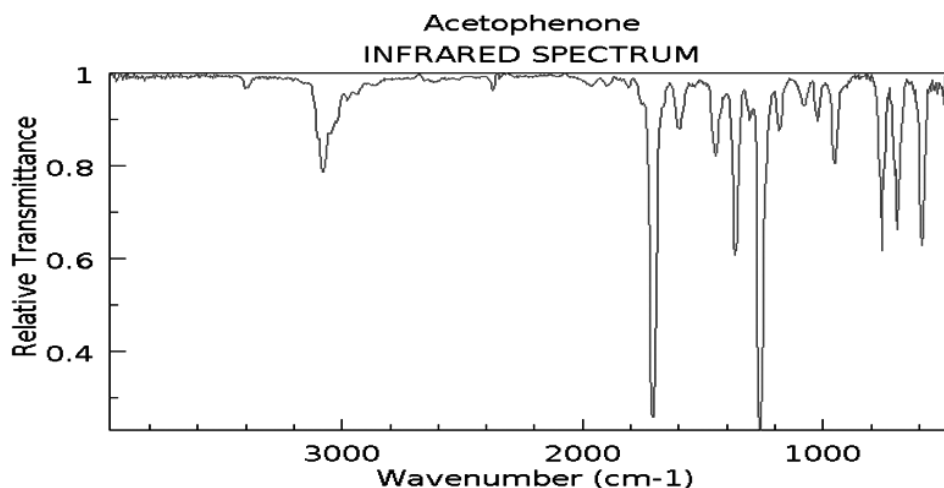
8. Acetone :

- i) The C=O stretching absorption for acetone 1718 cm^{-1} .
- ii) Two weak bands:
C-H stretching (asymmetric) absorption band at 2820 cm^{-1} .
And other C-H stretching (symmetric) absorption band near 2720 cm^{-1} .



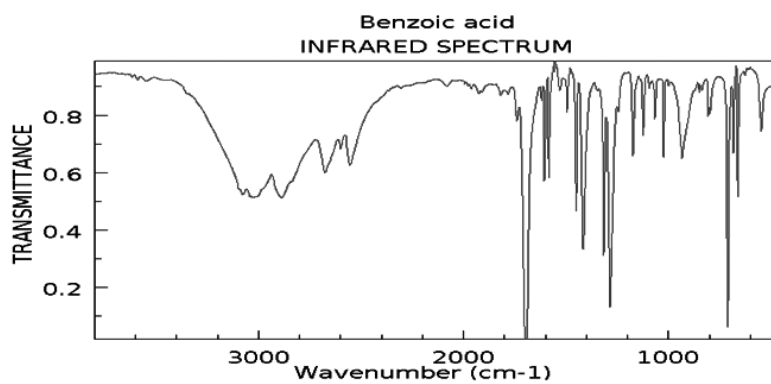
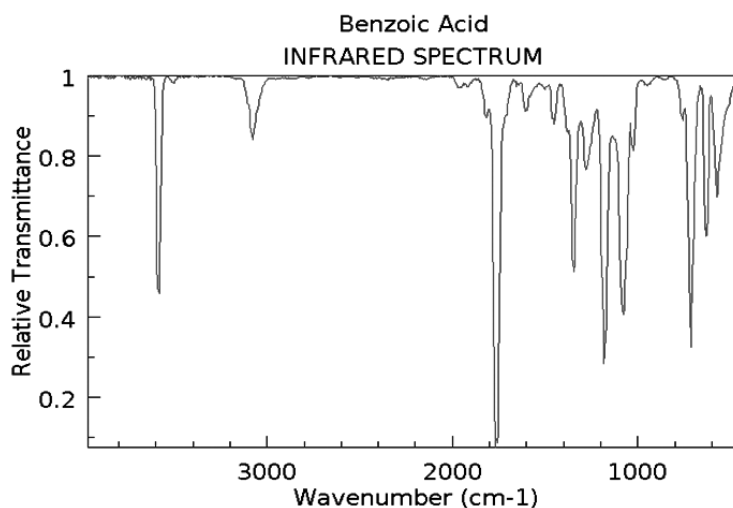
9. Acetophenone:

- i) The C=O stretching absorption for acetophenone 1690 cm^{-1} .
- ii) Aromatic C-H stretching at 3080 cm^{-1} .
- iii) STRETCHING of aromatic ring 1595 cm^{-1} .
- iv) Characteristic bands of aromatic substitution 745 cm^{-1} .
- v) C-H stretching in methyl group at 2850 cm^{-1} - 2950 cm^{-1} .



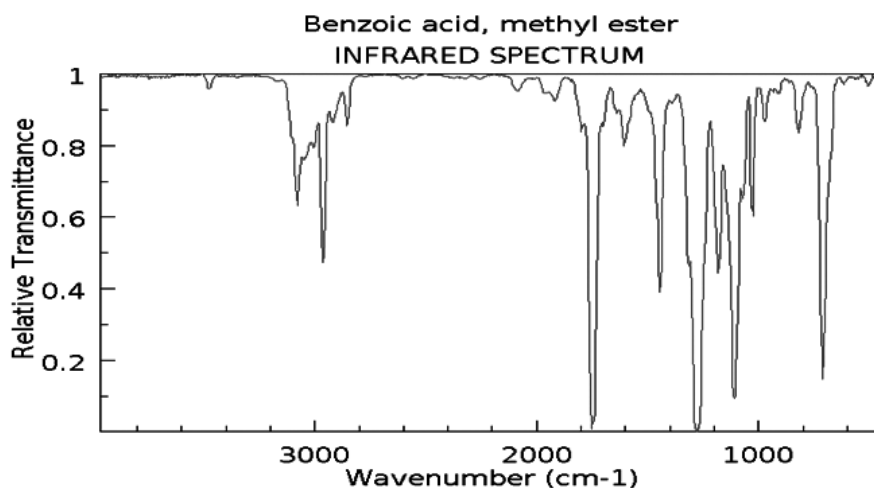
10. Benzoic acid:

- i) Aryl carboxylic acid, C=O stretching at 1700 cm^{-1} - 1680 cm^{-1} .
- ii) Carboxylic acid ,O-H stretching 3000 cm^{-1} - 2500 cm^{-1} .
- iii) STRETCHING of aromatic ring 1600 cm^{-1} - 1400 cm^{-1} .
- iv) Aromatic C-H stretching 3080 cm^{-1} .
- v) Characteristic bands of aromatic substitution 745 cm^{-1} .



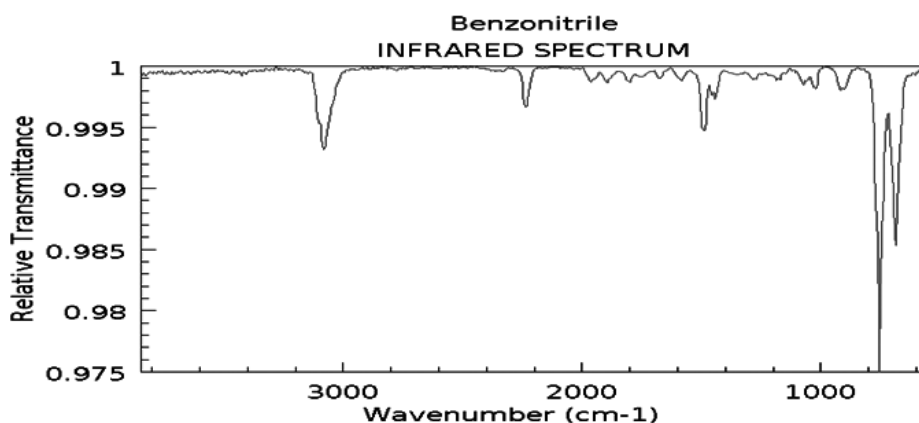
11. Methyl benzoate:

- i) Aryl ester, C=O stretching at 1730 cm^{-1} - 1715 cm^{-1} .
- ii) Carboxylic acid, O-H stretching 3000 cm^{-1} - 2500 cm^{-1} .
- iii) STRETCHING of aromatic ring 1600 cm^{-1} - 1400 cm^{-1} .
- iv) Aromatic C-H stretching 3080 cm^{-1} .
- v) Characteristic bands of aromatic substitution 745 cm^{-1} .



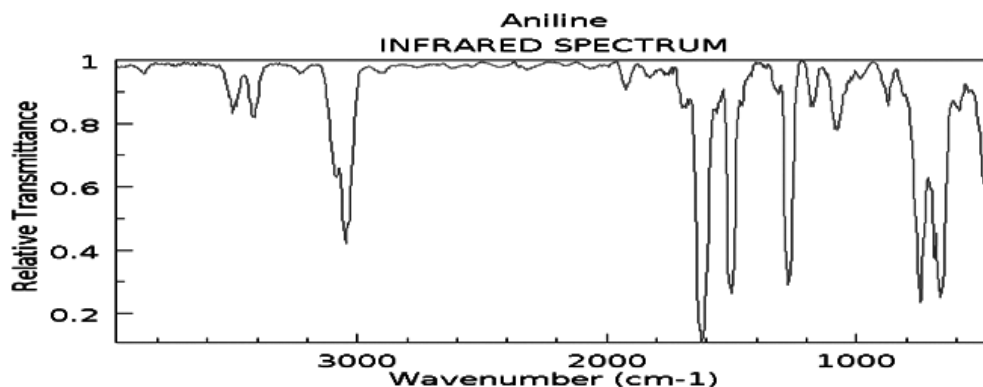
12. Phenyl cyanide: [Benzonitrile]

- i) Benzonitrile, stretching at 2230 cm^{-1} .
- ii) STRETCHING of aromatic ring 1600 cm^{-1} - 1400 cm^{-1} .
- iii) Aromatic C-H stretching 3080 cm^{-1} .
- iv) Characteristic bands of aromatic substitution 745 cm^{-1} .



13. Aniline:

- i) N-H stretching at 3600-3200.
- ii) Stretching of aromatic ring 1600 cm^{-1} - 1400 cm^{-1} .
- iii) Aromatic C-H stretching 3080 cm^{-1} .
- iv) Characteristic bands of aromatic substitution 745 cm^{-1} .



QUESTION BANK

- Q1. Explain the stretching and bending vibrations in I.R spectroscopy.
- Q2. State and explain the Hookes law.
- Q3. Give the brief information regarding I. R spectroscopy.
- Q4. Give the sampling method in I. R spectroscopy.
- Q5. Explain the following terms
- 1. Functional group region 2. Finger print region
 - 3. Fundamental bands 4. Overtones
- Q6. How will you distinguish 1-propanol, 2-propanol and 2-methyl-2-propanol?
- Q7. How will you interpret I.R. spectra of following compounds?
- i) Benzene ii) Phenol iii) Acetophenone
- Q8. How will you interpret I.R. spectra of following compounds?
- i) Ethane ii) Ethane iii) Ethyne
- Q9. How will you interpret I.R. spectra of following compounds?
- i) Acetaldehyde ii) Acetone iii) 1-propanol
- Q10. How will you interpret I.R. spectra of following compounds
- i) Benzaldehyde ii) Benzoic acid iii) Methyl benzoate.

...

Unit : III

Nuclear Magnetic Resonance Spectroscopy

Introduction

NMR or Nuclear Magnetic Resonance spectroscopy is a powerful and theoretically complex analytical tool. The chemical environment of specific nuclei is gathered from information obtained about the nuclei. NMR is a technique used to determine a compound's unique structure. It identifies the carbon-hydrogen (^1H -NMR), carbon- carbon (^{13}C -NMR) framework of an organic compound. Using this method and other instrumental methods including infrared and mass spectrometry, scientists are able to determine the entire structure of a molecule.

Principles of NMR spectroscopy

Nuclear spin and the splitting of energy levels in a magnetic field

Subatomic particles (electrons, protons and neutrons) can be imagined as spinning on their axis. In many atoms (such as ^{12}C) these spins are paired against each other, such that the nucleus of the atom has no overall spin. However, in some atoms (such as ^1H and ^{13}C) the nucleus does possess an overall spin. The rules for determining the net spin of a nucleus are as follows;

1. If the number of neutrons **and** the number of protons are both even, then the nucleus has **no spin**.
2. If the number of neutrons **plus** the number of protons is odd, then the nucleus has a half-integer spin (i.e. $1/2$, $3/2$, $5/2$)
3. If the number of neutrons **and** the number of protons is both odd, then the nucleus has an integer spin (i.e. 1, 2, 3) For ex.
 - 1] $^{12}_6\text{C}$, $^{16}_8\text{O}$, $^{32}_{16}\text{S}$ etc. those have spin quantum number zero, such nuclei have no angular momentum and magnetic properties.
 - 2] ^1H , ^{13}C , ^{14}N , ^{19}F , ^{31}P etc. possesses mass number = $1/2, 3/2, 5/2, \dots$.
 - 3] ^2H , ^{14}N etc. have spin quantum number = 1, 2, 3, $\dots$

Their NMR is difficult to study.

The overall spin, I , is important. Quantum mechanics tells us that a nucleus of spin I will have $2I + 1$ possible orientations.

A nucleus with spin $1/2$ will have 2 possible orientations in the absence of an external magnetic field, these orientations are of equal energy. If a magnetic field is applied, then the energy levels split. Each level is given a *magnetic quantum number*, m .

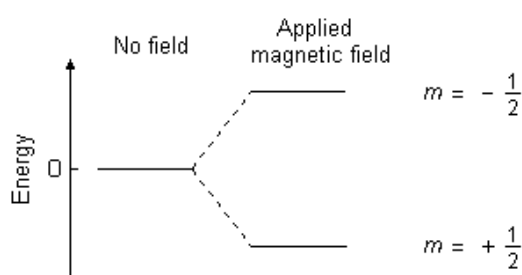
The atomic nucleus is a spinning charged particle, and it generates a magnetic field. Without

an external applied magnetic field, the nuclear spins are random and spin in random directions. But, when an external magnetic field is present, the nuclei align themselves either with or against the field of the external magnet.

Spin state: Protons that align with the external magnetic field. They are in a lower energy state.

Spin state: Protons that align against the external magnetic field. They are in a higher energy state.

Energy levels for a nucleus with spin quantum number 1/2



When the nucleus is in a magnetic field, the initial populations of the energy levels are determined by thermodynamics, as described by the Boltzmann distribution. This is very important, and it means that **the lower energy level will contain slightly more nuclei than the higher level**. It is possible to excite these nuclei into the higher level with electromagnetic radiation. The frequency of radiation needed is determined by the difference in energy between the energy levels.

Calculating transition energy - The nucleus has a positive charge and is spinning. This generates a small magnetic field. The nucleus therefore possesses a magnetic moment, μ , which is proportional to its spin, I .

$$\mu = \frac{\gamma I \hbar}{2 \pi}$$

The constant, γ , is called the *magnetogyric ratio* and is a fundamental nuclear constant which has a different value for every nucleus. $\hbar$ is Planck's constant.

The energy of a particular energy level is given by;

$$E = - \frac{\gamma \hbar}{2 \pi} m B$$

Where B is the strength of the magnetic field **at the nucleus**.

The difference in energy between levels (the transition energy) can be found from

$$\Delta E = \frac{\gamma \hbar B}{2 \pi}$$

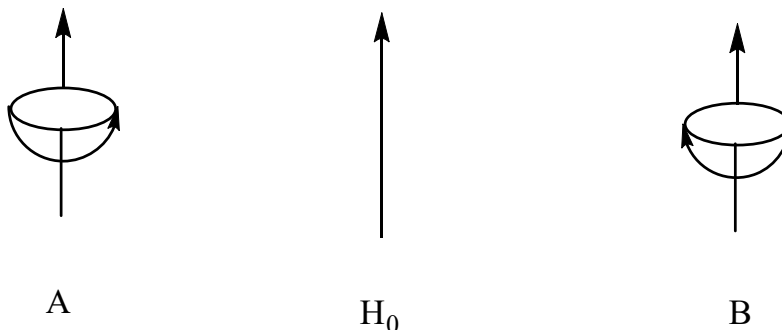
This means that if the magnetic field, B , is increased, so is ΔE . It also means that if a nucleus has a relatively large magnetogyric ratio, then ΔE is correspondingly large.

Orientation of Hydrogen Nucleus and Precessional motion of nuclei :

Nuclei of hydrogen has one proton may be regarded as spinning +vely charged unit. Since its spinning generate a tiny magnetic field (H) along its spinning axis

If this spinning nucleus is placed in an external magnetic field (H_0). its magnetic moment can be parallel to (A) or anti parallel to (B). to the direction of applied field. Parallel arrangement (A) is of lower energy and more stable due to applied magnetic field. Hydrogen nucleus absorb energy and flip the tiny proton magnet over the less stable arrangement (B) and energy required for flipping depends upon strength of applied magnetic field.

The nucleus absorbs this energy in the form of electromagnetic radiations (radio waves) or desirable frequency.

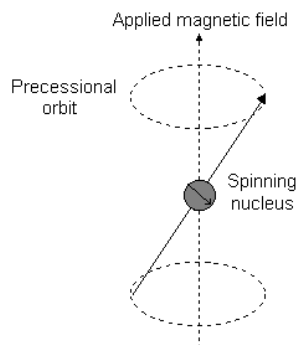


Applied magnetic field

Since nucleus is spinning, its rotation axis draws out a circle perpendicular to the applied field this motion of nucleus is called precessional or gyroscopic motion.

Let us consider that, the nucleus is spinning to give rise a magnetic moment μ . When nucleus is placed in power full uniform magnetic field (H_0) whose direction makes an angle θ with the axis of nuclear magnet . the external magnetic field exert a torque on the nucleus and nucleus precesses around the direction of the applied field.

When frequency of the rotating magnetic field and the frequency of precessing nucleus becomes equal , they are said to be in resonance and absorption or emission of energy by the nucleus occur.



The angular velocity of this precession is given by

$$\omega_0 = H_0 r$$

H_0 is applied magnetic field, r = gyrometric ratio.

$$\text{Angular frequency} = 2\pi \times \text{linear frequency} = 2\pi r$$

$$\text{Angular velocity} = 2\pi r = H_0$$

$$\text{Linear frequency} = H_0 / 2\pi$$

By applying a definite quantum energy $h\nu$, it is possible to flip a parallel orientation of nucleus to an antiparallel orientation in a given magnetic field of strength H_0 .

Instrumentation and Experimental procedure:

NMR Spectrophotometer consists of following four parts.

1. Powerful Magnet
2. Sweep Generator
3. Radio frequency oscillator.
4. Radio frequency detector.

1. Powerful magnet:

A powerful magnet generates a very strong homogenous field, order about 14,000 gauss is generally used.

2. Sweep generator:

It is used to supply D.C current to secondary small magnet. It also helps to vary the total applied field over a small range.

3. Radio frequency oscillator:

This coil is kept perpendicular to magnetic field and transmits radio-waves of some fixed frequency in the order of 60 or 1000 or 220MHz.

4. Radio frequency detector:

This coil is kept perpendicular to both the magnetic and oscillator coil. When the precessional frequency matches with radio frequency, the nuclei induce an e.m.f in the detector coil. The signal is amplified and sends to the detector, where graph is plotted.

Procedure:

The substance (20-25 mg) is dissolved in proper solvent [solvent is used CCl_4 , CS_2 , CDCl_3 , pyridine, trifluoroacetic acid, dimethyl sulphoxide etc. most ideal solvent is CCl_4] is placed in sample tube. The tube is kept between two magnet faces, which supply a strong magnetic field, at certain field strength. The energy required to flip the proton matches the energy of radiation absorption of energy is detected by appearances of signal in the spectrum. i.e. NMR spectrum.

Equivalent and non-equivalent protons

Chemically Equivalent Protons are protons that are in the same environment, and they must be identical in every way. They experience the same magnetic force, and therefore, will create overlapping signals on the spectrum. Each group of chemically equivalent protons gives rise to a signal. Therefore, we can determine how many sets of

equivalent protons there are in a molecule by looking at the number of signals (peaks) in its ^1H -NMR spectrum.

How do we determine how many equivalent protons there are?

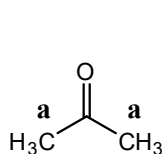
Protons that are aligned on a line of symmetry are equivalent. Another way is to replace the proton with deuterium to form two molecules, and if the two molecules are the same, then the two protons are equivalent. The third way to determine how many equivalent protons there are is to look at the atom attached to the proton (usually a carbon) and observe what that atom is bonded to, and then the atom bonded to that, all the way until a difference is observed. If there is no difference, the protons are equivalent. If there is a difference, the protons are not equivalent.

Are protons on the same carbon always equivalent?

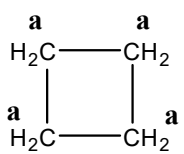
No. Usually, protons on the same carbon are equivalent. But, sometimes, they are not equivalent because they are not in the same environment. One proton could be trans and the other proton could be cis. This would create two different signals.

How many different absorption (signals) in the following compounds:

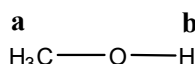
- a) Acetone b) Cyclobutane c) Methanol d) Diethylether e) Ethylamine f) Ethylbenzene g) Mesitylene



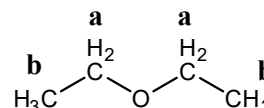
a) Acetone
(One signal)



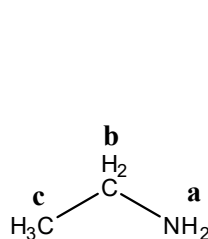
b) Cyclobutane
(One signal)



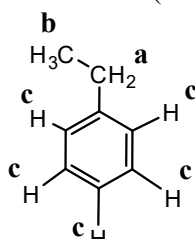
c) Methanol
(Two signal)



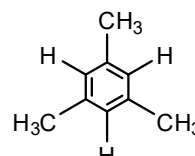
d) Diethylether
(Two signal)



e) Ethyl amine
(Three signal)

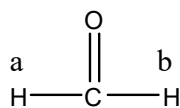


f) Ethylbenzene
(Three signal)

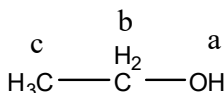


g) Mesitylene
(Two signal)

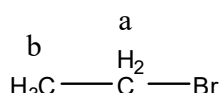
Number of absorption (signals) of a) Acetone b) Cyclobutane c) Methanol
d) Diethylether e) Ethylamine f) Ethylbenzene g) Mesitylene



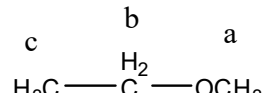
two signals



three signal



two signal



three signal

Position of Signals

The positions of the signals in an NMR spectrum are based on how far they are from the signal of the reference compound. This information tells us the kind of proton or protons that are responsible for the signal. Reference compound – Tetra-methylsilane (TMS) is usually used as the reference compound because it can easily be removed from the sample by evaporation due to its volatile properties. TMS is at a lower frequency than most other signals because its methyl protons are in a more electron dense environment than most protons are because silicon is less electronegative than carbon (which is a significant component of organic molecules). The position of the signals depends on the chemical shift.

Chemical Shift:

“The position of the PMR signals, shift from the position, at which proton should be absorbed in absence of shielding or deshielding effects . as this shift caused by the circulation of electrons in chemical bond” these are termed as **chemical shift**.

Thus, chemical shift is the position along the PMR spectrum at which resonance occurs for a particular nucleus in specific molecular environment.

It is a measure of how far the signal produced from the proton is from the reference compound signal, and it usually measured using the δ (delta) scale. The TMS or reference compound is at the zero position on the very left of the spectrum, and as it moves toward the left, the ppm values become larger. Ppm stands for parts per million, and it is the unit used to measure chemical shift. Proton chemical shifts cover a range of over 30 ppm, but the vast majorities appear in the region $\delta = 0\text{-}10$ ppm, where the origin is the chemical shift of tetramethylsilane. The chemical shift is identical for a specific proton regardless of the spectrometer used. The formula for the chemical shift is

$$\delta = \frac{[\nu_o(\text{H}) - \nu_o(\text{TMS})]}{[\text{Spectrometer Frequency in MHz}]}$$

Chemical shifts of all nuclei should be reported using δ values, with frequency and δ increasing from right to left. Many early papers on proton and multinuclear NMR used the opposite convention (not to mention other references) - in particular the τ scale was used in the early days on which tetramethylsilane (TMS) is taken as 10.0 ppm. Most τ values lie between ‘0’ and ‘10’ but there are some nuclei having negative τ values related by expression $\delta = 10 - \tau$.

Shielding and deshielding protons:

Shielding of protons:

When a molecule is placed in a magnetic field, electrons of molecule carrying -ve charge under the influence of external magnetic field and will circulate and circulating will generate their own magnetic field and this generated magnetic field is known as induced magnetic field. Which may be either reinforce or oppose the applied magnetic field.

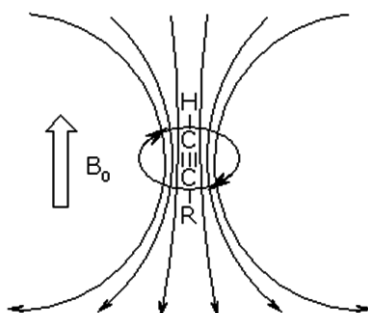
If induced magnetic field oppose the applied field the protons requires a stronger magnetic field to give a PMR signal, then the proton is said to be shielded and such protons experiences diamagnetic shielding.

The shielded protons requiring a stronger external magnetic field for giving PMR signal is said to absorb up field.

For ex. Acetylene molecule.

Acetylene molecule is linear and triple bond is symmetrical about the axis, if this axis aligned (bring to correct positions) with the applied external magnetic field (H_0) π electrons of the bond can circulate at right angle to the applied field, these circulating π electrons generate induced magnetic field, which oppose the external magnetic field (H_0) since protons lie along the magnetic axis of (H_0).

The magnetic lines of force generated by induced magnetic field of π electrons all to shield the protons.



Obviously, shielded protons of acetylene require a strong external magnetic field (H_0) for giving the PMR signal and hence due to shielding effect, PMR signal of acetylene proton is observed at higher field strength (up field)

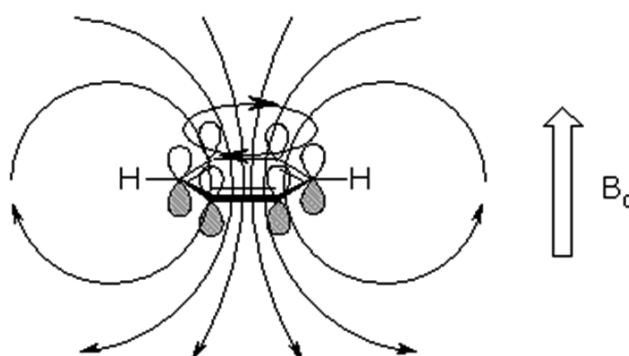
Deshielding of protons:

If induced magnetic field generated by circulating electrons, reinforces (increases) the applied magnetic field. The effective field strength which protons experiences, increases and protons require very a smaller applied field to give the PMR signal, since it requires only a smaller applied field, it is said to be absorb down field. Such protons is called deshielded proton and it experiences paramagnetic deshielding.

For ex. Benzene

Benzene is planar hexagonal molecule and lies in horizontal plane, π electrons cloud

lies above and below the plane of the benzene ring. Due to circulation of π electrons induced magnetic field is generated. Due to horizontal planar structure of benzene, protons of benzene lie in the region, where direction of magnetic lines of force of induced magnetic field and applied field are same. Hence benzene protons experience paramagnetic deshielding. This proton requires smaller applied field to give PMR signal. Hence due to deshielding effect, in benzene PMR signal of aromatic protons appears at lower field strength (down field).

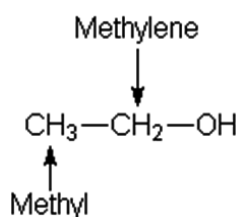


Magnetic anisotropy of an aromatic ring.

Spin - spin coupling : splitting of signals:

Coupling constant:

Consider the structure of ethanol;



The ^1H NMR spectrum of ethanol shows the methyl peak has been split into three peaks (a *triplet*) and the methylene peak has been split into four peaks (a *quartet*). This occurs because there is a small interaction (*coupling*) between the two groups of protons. The spacing between the peaks of the methyl triplet is equal to the spacing between the peaks of the methylene quartet. This spacing is measured in Hertz and is called the **coupling constant, J**.

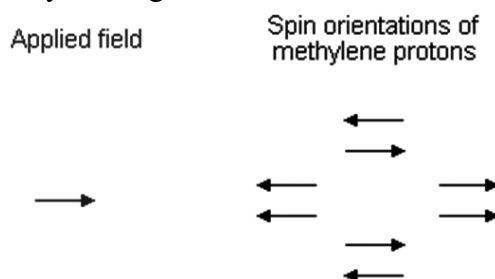
Splitting of signals:

Each signal in the spectrum represents one set of protons in a molecule. It is found that in certain molecules a single peak (singlet) is not observed but instead, a multiplet (a group of peak) is observed.

For ex. A molecule of $\text{H}_3\text{C}-\overset{\text{b}}{\underset{\text{a}}{\text{C}}}\text{H}_2-\text{Br}$ has two kinds of protons in it. It is expected that its PMR spectrum shows triplet (a) protons for CH_3 and quartet for (b) protons i.e. ($-\text{CH}_2-$)

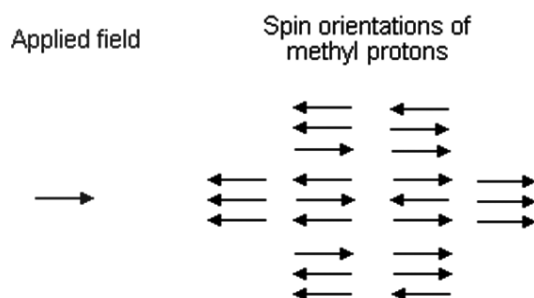
Splitting of PMR signal is called spin-spin coupling and splitting of signal is caused by the magnetic influence of hydrogens on adjacent atoms.

In $\text{H}_3\text{C}-\overset{\text{b}}{\underset{\text{a}}{\text{C}}}\text{H}_2-\text{Br}$ molecule, the spin of two protons ($-\text{CH}_2-$) can couple with the adjacent methyl group ($-\text{CH}_3$) in three different ways relative to the external magnetic field. The three different ways of alignment are as follows.

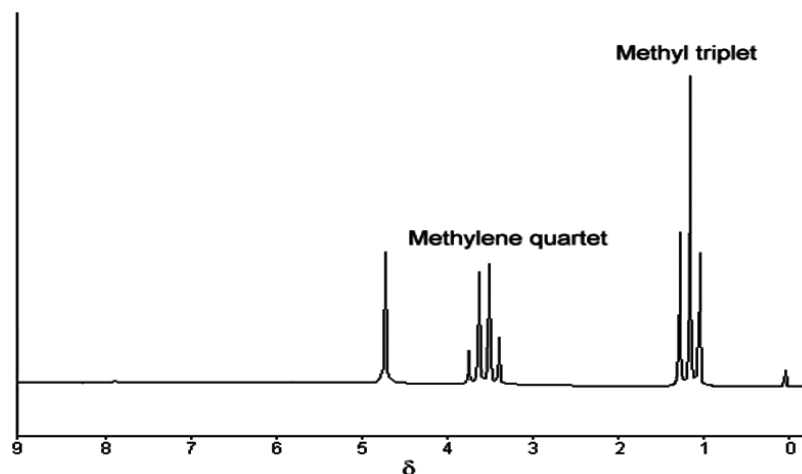


Thus, signal for $-\text{CH}_3$ protons (a) will be split into three peaks (triplets) which are equally spaced with peak intensities 1:2:1.

Similarly, the spin of three protons of $-\text{CH}_3$ group can couple with adjacent methylene group ($-\text{CH}_2-$) in four different ways relative to the external magnetic field.



Thus, signal from ($-\text{CH}_2-$) 'b' protons will be split into four peaks (quartet) which are equally spaced with peak intensities 1:3:3:1.



For ex. (2)

Similarly, PMR spectrum of 1,1-dibromoethane $\text{CH}_3\text{-CHBr}_2$ shows quartet for -CH protons (b-protons) because neighbouring protons are three and doublet for -CH_3 protons (a-protons) because neighbouring protons is one.

Thus, in general 'a' set of 'n' equivalent protons split up a signal (due to neighbouring protons) into a group of (n+1) peaks.

In a *first-order* spectrum (where the chemical shift between interacting groups is much larger than their coupling constant), interpretation of splitting patterns is quite straightforward;

- The multiplicity of a multiplet is given by the number of equivalent **protons in neighbouring atoms (n)** plus one, i.e. *the n + 1 rule*
- Equivalent nuclei do not interact with each other. The three methyl protons in ethanol cause splitting of the neighboring methylene protons; they do not cause splitting among themselves
- The coupling constant is not dependant on the applied field. Multiplet can be easily distinguished from closely spaced chemical shift peaks.

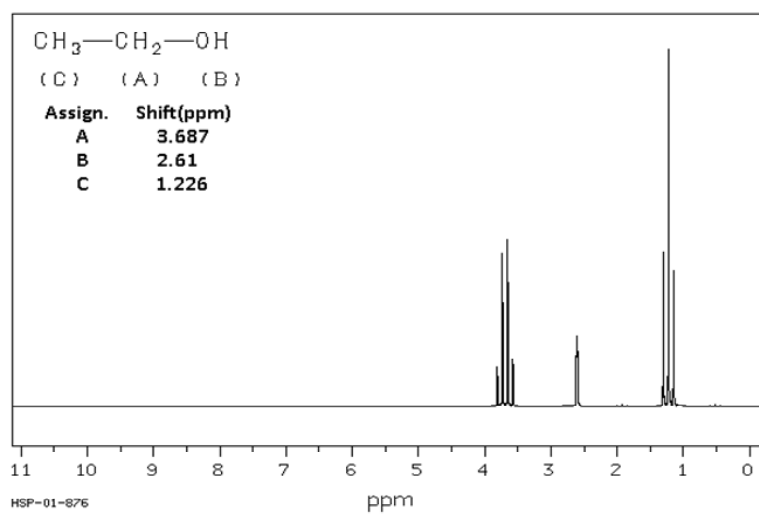
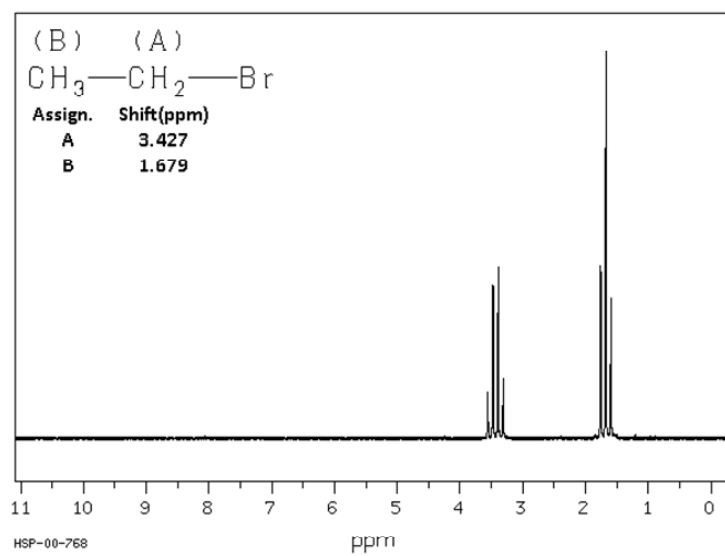
Magnitude of Some Typical Coupling Constants

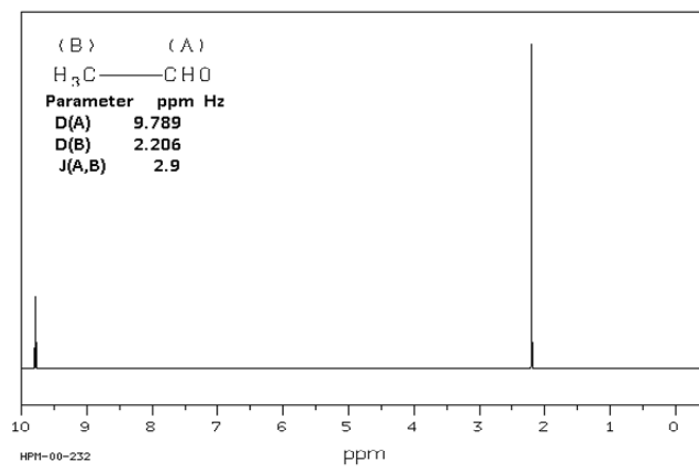
Structural Type	J (Hz)	Structural Type	J (Hz)
	0 (unless in a rigid ideal orientation)		12 to 18
$\text{H}_3\text{C}-\text{CH}_2-\text{X}$	6 to 8		7 to 12
	5 to 7		0.5 to 3
	2 to 12 (depends on dihedral angle and the nature of X and Y)		3 to 11 (depends on dihedral angle)
	0.5 to 3		2 to 3
	12 to 15 (must be diastereotopic)		o 6 to 9 m 1 to 3 p 0 to 1

Spin 1/2 nuclei include ^1H , ^{13}C , ^{19}F & ^{31}P . The spin-coupling interactions described above may occur between similar or dissimilar nuclei. If, for example, a ^{19}F is spin-coupled to a ^1H , both nuclei will appear as doublets having the same J constant. Spin coupling with nuclei having spin other than 1/2 is more complex and will not be discussed here.

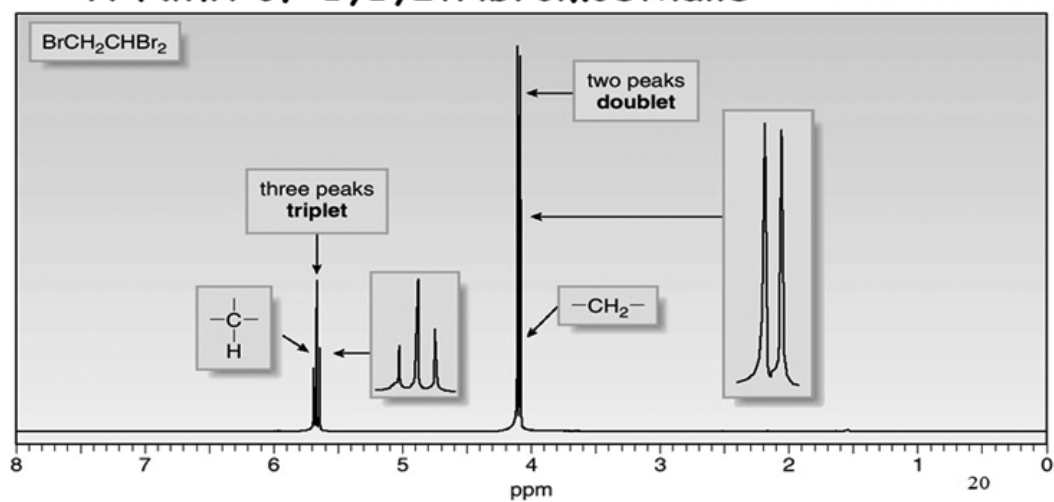
Table of Characteristic Proton NMR Shifts

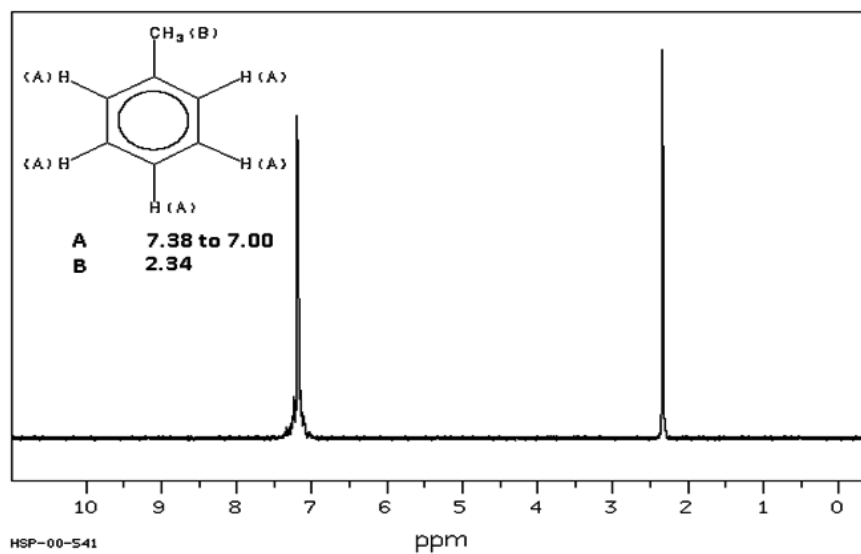
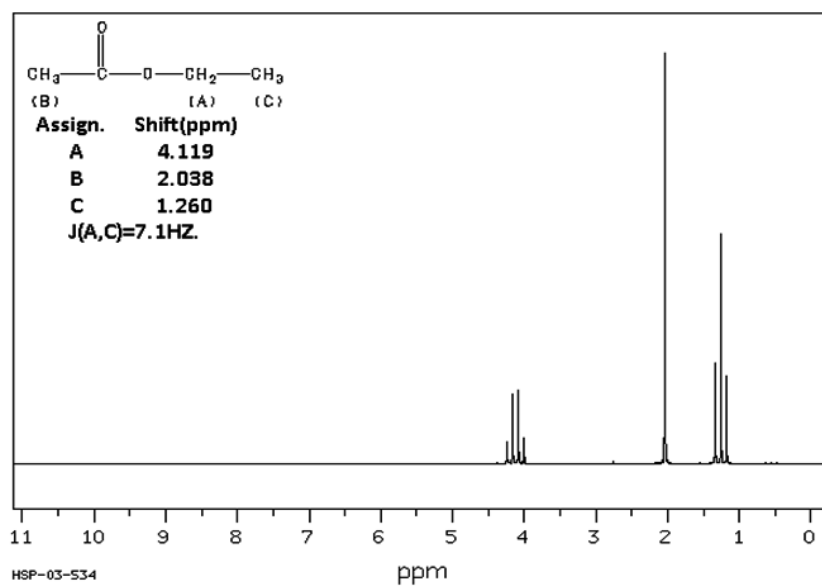
<i>type of proton</i>	<i>type of compound</i>	<i>chemical shift range, ppm</i>
RCH_3	primary aliphatic	0.9
R_2CH_2	secondary aliphatic	1.3
R_3CH	tertiary aliphatic	1.5
$\text{C}=\text{C}-\text{H}$	vinyllic	4.6-5.9
$\text{C}=\text{C}-\text{H}$	vinyllic, conjugated	5.5-7.5
$\text{C}(\text{triple bond})\text{C}-\text{H}$	acetylenic	02-Mar
$\text{Ar}-\text{H}$	aromatic	6-8.5
$\text{Ar}-\text{C}-\text{H}$	benzylic	2.2-3
$\text{C}=\text{C}-\text{CH}_3$	allylic	1.7
$\text{HC}-\text{F}$	fluorides	4-4.5
$\text{HC}-\text{Cl}$	chlorides	03-Apr
$\text{HC}-\text{Br}$	bromides	2.5-4
$\text{HC}-\text{I}$	iodides	02-Apr
$\text{HC}-\text{OH}$	alcohols	3.4-4
$\text{HC}-\text{OR}$	ethers	3.3-4
$\text{RCOO}-\text{CH}$	esters	3.7-4.1
$\text{HC}-\text{COOR}$	esters	2-2.2
$\text{HC}-\text{COOH}$	acids	2-2.6
$\text{HC}-\text{C}=\text{O}$	carbonyl compounds	2-2.7
RCHO	aldehydic	09-Oct
ROH	hydroxylic	02-Apr
ArOH	phenolic	04-Dec
$\text{C}=\text{C}-\text{OH}$	enolic	15-17
RCOOH	carboxylic	10.0-13.2
RNH_2	amino	01-May

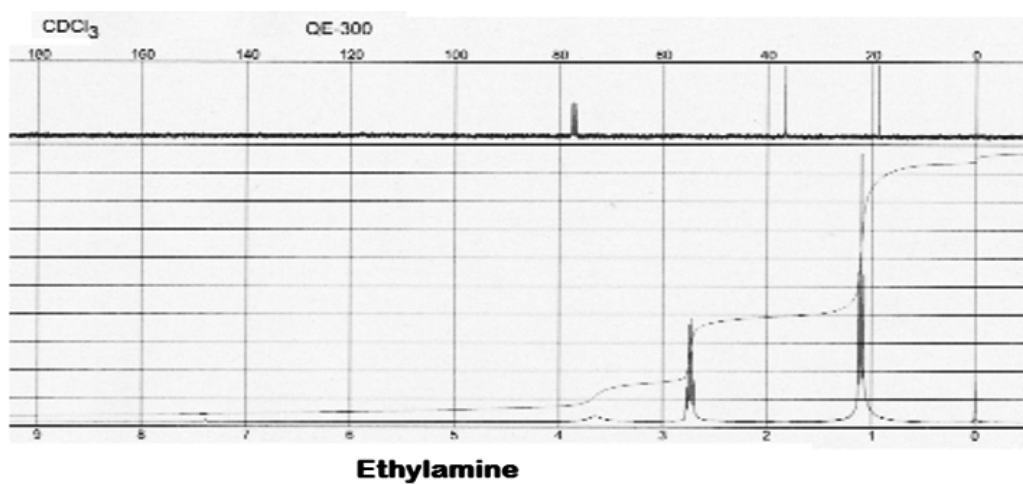
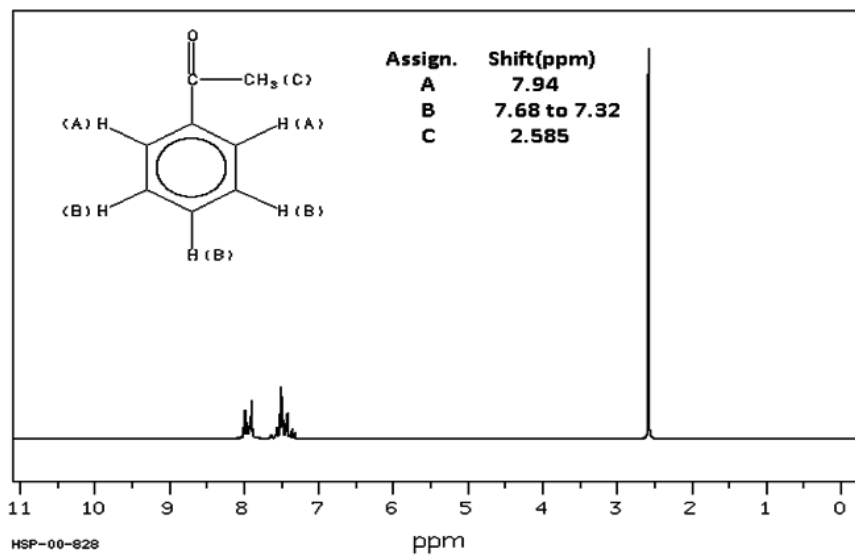


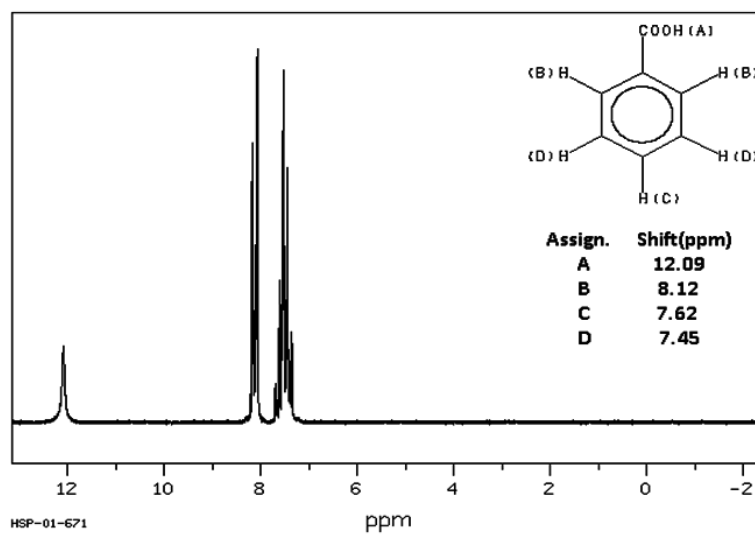
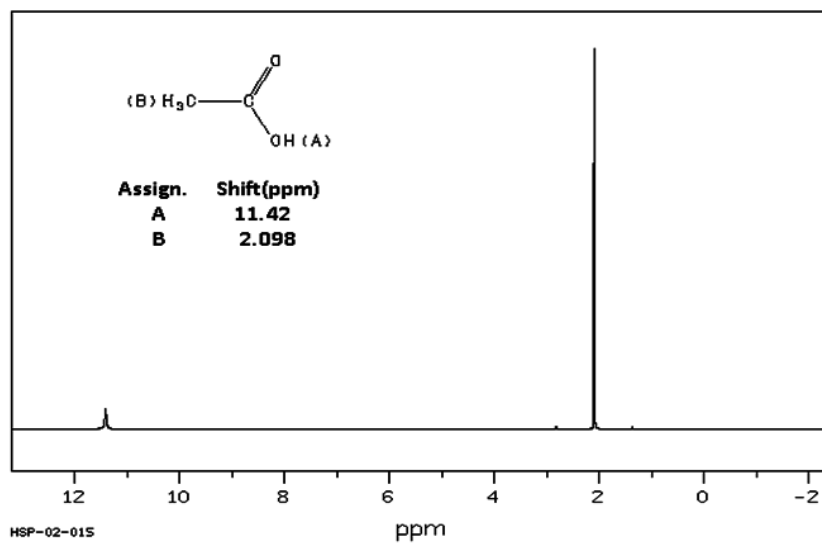


^1H NMR of 1,1,2tribromoethane









Solved Problems in NMR

1] **Molecular formula: C_3H_6O**

PMR (δ ppm): δ 2.05 (s, 6H)

MF indicates that compound contains three carbon atoms and in PMR spectrum, there is only one singlet for 6H, hence it must contain two $-CH_3$ groups must attached to electron withdrawing $C=O$ group.

Therefore molecular formula of compound is $CH_3-CO-CH_3$ Acetone

2] **MF $C_5H_{10}O$**

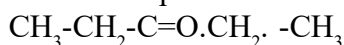
PMR (δ ppm): δ 1.05 (t, 6H, $J=6$ Hz), 2.4 (q, 4H, $J=6$ Hz),

Peak with same coupling constant (J) indicates that both groups are adjacent.

Peak at 1.05 for 6H indicates that compound must contains two $-CH_3$ groups. Moreover, this peak appears as triplet i.e. signal due to $-CH_3$ protons is split up by neighbouring protons in the form of $-CH_2$ Protons.

Similarly, another peak at 2.4 for 4H indicates that compound must contains two $-CH_2$ groups. This peak appears as quartet i.e. signal due to $-CH_2$ is split up by neighbouring three protons in the form of $-CH_3$ groups. $-CH_2$ groups are more deshielded (δ 2.4) than $-CH_3$ protons (δ 1.05) i.e.

$-CH_2$ groups must be attached to the electron withdrawing group $C=O$, Hence the structure of compound is.



3] **MF = C_8H_{10}**

PMR (δ ppm): δ 2.3 (q, 2H, $J=7$ Hz), 1.0 (t, 3H, $J=7$ Hz), δ 7.3 (s, 5H).

In PMR spectrum aromatic protons appears at δ 6.0 – 8.5. hence peak at δ 7.3 for 5H as singlet indicate that compound containing monosubstituted benzene ring is present. Hence, we account for

$C_8H_{10} - C_6H_5 = C_2H_5$ = another peak δ 2.3 (q, 2H, $J=7$ Hz), 1.0 (t, 3H, $J=7$ Hz), having same coupling constant indicates that compound must contains $-CH_2-CH_3$ group attached to benzene ring. Hence structure of compound is

ethyl benzene

4] **MF = C_8H_8O**

PMR (δ ppm): δ 2.8 (d, 2H, $J=6.5$ Hz), δ 7.2-7.6 (m, s, 5H), δ 9.78 (t, 1H, $J=6.5$ Hz)

Multiplet in the region δ 7.2-7.6 for five protons indicates that compound containing monosubstituted benzene ring. Acetaldehyde protons appear in down field region in the range

δ 9.78 as triplet indicates the presence of $-CH_2CHO$ group. It is supported by another peak with appears at δ 2.8 as doublet with same coupling constant. Hence the structure of the compound is 2-phenylacetaldehyde.

5] **MF = C_4H_9NO**

PMR (δ ppm): δ 1.10 (septet, 1H, $J=8$ Hz), δ 2.1 (d, $J=8$ Hz, 6H), δ 9.1 (s, 2H, exchangeable with D_2O)

Peak at δ 1.10 as septet for 1H indicates that -CH group is adjacent to two -CH₃ groups. It is supported by another peak at δ 2.1 as doublet for 6H with the same coupling constant. Hence compound must contain isopropyl group.

Protons on hetero atoms like N, O, S get replaced by deuterium and do not give any peak. Peak at δ 9.1 (high down field) as singlet for 2H exchangeable with D_2O indicates the presence of -NH₂ group. From the molecular formula we have to account for one carbon and one oxygen atom which must be in the form of -C=O group.

-NH₂ protons are deshielded as they are attached to electron withdrawing group -C=O. Hence structure of compound is.

6] MF = C₈H₈O₂

PMR (δ ppm): δ 2.35 (s, 3H), δ 7.10 (d, $J=9$ Hz, 2H), δ 7.95 (d, $J=9$ Hz, 2H), δ 10.5 (s, 1H, exchangeable with D_2O).

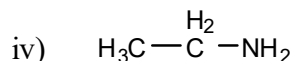
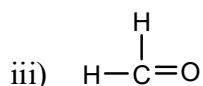
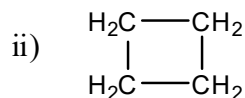
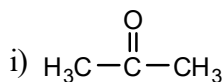
Peak at δ 7.10 as doublet for 2H and δ 7.95 as doublet for 2H with same coupling constant indicate the presence of para substituted benzene ring.

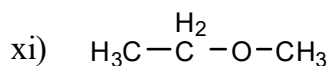
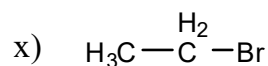
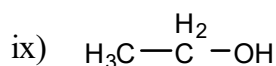
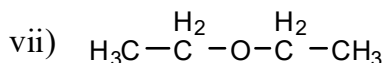
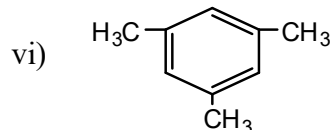
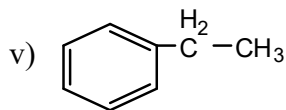
Peak at δ 2.35 as singlet for 3H indicates the presence of -CH₃ group, it is deshielded since it is attached to benzene ring.

In molecular formula there are two oxygen atoms and PMR spectrum exhibits peak at δ 10.5 exchangeable with D_2O which accounts for -OH proton of -COOH group. Hence structure of compound is

QUESTION BANK

- Q1. Explain the principle of NMR spectroscopy.
- Q2. Write note on Orientation of hydrogen nucleus.
- Q3. Give the instrumentation and experimental procedure for NMR spectroscopy.
- Q4. Explain Shielding and Deshielding protons with suitable examples.
- Q5. Explain Shielding effect by taking example of acetylene.
- Q6. Explain Deshielding effect by taking example of acetylene.
- Q7. What is Chemical shift? Explain with suitable example.
- Q8. How many signals are obtained for the following compounds.





Q9. Explain the terms (i) Spin-Spin Coupling (ii) Coupling Constant.

Q10. Based on PMR spectral data given below. Deduce the structure of the following compound. Justify the PMR spectral data.

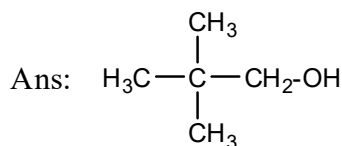
- a) M. F = $\text{C}_4\text{H}_8\text{O}_2$
PMR(δ ppm): δ 1.1(t, $j = 7$ Hz, 3H), δ 2.3(q, $j = 7$ Hz, 2H), δ 3.8(s, 3H)

Ans: $\text{CH}_3-\text{CH}_2\text{COOCH}_3$

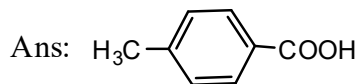
- b) M. F = $\text{C}_4\text{H}_8\text{O}_3$
PMR(δ ppm): δ 2.12(s, 3H), δ 2.6(t, $j = 6$ Hz, 2H), δ 2.82(t, $j = 6$ Hz, 2H), δ 11.0(s, H exchangeable with D_2O),

Ans: $\text{CH}_3-\text{O}-\text{CH}_2\text{CH}_2-\text{COOH}$

- c) M. F = $\text{C}_5\text{H}_{12}\text{O}$
PMR(δ ppm): δ 1.12(s, 9H), δ 3.4(s, 2H), δ 5.0(s, H exchangeable with D_2O),



- d) M. F = $\text{C}_8\text{H}_8\text{O}_2$
PMR(δ ppm): δ 2.35(s, 3H), δ 7.10(d, $j = 9$ Hz, 2H), δ 7.95(d, $j = 9$ Hz, 2H), δ 11.0(s, H exchangeable with D_2O),



Numerical problems on UV, IR and NMR

General spectral data given in table – 1, 2 and 3 is useful to solve the problems based on U.V, IR and NMR spectroscopy:

Table no.1

Chromophore group	Example	λ_{max}	E max	Transition
—C=C— 	ethylene	165	15000	Pi-Pi*
$\text{—C}\equiv\text{C—}$	Acetylene	190	8000	Pi-Pi*
—C=O 	Acetone	190	900	n- σ^*
		270	30	n- Pi*
HC=O 	Aldehyde	210	1200	Pi-Pi*
		290	16	n- Pi*
benzenoid ring	Benzene	180	60000	Pi- Pi* E ₁ -band
		200	8000	Pi- Pi* E ₂ -band
		255	215	Pi- Pi* B-band
Aromatic hydroxy compounds	Phenol	210	6200	Pi- Pi* E ₂ -band
		270	1450	Pi- Pi* B-band
	methoxy benzene	217	600	
		269		
	Aceto-phenone	245.5	9800	
-O-	ether	210		n - σ^*
-N=O	Nitrobutane	302	100	
—N=N—	Azomethane	348	04	pi- pi *
	Acetonitrile	160	05	pi- pi*
-NO ₂	Nitromethane	200	5000	pi- pi*

**Table no. 2: IR group frequency bands-region/
Characteristics Infrared absorption bands of some common functional groups:-**

Sr. no.	Functional group	compound	Wave number cm^{-1}
1	O-H	Alcohol, Carboxylic acids	3600-3200
2	$\begin{array}{c} \text{—NH} \\ \end{array}$	Amines and amides	3600-3200
3	$\equiv\text{CH}$	Acetylene	3600-3200
4	$\begin{array}{c} \text{=CH} \\ \end{array}$	Alkenes	3100-3000
5	Ar-H	Aromatic	3100-3000
6	$\begin{array}{c} \\ \text{—CH} \\ \end{array}$	Saturated alkanes	3000-2800
7	C-H band -CHO	Aldehyde	2900-2700
8	—S-H	Thioles	2950-2550
9	$\text{—C}\equiv\text{C—}$	Alkynes	2200-2100
10	$\text{—C}\equiv\text{N}$	Nitriles	2280-2240
11	$\begin{array}{c} \text{—C=O} \\ \end{array}$	Aldehydes, Ketones. Acids, Esters & Amides	1870-1650
12	$\begin{array}{c} \text{—C=C—} \\ \quad \end{array}$	Alkenes	1680-1620
13	$\begin{array}{c} \text{—C} \cdots \text{C—} \\ \quad \end{array}$	Aromatic ring	1600-1400 (4-bands)
14	—NO_2	Nitro compounds	1560-1575 1355-1345
15	$\begin{array}{c} \quad \\ \text{—C—O—C—} \\ \quad \end{array}$	Ethers	1270-1050
16	$\begin{array}{c} \\ \text{—C—X} \\ \end{array}$	Halo alkanes	750-500

Table.3 : PMR Chemical shift data. (δ ppm)

<i>type of proton</i>	<i>type of compound</i>	<i>chemical shift range,</i>
RCH_3	primary aliphatic	0.9
R_2CH_2	secondary aliphatic	1.3
R_3CH	tertiary aliphatic	1.5
$\text{C}=\text{C}-\text{H}$	vinyllic	4.6-5.9
$\text{C}=\text{C}-\text{H}$	vinyllic, conjugated	5.5-7.5
$\text{C}(\text{triple bond})\text{C}-\text{H}$	acetylenic	2-3.
$\text{Ar}-\text{H}$	aromatic	6-8.5
$\text{Ar}-\text{C}-\text{H}$	benzylic	2.2-3
$\text{C}=\text{C}-\text{CH}_3$	allylic	1.7
$\text{HC}-\text{F}$	fluorides	4-4.5
$\text{HC}-\text{Cl}$	chlorides	3-4.
$\text{HC}-\text{Br}$	bromides	2.5-4
$\text{HC}-\text{I}$	iodides	2-4.
$\text{HC}-\text{OH}$	alcohols	3.4-4
$\text{HC}-\text{OR}$	ethers	3.3-4
$\text{RCOO}-\text{CH}$	esters	3.7-4.1
$\text{HC}-\text{COOR}$	esters	2-2.2
$\text{HC}-\text{COOH}$	acids	2-2.6
$\text{HC}-\text{C}=\text{O}$	carbonyl compounds	2-2.7
RCHO	aldehydic	9-10.
ROH	hydroxylic	2-4.
ArOH	phenolic	4-12.
$\text{C}=\text{C}-\text{OH}$	enolic	15-17
RCOOH	carboxylic	10.0-13.2
RNH_2	amino	1-5.

Double bond and/or ring equivalent:

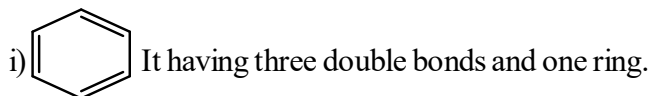
If the molecular formula of the compound is given, then the number of bonds or/ and ring equivalent DBE can be easily calculated.

I] Type A: If the compound is hydrocarbon with general formula C_xH_y , then

$$\text{DBE} = X+1- Y/2 \quad \text{OR} \quad C+1 - H/2$$

For ex. C_6H_6 the number of DBE in it

$$\text{DBE} = 6+1 - 6/2 = 4 \text{ and possible structure for given molecular formula}$$



ii) $\text{H}_2\text{C}=\underset{\text{H}}{\text{C}}-\text{C}\equiv\text{C}-\underset{\text{H}}{\text{C}}=\text{CH}_2$ It having two double bonds one triple bond.
A triple bond may be regarded as equivalent to two double bonds. The presence of triple bond. $\left[\text{C}\equiv\text{C}, \text{C}\equiv\text{N} \right]$

III] Type B: if the compound contains one or more divalent atoms (sulphur, oxygen) in addition to the elements carbon and hydrogen. Then the presence of divalent atom can be ignored, while calculating DBE.

$$\text{DBE} = \text{X} + 1 - \text{Y}/2 \quad \text{OR} \quad \text{C} + 1 - \text{H}/2$$

For ex. Organic compound with molecular formula. (i) $\text{C}_3\text{H}_8\text{O}_3$ (ii) $\text{C}_6\text{H}_6\text{O}_2$

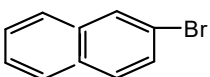
I) $\text{DBE} = 3 + 1 - 8/2 = 0$ i.e. it does not contains double bond or ring.

II) $\text{DBE} = 6 + 1 - 6/2 = 7 - 3 = 4$. It contains three double bonds and one ring.

III] Type C: if molecular formula of compound contains some monovalent element like halogens [Cl, Br, I etc.] then for calculating the number of DBE in its structural formula.

$$\text{DBE} = \text{x} + 1 - \text{y} + \text{z}/2; \quad \text{or} \quad \text{DBE} = \text{C} + 1 - \text{H} + \text{X}/2$$

for ex. consider a compound with molecular formula $\text{C}_{10}\text{H}_7\text{Br}$. The number of DBE in the compound is equal to,

$$10 + 1 - 7 + 1/2; \quad 11 - 4 = 7; \quad \text{$$

it contains five double bonds and two rings.

IV] Type D: If compound contains nitrogen atom or some trivalent phosphorous atom. The number of trivalent atoms subtracted from number of hydrogen atoms present in molecular formula.. $\text{C}_x\text{H}_y\text{N}_z$.

$$\text{DBE} = \text{x} + 1 - \text{y} - \text{z}/2 \quad \text{or} \quad \text{DBE} = \text{C} + 1 - \text{H} - \text{N}/2$$

for ex. 1. $\text{C}_{12}\text{H}_{12}\text{N}_2$ 2. $\text{C}_6\text{H}_8\text{O}_3\text{N}_2$

$$1. \quad \text{DBE} = 12 + 1 - 12 - 2/2 : \quad 13 - 5 = 8.$$

$$2. \quad \text{DBE} = 6 + 1 - 8 - 2/2; \quad 7 - 3 = 4.$$

Solved combined problems based on UV, IR, and NMR data:

1] An organic compound contains $\text{C}_4\text{H}_8\text{O}$. In UV it gives a characteristic band at 275 mu,

ϵ_{max} 17. In IR band are formed at 2941-2857(m)
1715(s) and
1460 (m).

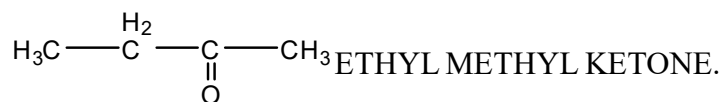
In NMR, three signals appears at i) 7.5 τ or 2.5 quartet, (2H)

ii) 7.88 τ singlet (3H)

iii) 8.93 τ triplet, (3H) determine the structural formula.

Ans:-

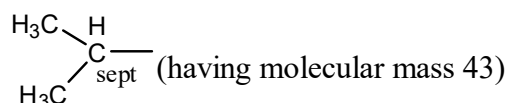
1. Absorption at 275 cm^{-1} , $\epsilon_{\text{max}} 17$ is characteristic of a carbonyl group. Due to $n \rightarrow \pi^*$ transition.
2. a) the absorption at $2941\text{--}2857\text{ cm}^{-1}$ in IR spectrum is due to --C--H stretching.
b) at 1715 cm^{-1} is characteristic of saturated ketonic group.
c) at 1460 cm^{-1} may be due to --C--H bending.
3. i) the presence of triplet at 8.93τ triplet, (3H) and quartet at 7.5τ or 2.5 quartet, (2H) is characteristic of $\text{H}_3\text{C--CH}_2$ group in the compound.
ii) the singlet at 7.88τ singlet (3H) is due to methyl group adjacent to a carbonyl group. Hence the structure of compound is



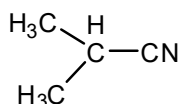
- 2] An organic compound with molecular mass 69 and molecular formula $\text{C}_4\text{H}_7\text{N}$.
It transparent above 200 nm
The absorption bands in IR spectrum, are a) 2941 cm^{-1} (m).
b) 2273 cm^{-1} (m). and
c) 1460 cm^{-1} (m).
in NMR, two signals are formed, a) one is septet at 7.28τ ($J=6.7\text{ cps}$, 4.2 square)
b) doublet at 8.67τ ($J=6.7\text{ cps}$, 2.8 square).
determine the structural formula.

Ans:-

1. The UV spectrum is transparent above 200 nm . shows absence of conjugation and carbonyl group.
2. In IR spectrum, a) the signal at 2941 cm^{-1} (m) indicate --C--H stretching and 1460 cm^{-1} (m) indicate C-C stretching. And b) signal at 2273 cm^{-1} (m) indicate the presence of CN group.
3. In NMR one signal septet at 7.28τ is a part of structure



Remaining 26 mass unit corresponds to CN group, therefore structure of compound is



- 3] A hydrocarbon containing molecular formula C_4H_8 .
i) it transparent above 210 nm , in UV spectrum
ii) in its infra red spectrum, bands are formed at a) 3022 cm^{-1} , 1676 cm^{-1} and at 965 cm^{-1}

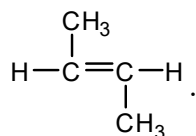
(s).

iii) Two signals appears in its NMR spectrum a) 8.40 τ doublet and 4.45 τ quartet in the integral area ratio at 3:1 respectively, determine structural formula of the compound.

Ans:-

1. The UV spectrum is transparent above 210 nm, shows the absence of conjugation and carbonyl group.
2. In IR, a) absorption at 3022 cm^{-1} (m) C-H stretching in aromatic compound or =CH stretching. Since carbonyl group is absent.
b) and bond at 1676 (m) may be due to C=C stretching. Thus the hydrocarbon must be unsaturated.
c) bond at 965 cm^{-1} (s), indicate trans alkenes.
3. In NMR, two signals are formed 8.40 τ doublet indicate methyl group attached to =CH and second signal due to one proton quartet i.e.

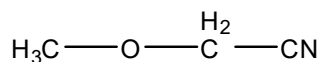
$\text{H}_3\text{C}-\underset{\text{H}}{\text{C}}=$ and its molecular mass is 28. The molecular formula is double of it. Hence probable structure is



- 4] A compound with molecular mass 71.
 - i) is transparent in UV spectrum.
 - ii) In IR bands are formed at
 - a) 2941-2857 cm^{-1} ,
 - b) 2247 cm^{-1} and
 - c) 1460 cm^{-1} .
 - iii) Two signals are formed at i) 5.78 τ (16.8 square) and 6.51 τ (23.9 square)

Ans:-

1. In IR spectrum band at 2941 cm^{-1} (m) indicate -C-H stretching and 1460 cm^{-1} (m) indicate C-C stretching. and band at 2247 cm^{-1} indicate the presence of CN group.
2. Two signal formed in NMR are, two sets of protons are in the ratio 2:3 thus, CH_3 and CH_2 may be part of structure. Thus, CH_3 , CH_2 and CN are the part of structure. And mole. Mass 55 and total mass given is 71. Remaining mass 16 corresponding to an atom of oxygen.
3. Thus the probable structure of compound is



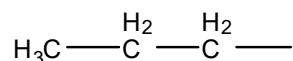
- 5] An organic compound with molecular mass 88 absorb at 206 nm, ϵ_{max} 50,
In IR medium absorb at on bands formed at i) 3049-2924 and ii) 1445 cm^{-1} . also

strong absorption band at 1736 cm⁻¹ and following signals are formed in its NMR spectrum.

- i) 1.93 τ singlet (5.9 sq.)
- ii) 5.88 τ triplet (J= 7.0, 12.2 sq.)
- iii) 8.33 τ sextet (J= 7.0, 11.6 sq.) and
- iv) 9.05 τ triplet (J= 7.0, 18.6 sq.).

Ans:-

1. In UV an absorption band at 206 nm, ϵ max 50 does not give any definite information/presence of C=O group.
2. In IR, i) formation of strong absorption band 1736 cm⁻¹ shows the presence of an ester.
ii) The bands at 3049-2924 and 1445 cm⁻¹ due to C-H stretch, and C-C stretch and C=O stretch respectively.
3. The set of protons with different chemical shift are in the ratio 1:2:2:3. The formation of triplet, sextet and triplet with the same coupling constant (J=7.0) shows that



as the part of structure. A one proton singlet at very low field suggest as -CH also as

a part of structure. This amount to 56 mass units. $\text{H}_3\text{C}-\overset{\text{H}_2}{\text{C}}-\overset{\text{H}_2}{\text{C}}-\text{O}-\overset{\text{O}}{\parallel}\text{CH}$.

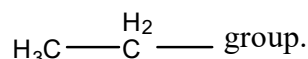
[56+32=88]

[C=O structure for acid appears at 1715-1720 cm⁻¹]

- 6] A compound with molecular formula C₄H₈O₃ and having mass 104. Is transparent below 210nm.
 - i) In IR spectrum, the medium bands formed are i) 3125- 2857cm⁻¹ and 1449 cm⁻¹ (s). A strong band formed at 1718 cm⁻¹ and also weak bands at 2695 cm⁻¹ and 2625 cm⁻¹.
 - ii) In NMR spectrum following signals are observed i) -0.95 τ singlet (5.4 sq.),
ii) 5.87 τ singlet (11.2 sq.),
iii) 6.34 τ quartet (J= 7.1, 10.6 sq.) and
iv) 8.73 τ triplet (J= 7.1, 16.2 sq.),

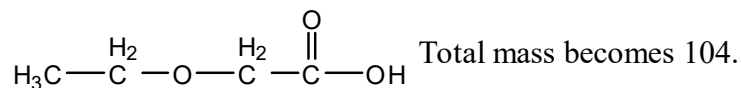
Ans:-

1. In UV, absorption band transparent below 210nm indicates n $\rightarrow$ π^* transition i.e. C=O gr.
2. a) The broad band 3125- 2857cm⁻¹ appears due to O-H stretching. And strong bond formed at 1718 cm⁻¹ results presence of C=O group.
3. In NMR spectrum, -0.95 τ singlet (5.4 sq.) results the formation -COOH group, and 6.34 τ quartet (J= 7.1, 10.6 sq.) and 8.73 τ triplet (J= 7.1, 16.2 sq.) indicate the formation of



5.87 τ singlets (11.2 sq.) indicate the presence of -CH₂- group.

There fore possible structure is

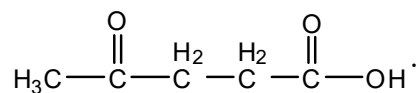


7] A compound with molecular weight 116 gave the following spectral information.

- UV, 283 mμ, ε max 50.
- IR, a) 3000-2500 b) 1715(s) c) 1345(w) cm⁻¹.
- NMR, 7.88 τ singlet, (3H), 7.40 τ triplet (2H), 7.75 τ triplet (2H), and 1.1 τ singlet (1H).

Ans:-

- In UV, absorption at 283 mμ, ε max 50 of low intensity indicates presence of -C=O group.
- In IR,
 - the presence of -C=O group is confirmed by a strong band at 1715 cm⁻¹.
 - A very broad band at 3000-2500 cm⁻¹ is most characteristic of acid (O-H stretching) and it appears as a result of hydrogen bonding.
- In NMR, a) the presence of an acid group is also shown by NMR which gives signal singlet at -ve τ value. Thus compound contains -C=O and -COOH groups.
 b) 7.88 τ singlet (3H) indicates presence of -CH₃ group.
 c) 7.40 τ triplet (2H), 7.75 τ triplet (2H) indicates the presence of -CH₂-CH₂- .
 Hence compound with this structure is

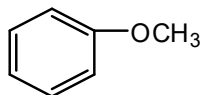


- Molecular formula: C₇H₈O.
 UV: 230 nm (ε max 1000), 270 nm (ε max 600).
 IR: 3100, 2950, 1600, 1500, 1250, 750, AND 700 cm⁻¹.
 NMR: (δ ppm) , δ 3.8 (s, 3H), δ 6.8-7.2 (m, 5H).

Ans:-

- In UV; absorption bands at 230 nm (ε max 1000), 270 nm (ε max 600) indicates the presence of E₂ band and B- band of benzene ring.
- In IR spectrum the band at 3100 cm⁻¹ due to -C-H stretching of benzene ring, band at 2950 cm⁻¹ is due to -C-H stretching of aliphatic alkyl group. 1600, 1500 cm⁻¹ indicate the -C=C- benzene ring. And band at 1250 cm⁻¹ is due to C-O-C asymmetric stretching of aromatic ether. 750, AND 700 cm⁻¹ bands indicates the presence of monosubstituted benzene.
- In NMR, δ 3.8 (s, 3H), peak due to -CH protons. And the presence of oxygen atom in molecular formula accounts for -OCH₃ group.
- As -CH₃ group attached to electronegative oxygen atom. δ 6.8-7.2 (m, 5H) represent

multiplet for 5H in benzene ring. Hence the structure of the compound is



9. Molecular formula: $C_6H_{12}O$
 UV: 282nm (ϵ max 221)
 IR: 2950-2840 cm^{-1} , 1710 cm^{-1} .
 PMR: (δ ppm), δ 1.2 (s, 3H), δ 2.1 (s, 9H).

Ans: -

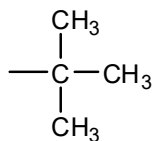
In UV spectrum absorption band at 282nm (ϵ max 221) indicates the presence of carbonyl group.

In IR spectrum the absorption band at 2950-2840 cm^{-1} , due to -C-H stretching of alkyl group.

And the band at 1710 cm^{-1} due to C=O group present.

In PMR: spectrum, the peak at δ 1.2 (s, 3H), as singlet for 3H indicate the presence of -CH₃ group.

And the presence of singlet peak at δ 2.1 (s, 9H) indicate the presence of three -CH₃ group at same carbon atom, i.e.



Hence the presence of CH₃, C=O and in the structure, there fore possible structure is.

10. Molecular formula: $C_8H_8O_2$
 In UV: 202nm (ϵ max 7900), 255nm (ϵ max 215),
 IR: broad band between 3300- 2700 cm^{-1} , 1700 cm^{-1} , 1600, 1500, 750, 700 cm^{-1} .
 PMR: (δ ppm), δ 3.5 (s, 12 mm), δ 7.2 (s, 30mm), δ 12.3 (s, 6 mm exchangeable with D₂O),

Ans:

In UV:

Spectrum absorption band at 202 nm and 255 nm indicate the presence of E₂ band and B band of benzene ring.

In IR:

Broad band between 3300- 2700 cm^{-1} indicate the presence of O-H stretching of -COOH group.

1700 cm^{-1} this band indicate the presence of -C=O group in -COOH..

Band at 1600, 1500 cm^{-1} indicate the presence of benzene ring. -C-H deformation

bands at 750, 700 cm^{-1} indicate the presence of mono-substituted benzene.

In PMR: singlet peak at δ 3.5 (s, 12 mm), indicate the presence of two protons, which represent s $-\text{CH}_2$ group. Singlet peak at δ 7.2 (s, 30mm), indicate the presence of 5H of benzene ring with mono-substitution. Singlet peak with exchangeable D_2O confirms the presence of O-H of COOH group.

Hence, the presence of $-\text{CH}_2$ group, $-\text{COOH}$ group and one benzene ring gives possible structure.

11. Molecular formula: $\text{C}_3\text{H}_8\text{O}$

In UV: transparent above λ max 210.

IR: broad band 3400 cm^{-1} , 2890 cm^{-1} , 1050 cm^{-1} .

PMR: (δ ppm), δ 1.2 (t, J = 7.5 Hz, 3H), δ 2.6 (sextet, 7.5 Hz, 2H), δ 3.5 (t, J =7.5 Hz, 2H), δ 4.5 (s, 1H, exchangeable with D_2O).

Ans:

In UV:

Spectrum absorption band above 210 nm indicate the absence of carbonyl group and conjugation.

In IR:

Absorption band at broad band 3400 cm^{-1} due to $-\text{OH}$ stretching. Band at 2890 cm^{-1} , indicate the $-\text{CH}$ stretching of alkyl group. And 1050 cm^{-1} indicate the $-\text{CO}$ stretch of $-\text{CH}_2\text{OH}$ group.

In PMR:

Triplet at δ 1.2 (t, J = 7.5 Hz, 3H), δ 2.6 (sextet, 7.5 Hz, 2H), δ 3.5 (t, J =7.5 Hz, 2H)

indicate the presence of $\text{H}_3\text{C}-\overset{\text{H}_2}{\text{C}}-\text{CH}_2$ group.

Singlet at δ 4.5, exchangeable with D_2O indicate the presence of $-\text{OH}$ group.

Hence, the presence of group and $-\text{OH}$ group gives possible structure.

12. Molecular formula: $\text{C}_3\text{H}_8\text{O}$

In UV: transparent above λ max 210.

IR: broad band 3500 cm^{-1} , 2910 cm^{-1} , 1100 cm^{-1} .

PMR: (δ ppm), δ 1.2 (d, J = 6 Hz, 6H), δ 3.8 (septet, 6 Hz, 1H), δ 4.3 (s, 1H, exchangeable with D_2O).

Ans:

In UV:

Spectrum absorption band above 210 nm indicate the absence of carbonyl group and conjugation.

In IR:

Absorption band at broad band 3350 cm^{-1} due to $-\text{OH}$ stretching. Band at 2910 cm^{-1} ,

indicate the -CH stretching of alkyl group. And 1100 cm^{-1} is a characteristic of -CO stretch of secondary alcohol i.e. -CHOH group.

In PMR:

doublet at δ 1.2 (d, $J = 6\text{ Hz}$, 6H), and δ 3.8 (septet, 6 Hz , 1H), indicate the presence of group.

Singlet at δ 4.3, exchangeable with D_2O indicate the presence of -OH group.

Hence, the presence of group and -OH group gives possible structure.

13. Molecular formula: $\text{C}_4\text{H}_{10}\text{O}$

In UV: transparent above λ_{max} 210.

IR: broad band 3300 cm^{-1} , 2970 cm^{-1} , 1150 cm^{-1} .

PMR: (δ ppm), δ 1.3 (s, 9H), δ 4.2 (s, 1H, exchangeable with D_2O).

Ans:

In UV:

Spectrum absorption band above 210 nm indicate the absence of carbonyl group and conjugation.

In IR:

Absorption band at broad band 3300 cm^{-1} due to -OH stretching. Band at 2970 cm^{-1} , indicate the -CH stretching of alkyl group. And absorption band at 1150 cm^{-1} is a characteristic of -CO stretch of tertiary alcohol i.e. -C-OH group.

In PMR:

Singlet at δ 1.3 (s, 9H) indicate the presence of group.

Singlet at δ 4.2, exchangeable with D_2O indicate the presence of -OH group.

Hence, the presence of group and -OH group gives possible structure.

14. Molecular formula: $\text{C}_2\text{H}_4\text{O}_2$

In UV: λ_{max} 204 (ϵ_{max} 50).

IR: broad band $3100\text{-}2700\text{ cm}^{-1}$, 1720 cm^{-1} .

PMR: (δ ppm), δ 2.1 (s, 3H), δ 11.8 (s, 1H, exchangeable with D_2O).

Ans:

In UV:

Spectrum absorption band at 204 nm indicate the presence of carbonyl group of -COOH group and due to $n\text{-}\pi^*$ transition.

In IR:

broad band $3100\text{-}2700\text{ cm}^{-1}$ due to -OH stretching of -COOH group. and band at 1720 cm^{-1} .

indicate the presence of -C=O stretching of -COOH group.

In PMR:

Singlet at δ 2.1 (s, 3H) indicate the presence of -CH_3 group and its protons are

deshielded as attached with electron withdrawing group. and

Singlet at δ **11.8** (s, 1H, exchangeable with D_2O) indicate the presence of H of -COOH group.

Hence, the presence of $-CH_3$ group and -COOH group gives possible structure.



15. Molecular formula: C_2H_5Cl

In UV: transparent above λ max 210.

IR: 2980 cm^{-1} , 750 cm^{-1} .

PMR: (δ **ppm**), δ 1.48 (t, 3H, $J=7Hz$), δ **3.57** (q, 2H, $J=7Hz$).

Ans:

In UV:

Spectrum absorption band above 210 nm, indicate the absence of carbonyl group and conjugation.

In IR:

Absorption at 2980 cm^{-1} due to $-CH$ stretching of alkyl group. and band at 750 cm^{-1} indicate the

$-C-Cl$ stretching.

In PMR:

Triplet at δ 1.48 (t, 3H, $J=7Hz$) indicate the presence of $-CH_3$ group and

Quartet at δ **3.57** (q, 2H, $J=7Hz$). indicate the presence of CH_2 group. peaks have same coupling constant which indicate that group are adjacent to one another.

Hence, the presence of $-CH_3$ group, $-CH_2$ group and $-Cl$ gives possible structure.



16. Molecular formula: $C_2H_5O_2N$

In UV: λ max 274 (ϵ max 15).

IR: band at 2980 cm^{-1} , 1530 cm^{-1} , 1350 cm^{-1} .

PMR: (δ **ppm**), δ 1.0 (t, 3H, $J=7Hz$), δ 4.3 (q, 2H, $J=7Hz$).

Ans: -

In UV : Spectrum absorption band at 274 nm indicate the presence of $-NO_2$ group due to $n-\pi^*$ transition.

In IR : Absorption at 2980 cm^{-1} due to $-CH$ stretching of alkyl group. and band at 1530 and 1350 cm^{-1} due to asymmetric and symmetric stretching of $-NO_2$ group resply.

PMR:

Triplet at δ 1.0 (t, 3H, $J=7Hz$), indicate the presence of $-CH_3$ group and

Quartet at δ 4.3 (q, 2H, $J=7Hz$). indicate the presence of CH_2 group. peaks have same coupling constant which indicate that group are adjacent to one another.

Hence, the presence of $-CH_3$ group, $-CH_2$ group and $-NO_2$ group gives possible structure.



17. Molecular formula: C_4H_8O
In UV: λ max 283(ϵ max 20).
IR: band at 2940 cm^{-1} , 1710 cm^{-1} .
PMR: (δ ppm), δ 1.05 (t, 3H, J= 7Hz), δ 2.4 (q, 2H, J= 7Hz) δ 2.1 (s, 3H,).

Ans:-

In UV:

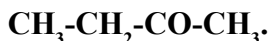
Spectrum absorption band at 283nm indicate the presence of carbonyl group of aldehyde or ketone.

In IR:

broad band 2940 cm^{-1} due to $-C-H$ stretching of alkyl group. And band at 1710 cm^{-1} indicate the presence of $-C=O$ stretching of aliphatic keto group band is due to $-C=O$.

PMR:

Triplet at δ 1.05 (t, 3H, J= 7Hz), indicate the presence of $-CH_3$ group and Quartet at δ 2.4 (q, 2H, J= 7Hz) indicate the presence of CH_2 group. Peaks have same coupling constant which indicate that group are adjacent to one another i.e. CH_3-CH_2- group. δ 2.1 (s, 3H,) for 3H indicate the presence of $-CH_3$ group. Proton are shielded as $-CH_3$ group is attached to electron withdrawing group Hence, the presence of CH_3-CH_2- group $-CH_3$ group and $-C=O$ group gives possible structure.



18. Molecular formula: C_3H_6O
In UV: λ max 290(ϵ max 20).
IR: band at 2980 cm^{-1} , 2720 cm^{-1} , 1740 cm^{-1} .
PMR: (δ ppm), δ 1.1 (t, 3H, J= 6Hz), δ 2.5 (quintet, 2H, J= 6Hz) δ 9.6 (t, 1H,).

Ans:-

In UV:

Spectrum absorption band at 290nm indicate the presence of carbonyl group of aldehyde or ketone.

In IR:

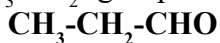
Absorption band 2980 cm^{-1} due to $-C-H$ stretching of alkyl group, band at 1740 cm^{-1} indicate the presence of $-C=O$ stretching of aliphatic keto group band is due to $-C=O$ and band at 2720 cm^{-1} indicate strong absorption of $-C=O$ group.

PMR:

Triplet at δ 1.1 (t, 3H, J= 6Hz), indicate the presence of $-CH_3$ group and Quintet at δ 2.5 (quintet, 2H, J= 6Hz) indicate the presence of CH_2 group. Peaks have same coupling constant which indicate that group are adjacent to one another i.e.

CH₃-CH₂- group. δ 9.6 (t, 1H,) for 1H indicate the presence of -CHO group adjacent to -CH₂ group.

Hence, the presence of CH₃-CH₂- group and -CHO group gives possible structure.



19. Molecular formula: C₃H₆O

In UV: λ max transparent above 210.

IR: Broad band at 3400 cm⁻¹, 2970 cm⁻¹,

PMR: (δ ppm), δ 2.5 (s, 2H, exchangeable with D₂O), δ 3.68 (t, 4H).

Ans:-

In UV:

Spectrum absorption band at 210nm indicate the absence of carbonyl group and conjugation.

In IR:

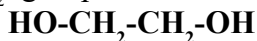
Absorption of broad band at 3400 cm⁻¹ due to -O-H stretching. Band at 2970 cm⁻¹.

Indicate the presence of -C-H stretching.

PMR:

δ 2.5 (s, 2H, exchangeable with D₂O) indicate the presence of two -OH groups and triplet at δ 3.68 (t, 4H) indicate the presence of two CH₂ groups.

Hence, the presence of CH₂-CH₂- group and two -OH groups gives possible structure.



20. Molecular formula: C₃H₆N

In UV: λ max transparent above 210.

IR: band at 2980 cm⁻¹, 2250 cm⁻¹,

PMR: (δ ppm), δ 1.1 (t, 3H, J= 6Hz), δ 3.5(q, 2H, J= 7Hz).

Ans:-

In UV:

Spectrum absorption band at 210nm indicate the absence of carbonyl group and conjugation.

In IR:

Absorption band 2980 cm⁻¹ due to -C-H stretching of alkyl group and 2250 cm⁻¹ indicate the presence of group.

PMR:

Triplet at δ 1.1 (t, 3H, J= 6Hz), indicate the presence of -CH₃ group and

Quartet at δ 3.5(q, 2H, J= 7Hz) indicate the presence of CH₂ group, protons are deshielded as -CH₂ group attached to electron withdrawing group.

Hence, the presence of -CH₃ group, -CH₂ group and group gives possible structure.

...

Unit: IV

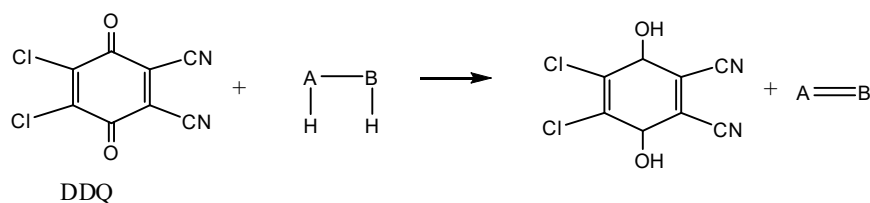
Organic Reagents and Name Reactions

Organic Reagents:

1) DDQ [2,3-DICHLORO-5,6-DICYANO-BENZOQUINONE]

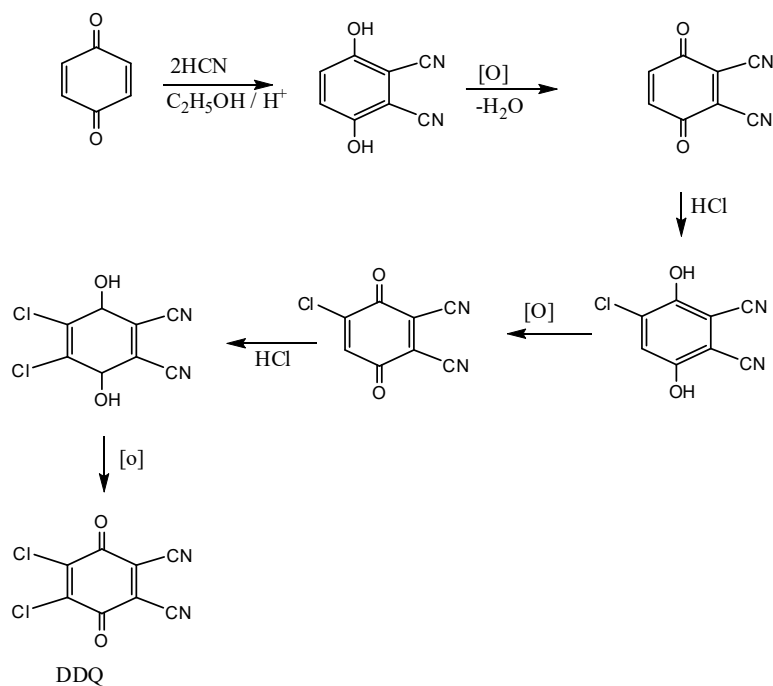
2,3-DICHLORO-5,6-DICYANO-BENZOQUINONE [DDQ] is a powerful dehydrogenating agent.

Reaction with DDQ may be carried out in the inert solvent such as benzene, toluene, dioxane, THF, or acid but dioxane and hydrocarbon solvents are often preferred, because DDQ.H₂ formed in these solvents is insoluble and can be removed by filtration.



Synthesis of DDQ:

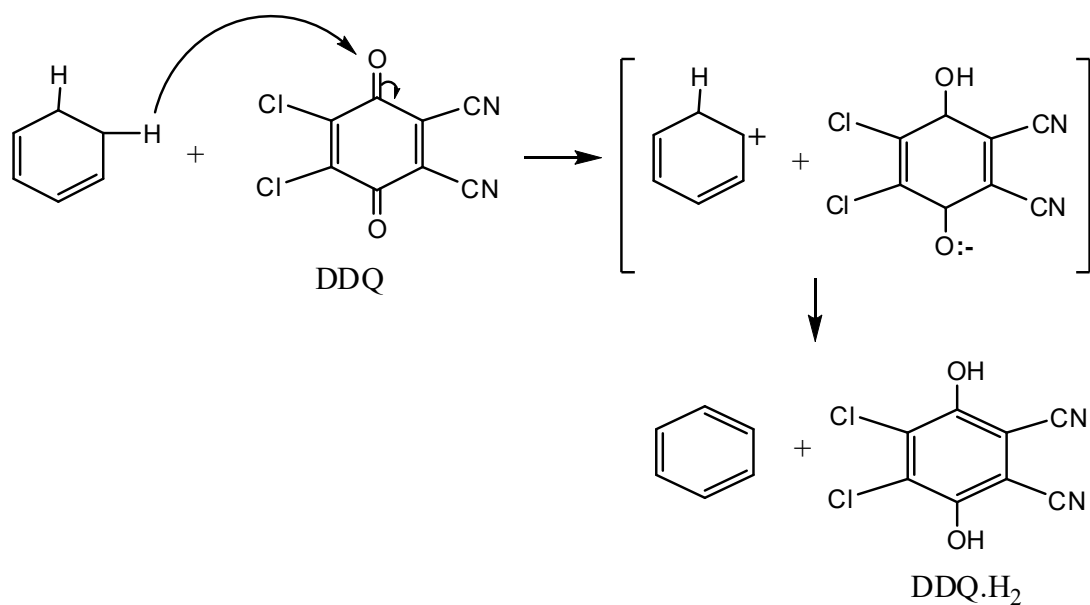
It is synthesized by the method of Thiele and Ganther.



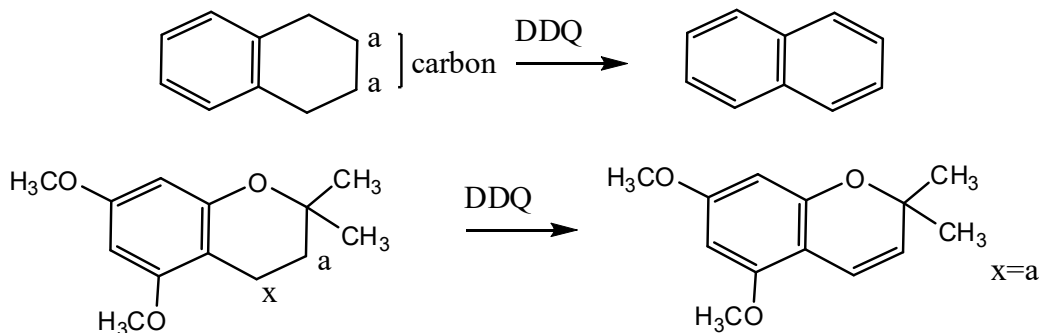
Mechanism:

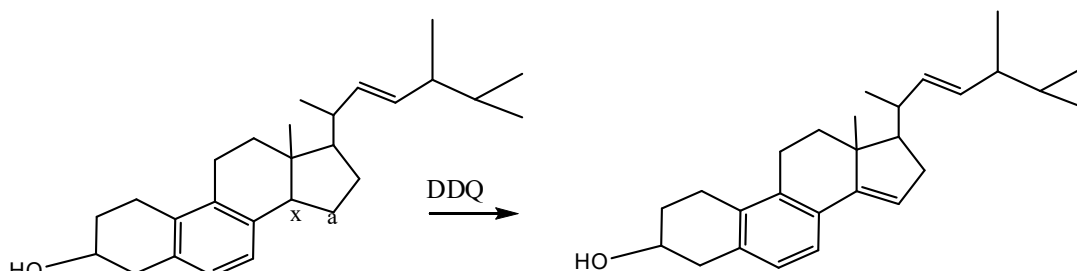
The mechanism of dehydrogenation with DDQ involve

- Transfer of hydride ion for substrate to the quinone oxygen
- Transfer of proton to phenolate ion i.e DDQ reduced to DDQ. H₂

**Synthetic application of DDQ:****I] Benzylic oxidation:**

Dehydrogenation by DDQ can only be possible if benzylic carbon have one hydrogen each

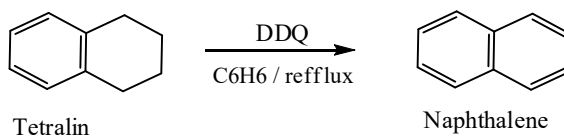




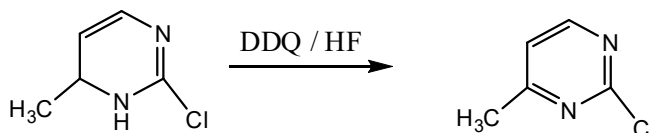
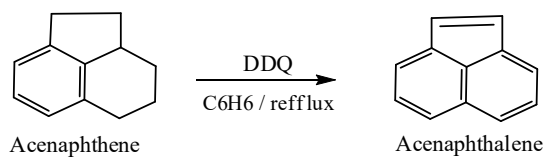
II] Aromatization:

DDQ is an effective reagent for the dehydrogenation of hydroaromatic compound. Aromatization is easily obtained if there are already one or two double bonds in the ring or if the ring fused with an aromatic ring.

For ex: i) **it convert tetralin into naphthalene.**

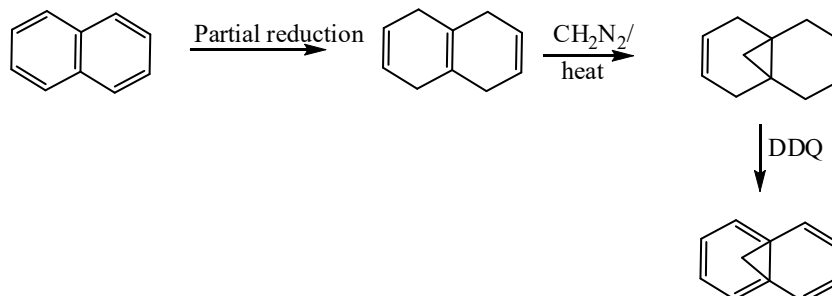


iii) **Acenaphthene into acenaphthalene.**



i) **Annulene Synthesis:-**

DDQ also used for the synthesis of non-benzenoid aromatic system. It is a useful reagent for annulene [10] of the type (I).

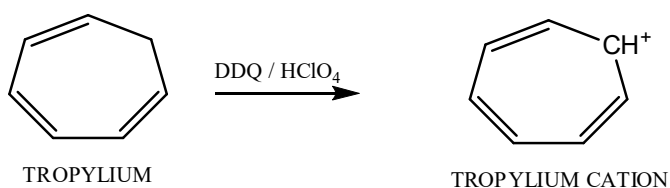


ii) Allylic oxidation:-

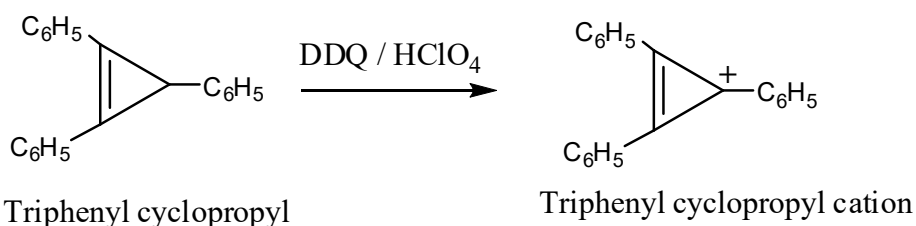
Allylic oxidation is given by the compound having at least one allylic hydrogen atom. Such type of reaction is accomplished most readily, if there are already one or two double bonds in the ring. Such type of substrate is useful for the preparation of stable aromatic cation.

For ex:-

Tropylium cation:



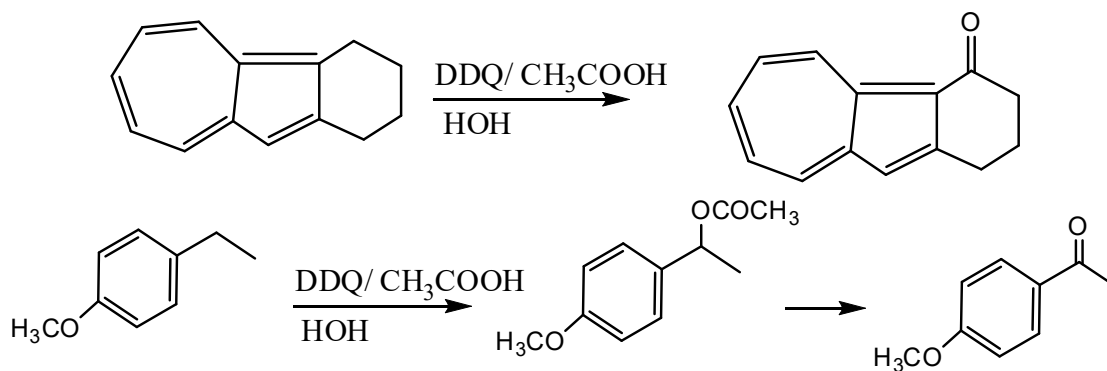
Triphenyl cyclopropyl cation:



iii) Oxidation of benzylic and allylic alkyl group:

DDQ can oxidize benzylic or allylic alkyl group to carbonyl group.

Benzylic oxidation by DDQ in aq. Acetic acid proceeds via an intermediate, benzylic acetate, which is hydrolysed under the reaction condition.



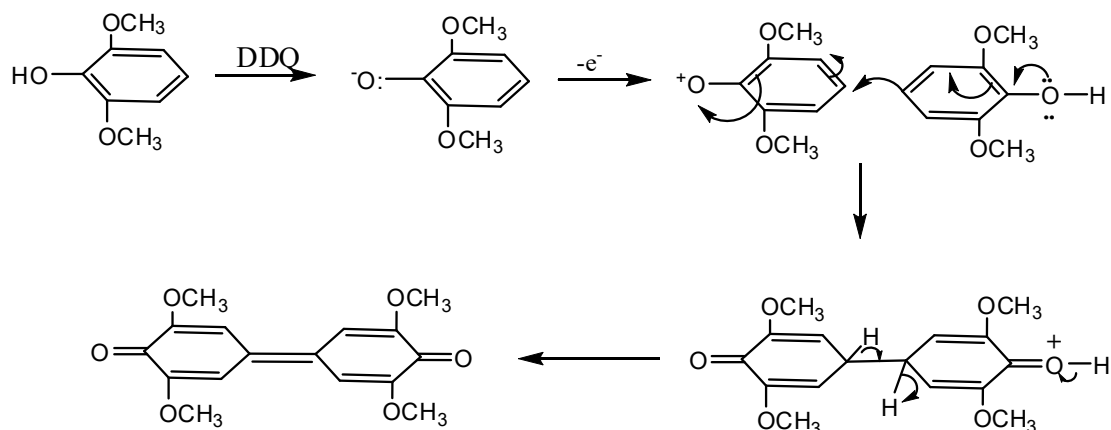
iv) Oxidation of phenol:

Phenol undergo a wide variety of reactions with DDQ.

a) Monohydric phenol:

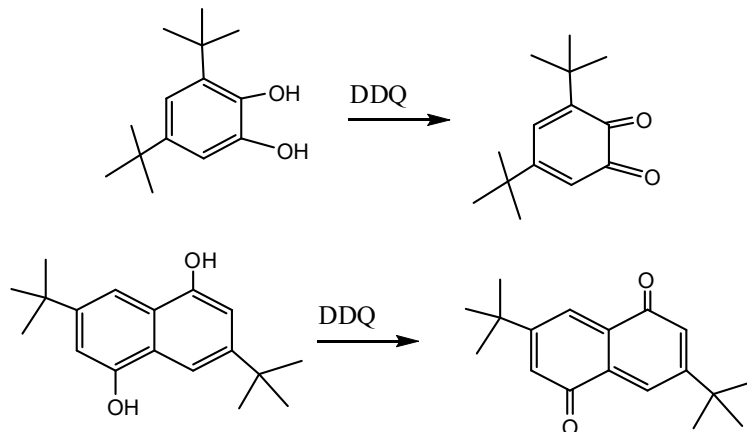
Phenols having free para position undergo dimerisation reaction.

Ex; oxidation of 2,6-disubstituted phenol, give oxidative dimerisation reaction.



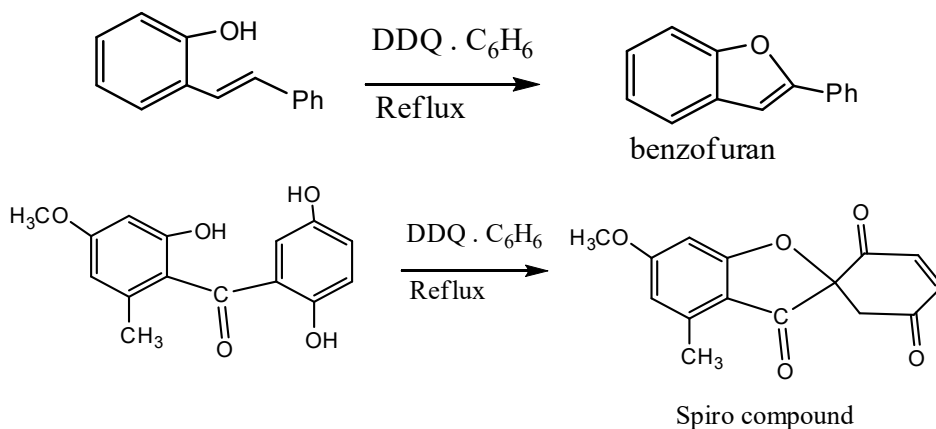
b) Dihydric phenols:

Dihydric phenol on oxidation with DDQ convert into quinone.



viii) Phenolic cyclisation:

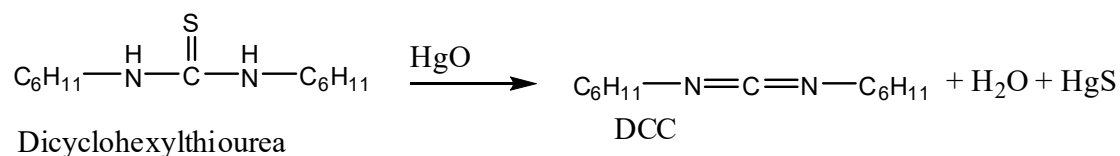
Cyclodehydrogenation reaction of phenols leads to formation of oxygen heterocycles. This reaction takes place only in non-polar solvents and has given products like benzofuran, spiro compound.



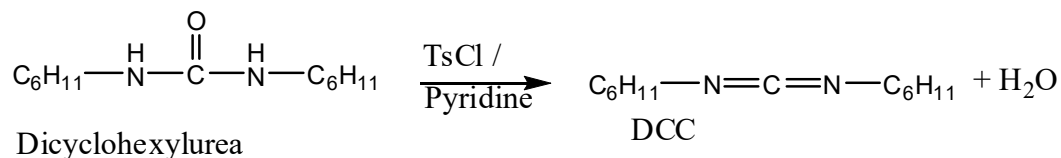
2] 1,3-DicycloHexylcarbodiimide[DCC]

SYNTHESIS:

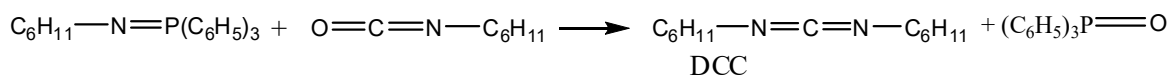
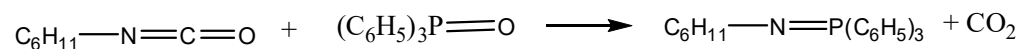
i) DCC is usually prepared by oxidation of dicyclohexylthiourea by using HgO.



ii) DCC is prepared by dehydration of dicyclohexylurea using TsCl or pyridine.

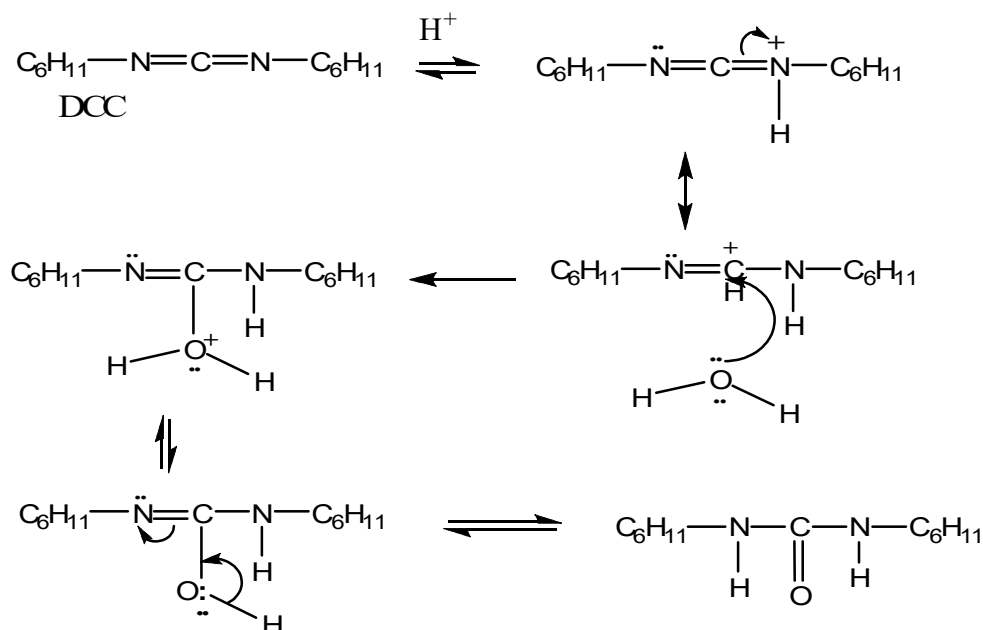


iii) DCC is prepared from cyclohexylisocyanide and $\text{Ph}_3\text{P}=\text{O}$.



Chemical Properties:

DCC reacts with water in the presence of acid and converts into N,N-dicyclohexylurea. Due to this property, DCC is used as a dehydrating agent under mild conditions.

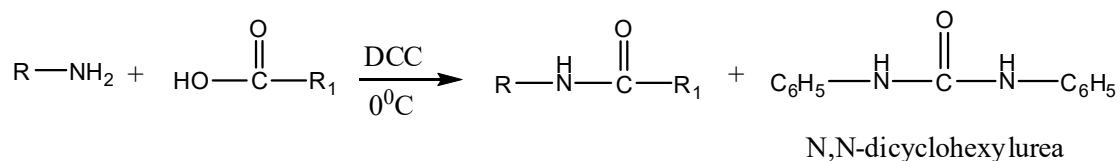


From the above it is clear that carbodiimide carbon of DCC is electrophile due to two highly electronegative nitrogen atom and therefore DCC gives nucleophilic addition reaction. At this carbon and reaction is catalysed by acid and nucleophile is used as water.

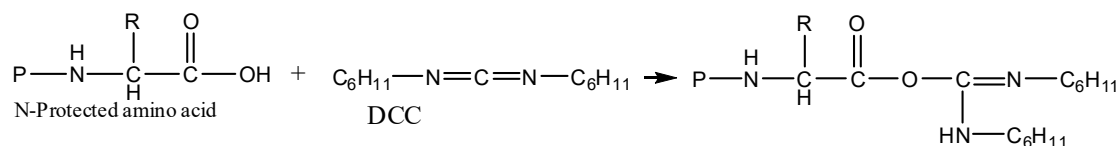
DCC is a powerful dehydrating agent commonly used for the preparation of amide, ester, anhydride, oxidation alcohol to ketone, conversion of primary amide to nitriles and β -hydroxy ketone to α,β -unsaturated ketone.

Synthetic application:

1] AMIDE FORMATION: DCC is used in the peptide synthesis and in other amide bond formation reactions of primary and secondary amines with carboxylic acids.



Amide formation is coupling reaction between acid and amide and the catalyst is known as coupling agent or acylation catalyst. for one mole of N- Protected amino acid react with DCC to give amide.

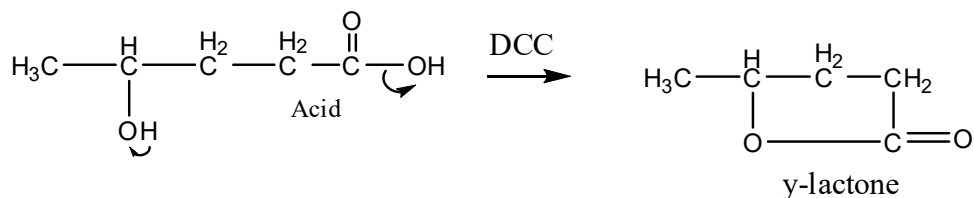


$$\begin{array}{c} \text{R} \quad \text{O} \\ | \quad || \\ \text{P}-\text{N}-\text{C}-\text{C}-\text{O}-\text{C}=\text{N}-\text{C}_6\text{H}_{11} \\ | \quad | \\ \text{H} \quad \text{H} \\ \text{HN}-\text{C}_6\text{H}_{11} \end{array} + \begin{array}{c} \text{H} \\ | \\ \text{H}_2\text{N}-\text{C}-\text{C}-\text{P} \\ | \quad || \\ \text{R} \quad \text{O} \end{array}$$

C-Protected amino acid

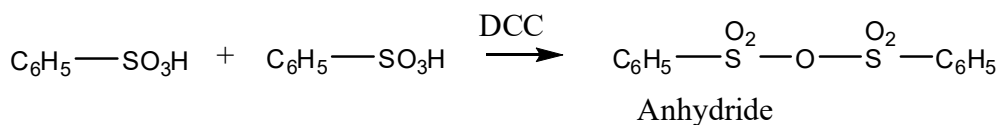
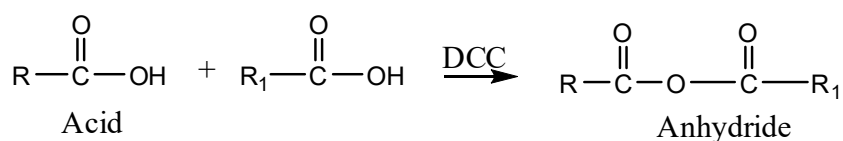

$$\begin{array}{ccccccc} \text{O} & & & & \text{O} & & \\ \parallel & & & & \parallel & & \\ \text{R}-\text{C}-\text{OH} & + & \text{H}-\text{O}-\text{R}_1 & \xrightarrow{\text{DCC}} & \text{R}-\text{C}-\text{O}-\text{R}_1 & + & \text{DCC} + \text{H}_2\text{O} \\ \text{Acid} & & \text{Alcohol} & & \text{Ester} & & \end{array}$$

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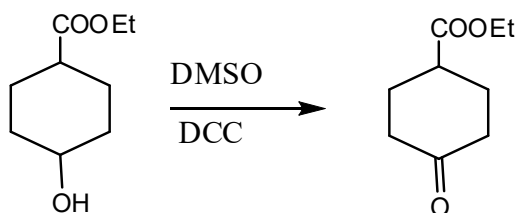
III] Anhydride formation:

DCC is simplest and most effective reagent for the preparation of symmetrical anhydride.



IV] Oxidation of alcohol:

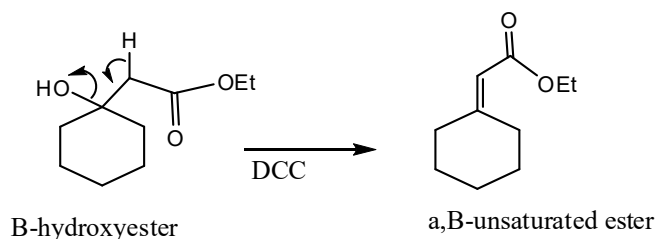
The oxidation of primary and secondary alcohol to aldehydes and ketones respectively carried out by reaction with DMSO activated by DCC and this oxidation is known as Moffatt oxidation.



V] Dehydration of β -hydroxy ketones and ester:

β -hydroxy ketones and β -hydroxy ester can be dehydrated by using DCC to give α,β -unsaturated ketone and ester respectively

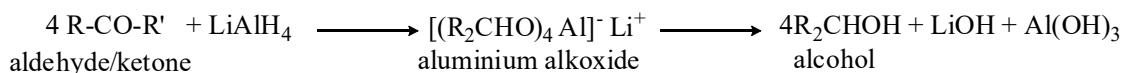




3] LITHIUM ALUMINIUM HYDRIDE [LiAlH₄]

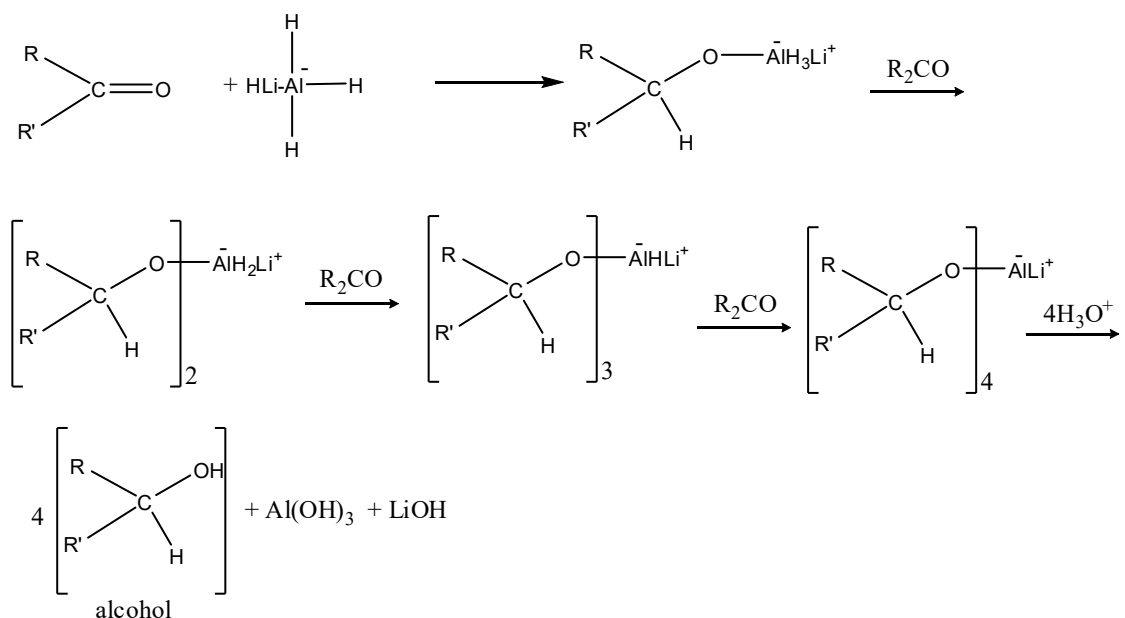
By LiAlH₄, aldehydes and ketones reduced to alcohol, initial product is the aluminium salt of the alcohol (aluminium alkoxide) which is treated with aqueous acid to yield free alcohol (primary and secondary).

One mole of LiAlH₄ reduces four mole of carbonyl compounds.



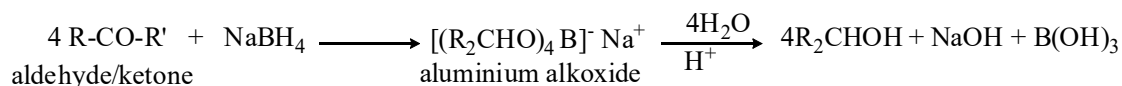
Mechanism:

Since LiAlH₄ and NaBH₄ are nucleophilic reagents normally attack polarized multiple bonds such as C=O or CN by transfer of hydride ion to the more positive atom. Further with both reagents all the four hydride ions may be used for reduction, the hydride ions are transferred in a stepwise process as illustrated below for the reduction of ketone.



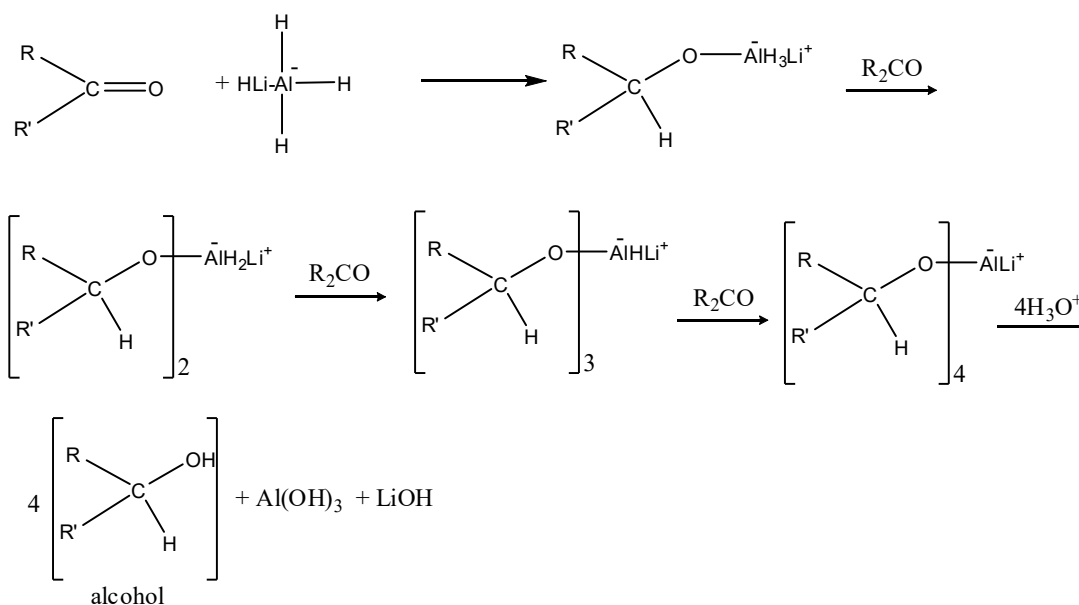
4] SODIUM BOROHYDRIDE; [NaBH₄]

Sodium borohydride is a reducing agent it reduced by transfer of hydride ions to substrate as in the case of lithium aluminium hydride (LiAlH₄)



Mechanism:

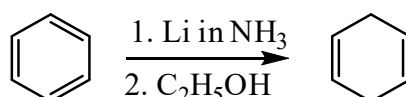
Since LiAlH₄ and NaBH₄ are nucleophilic reagents normally attack polarized multiple bonds such as C=O or CN by transfer of hydride ion to the more positive atom. Further with both reagents all the four hydride ions may be used for reduction, the hydride ion are transferred in a stepwise process as illustrated below for the reduction of ketone.

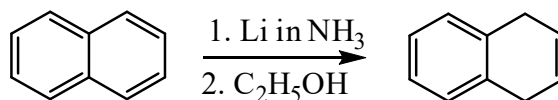


5] BIRCH REDUCTION:

When aromatic rings are reduced with sodium, potassium or lithium in liquid ammonia or amine in the presence of alcohol, addition of hydrogen takes place at position 1 and 4 to give unconjugated diene. This reaction is called Birch reduction.

For ex. Benzene gives 1,4-dihydrocyclohexadiene and naphthalene gives 1,4-dihydronaphthalene.

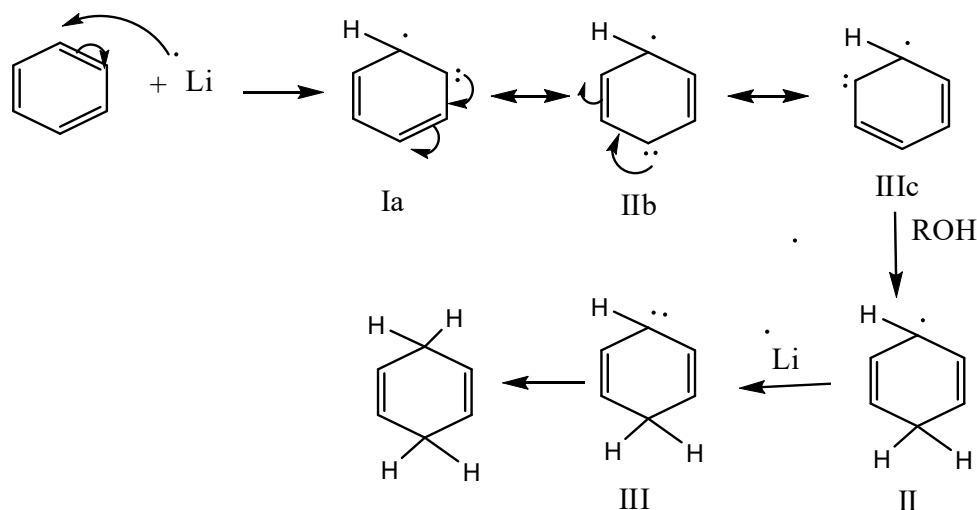




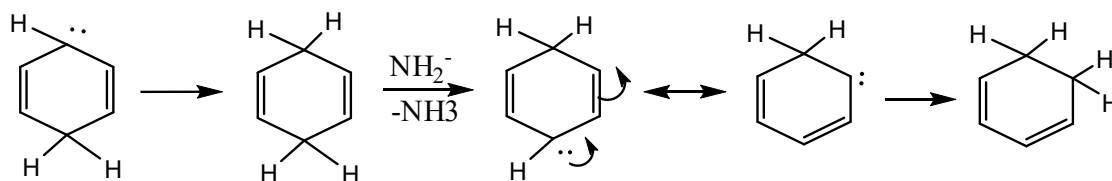
Liquid ammonia serves as solvent. Primary amines also used as solvent with advantage. At higher temperature.

Mechanism:

The accepted mechanism of reduction involves the following sequential steps. The metal transfer one electron to the benzene ring to produce a resonance stabilized anion radical (Ia- I c) which accept a proton from the alcohol to form radical (II). The addition of an electron from the metal to the radical produces an anion (III) which subsequently takes up a proton from the alcohol to give the dihydro product.



At higher temperature ammonia becomes the proton source and alcohol need not be used. the amide ion formed is a strong base and isomerizes the 1,4-dihydro product to 1,2-dihydro product.



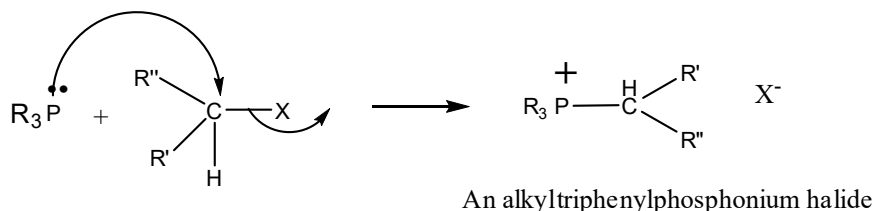
Name Reactions:

6] WITTIG REACTION:

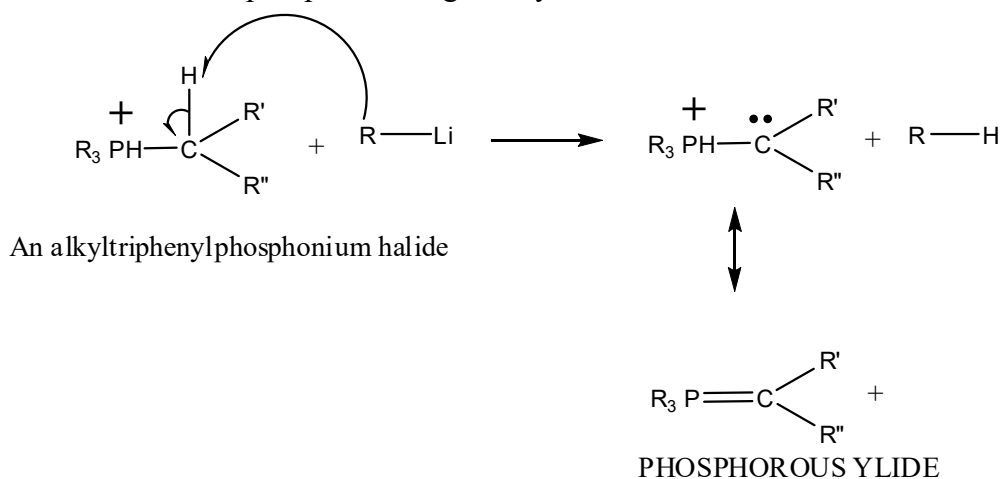
The reaction of aldehydes and ketones with phosphorane or phosphonium ylide to produce an alkene is known as Wittig reaction.

Phosphorus ylides for this reaction are prepared from triphenylphosphine and alkyl halides which has at least one α -hydrogen atom i.e. (primary and secondary alkyl halides)

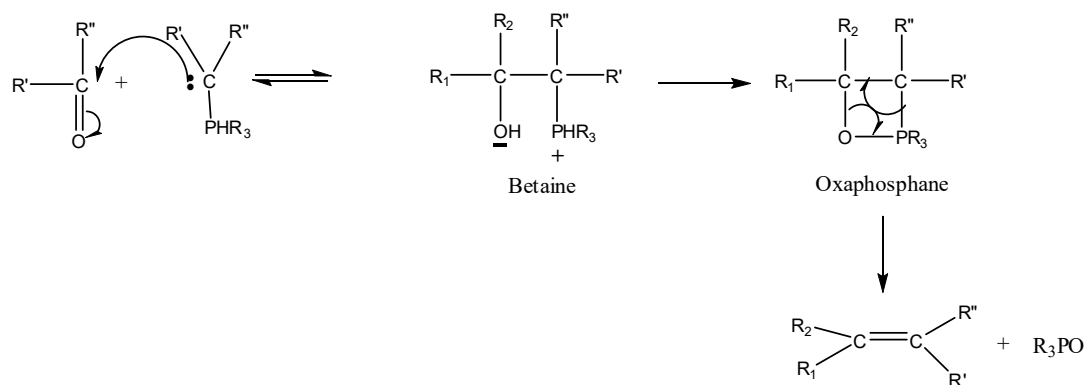
Reaction: triphenyl phosphine is an excellent nucleophile and a weak base it reacts readily with primary and secondary alkyl halides by an S_N2 mechanism to give alkyl triphenylphosphonium salt.



A strong base usually alkyl lithium, sodium hydride or sodamide removes a proton from the carbon that is attached to phosphorous to give an ylide.



The carbon of the ylide is a nucleophile and gives nucleophilic addition reaction with carbonyl carbon to form betaine which leads to the formation of a four membered ring. And oxaphosphetane. Oxaphosphetane is strained and unstable gives alkene and trialkylphosphene oxide.

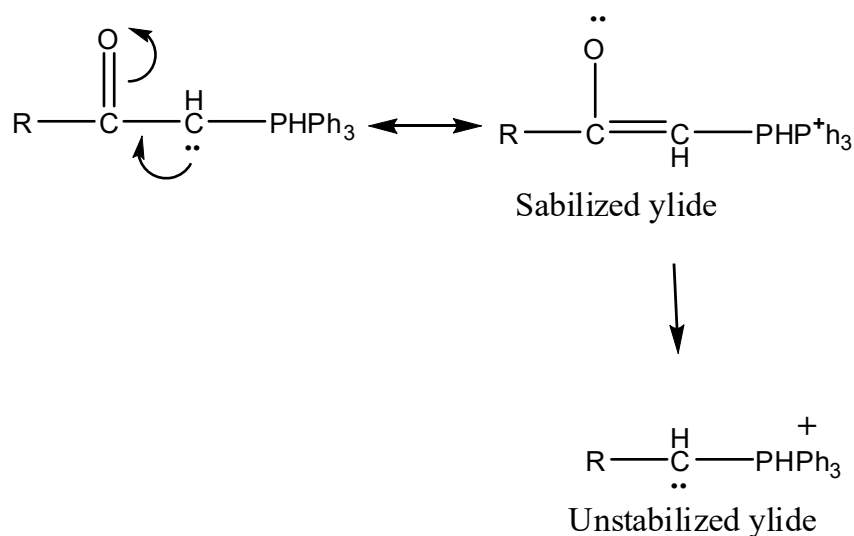


Mechanism of Wittig reaction

Stereo selectivity in the Wittig Reaction:

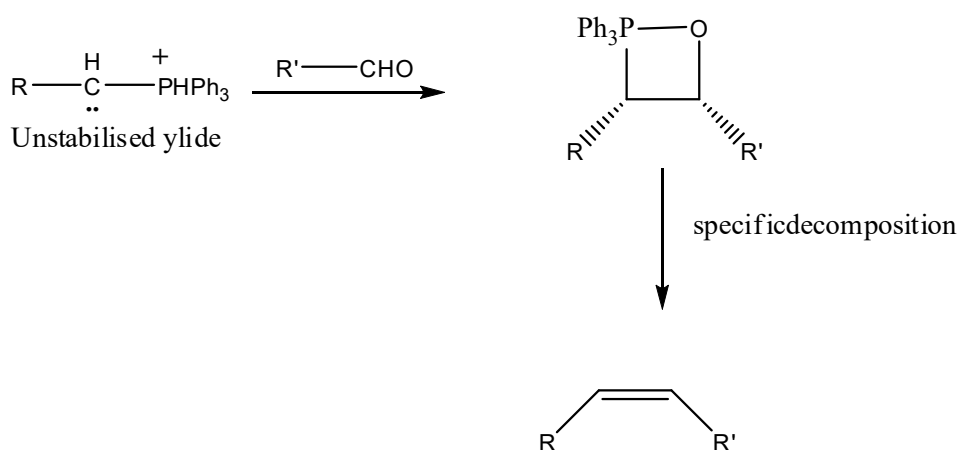
Although the mixture of (E) and (Z) isomers may result in this reaction, but even then some reactions are (Z) selective and some reactions are (E) selective. Stereoselectivity of the reaction can depend upon the nature of the substituents on the carbon atom of the ylide.

With a stabilized ylide the Wittig reaction is E selective, and with an unstabilized ylide the reaction is Z selective. Ylides containing anion-stabilized substituents adjacent to the negative charge (such as a carbonyl group) are known as stabilized ylides. The rest are called unstabilized ylides.



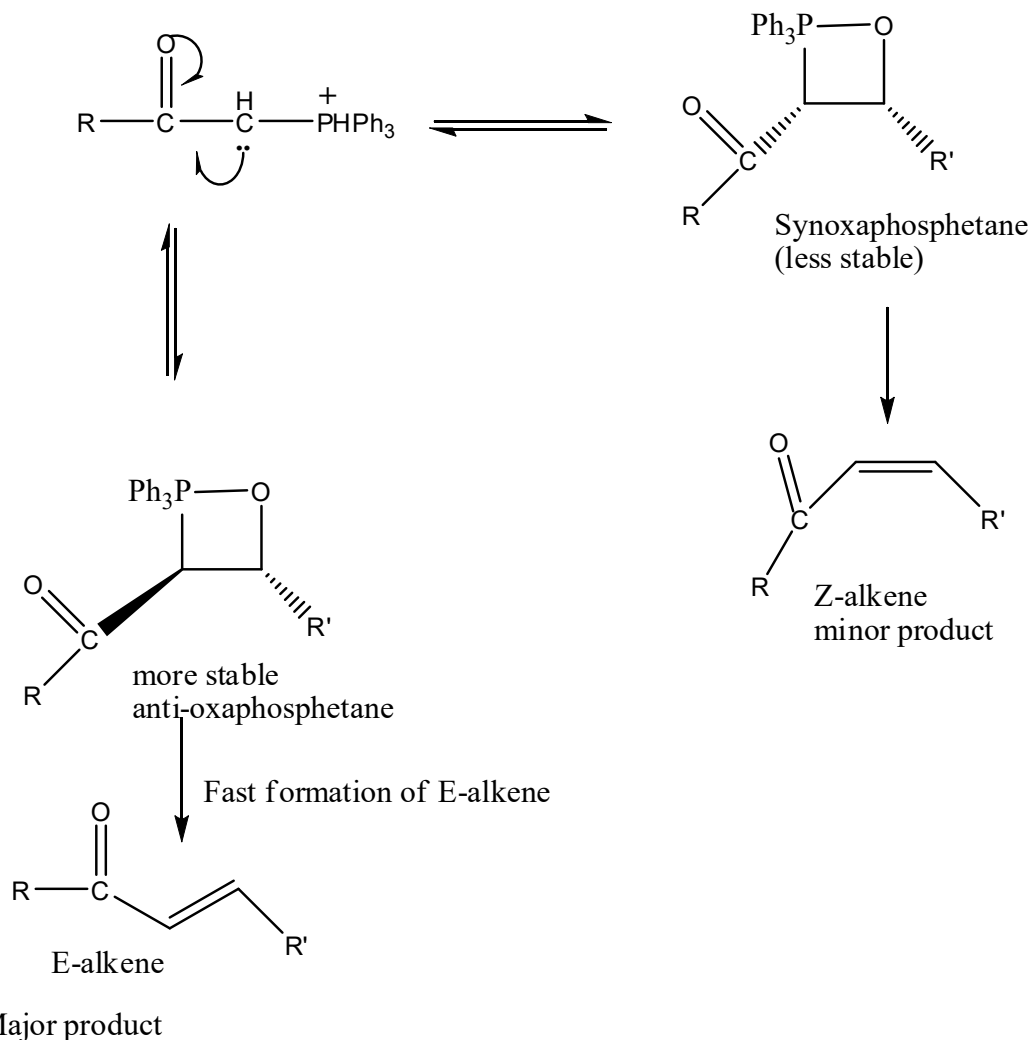
R = H / OR / alkyl

Formation of Z-alkene from unstabilised ylide;



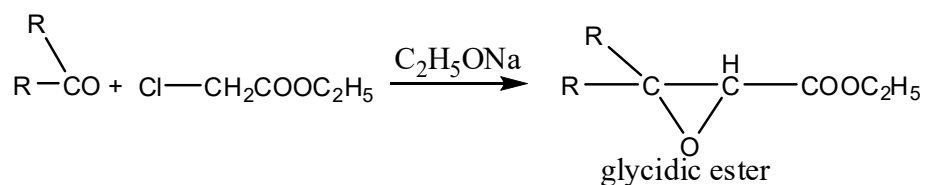
Formation of Z-alkene from unstabilised ylide

Formation of E-alkene from stabilized ylide:



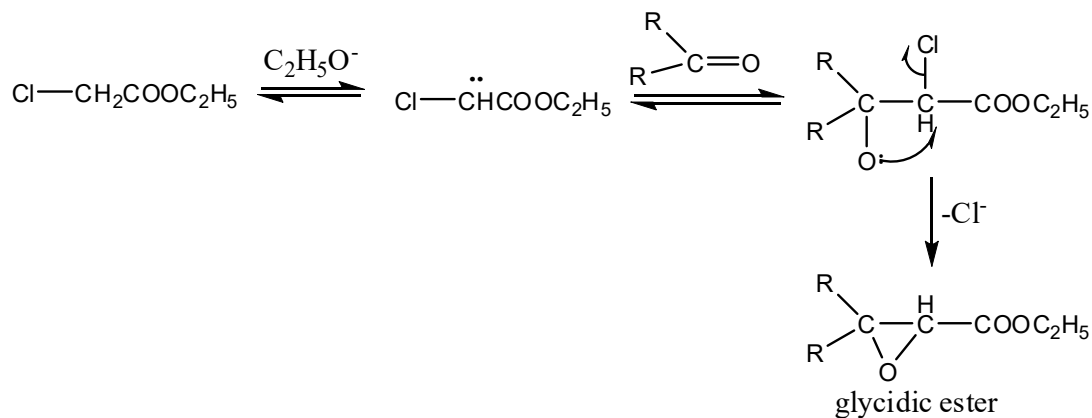
7] DARZEN CONDENSATION:

This reaction involves the condensation of an aldehydes or ketone with an α -halogen ester in the presence of sodium ethoxide or sodsamide to give an α,β -epoxyester (glycidic ester)



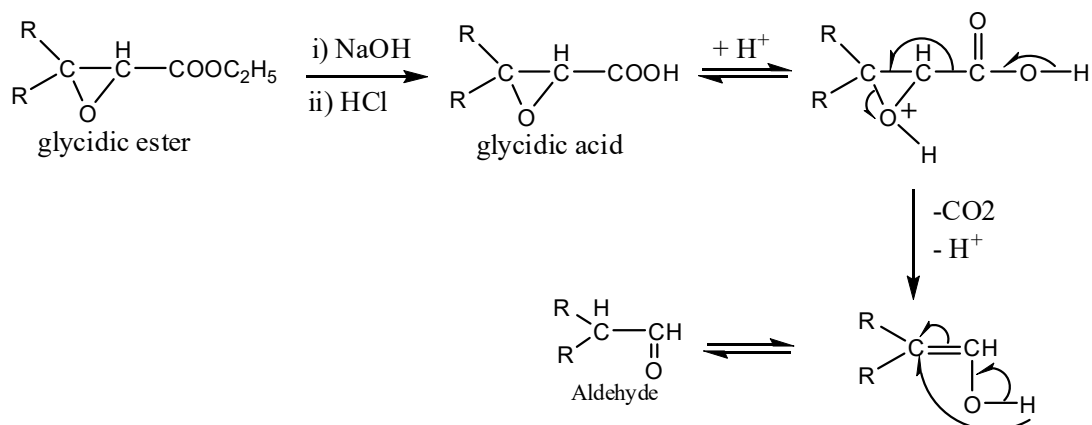
Mechanism:

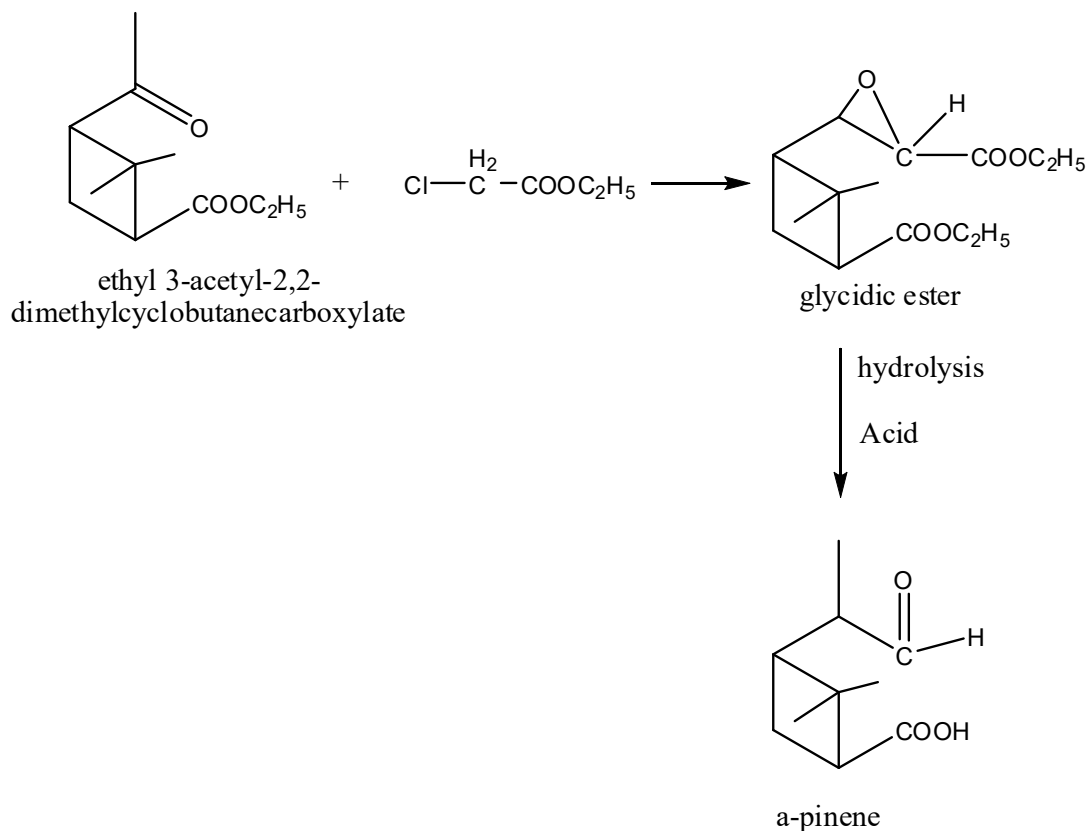
This follows the following path

**Synthetic Application:-**

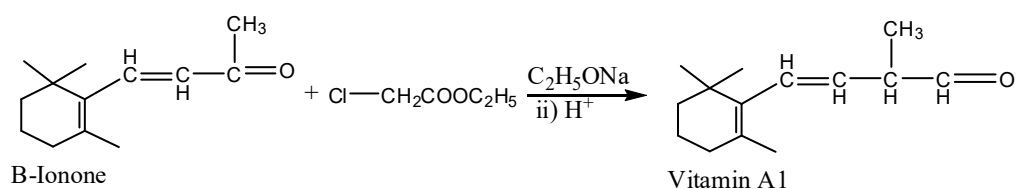
i) Synthesis of Aldehyde / ketone

Decarboxylation of glycidic ester: the epoxy ester obtained above gives salt of the epoxy acid on alkaline hydrolysis, which on further treatment with acid undergoes decarboxylation and epoxide ring opening to form an aldehydes or ketone.

ii) Synthesis of α -pinene:

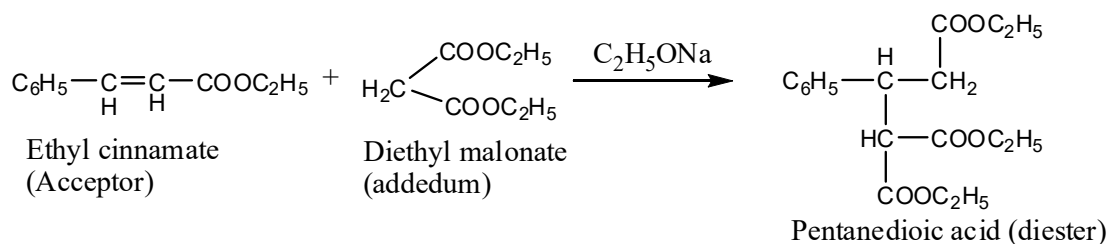


iii) Synthesis of Vitamin A1:



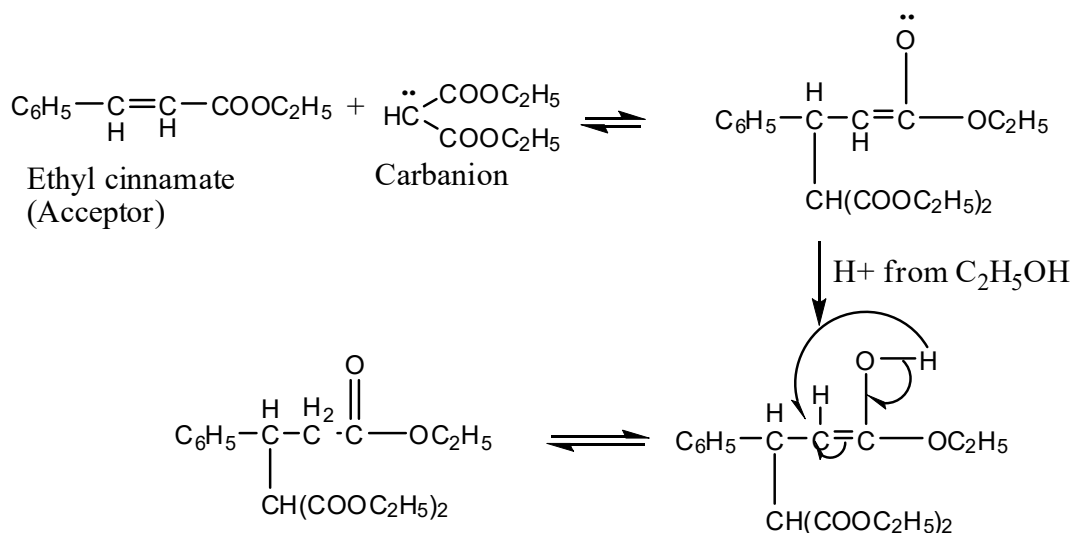
8] MICHAEL REACTION:

This is the addition reaction between an α,β -unsaturated keto compound (acceptor) and a compound with an active methylene group (addendum) in the presence of a base. A Michael systematically investigated the reaction between diethyl malonate and ethyl cinnamate in the presence of sodium ethoxide to afford a substituted pentanedioic acid diester.



Mechanism:-

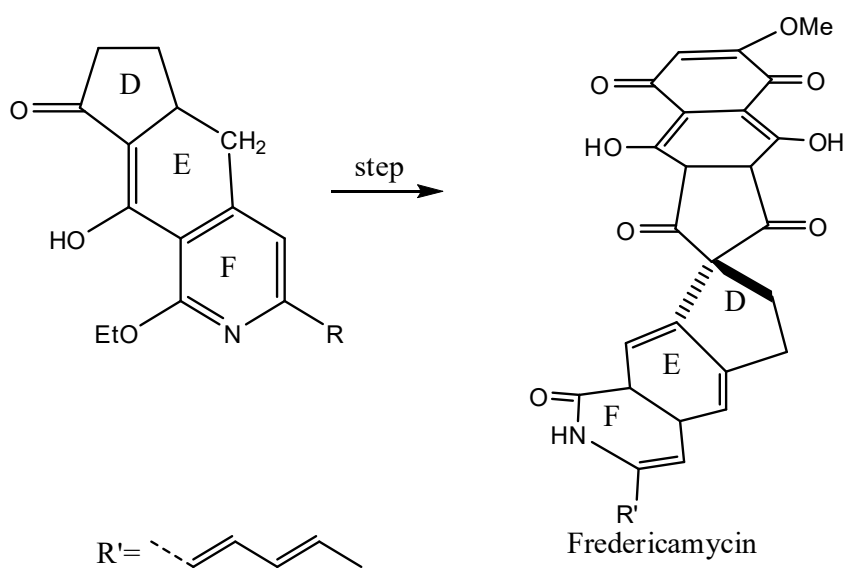
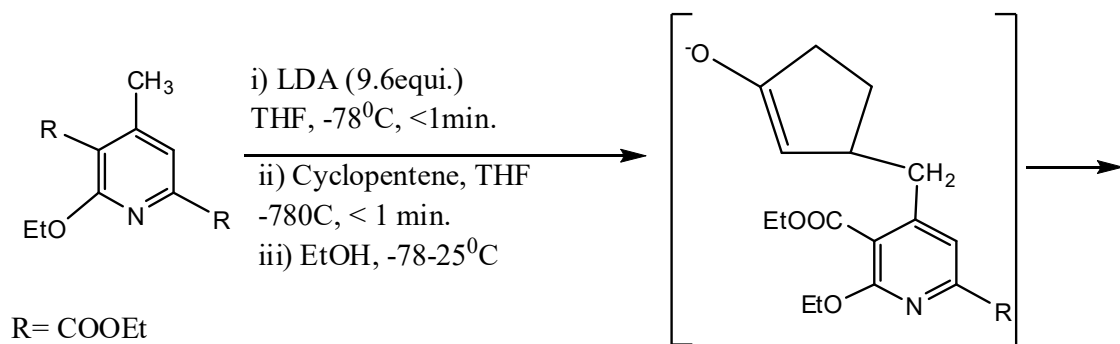
The mechanism is illustrated with the addition of a malonate anion across the double bond of the ethyl cinnamate. The reaction is reversible in protic solvents and thermodynamically most stable product usually predominates.



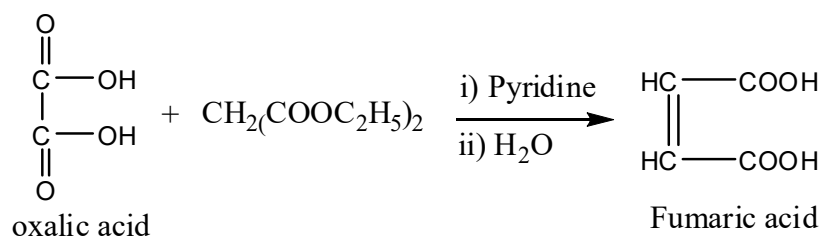
Synthetic Application:-

1] Synthesis of Fredericamycin A:

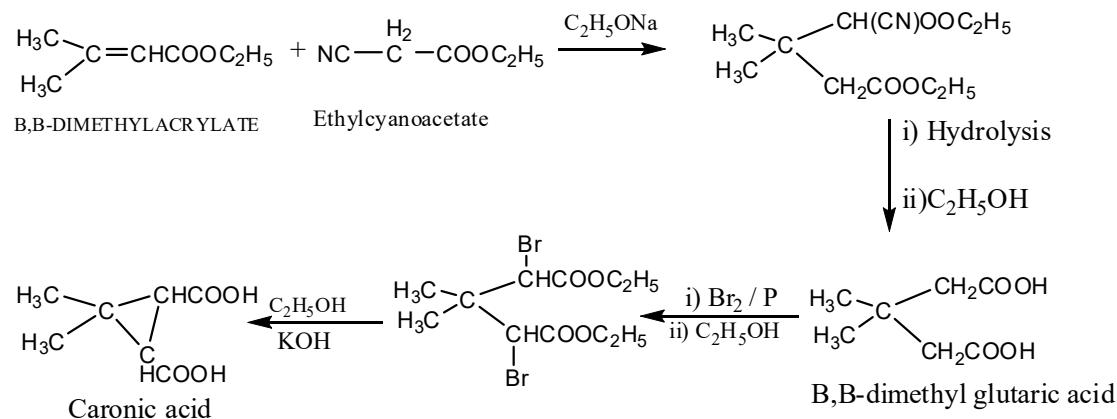
The highly substituted 4-methyl pyridine precursor was treated with excess LDA (Lithium diisopropyl amide) followed by addition of cyclopentenone, the Michael adduct underwent an intramolecular acylation with ester functionality in situ to afford the desired DEF tricycle.



2] Synthesis of dicarboxylic acids:-

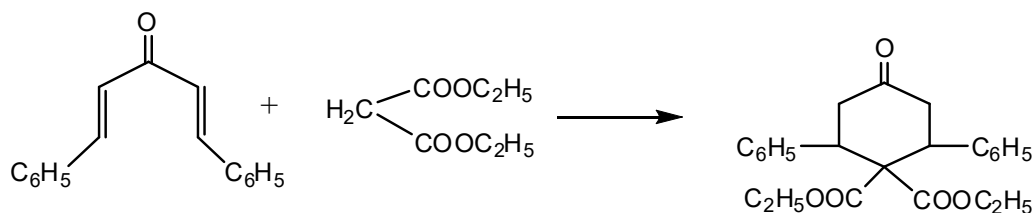


3] Synthesis of Cyclopropane derivatives, e.g. Caronic acid :



4] Synthesis of ring compounds:

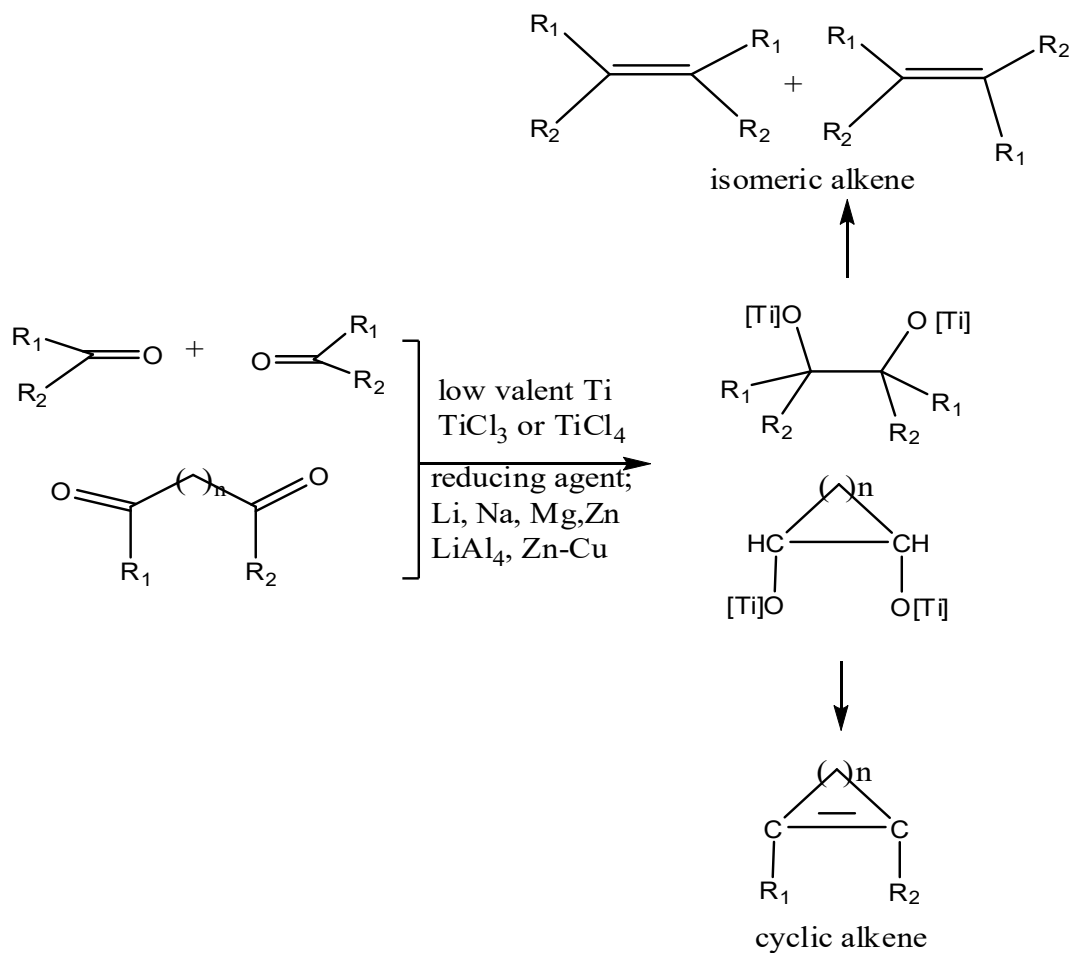
Double Michael addition are often employed for synthesizing ring compounds.



9] MECMURRY REACTION AND COUPLING:-

McMurry independently discovered that the treatment of carbonyl compounds with low valent titanium led to olifinic coupled products.

The reductive coupling of carbonyl compounds using low valent titanium compounds to form corresponding alkene is known as the McMurry reaction.

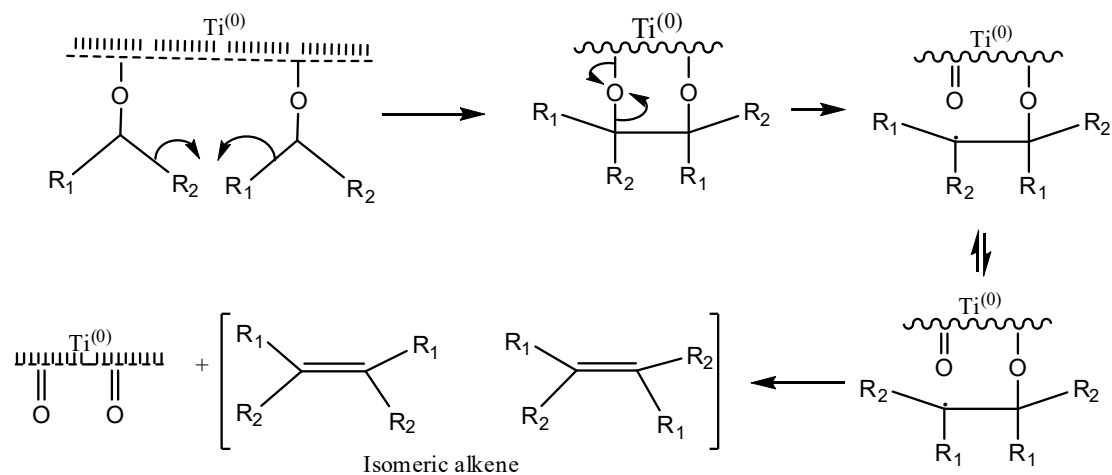


MECHANISM:

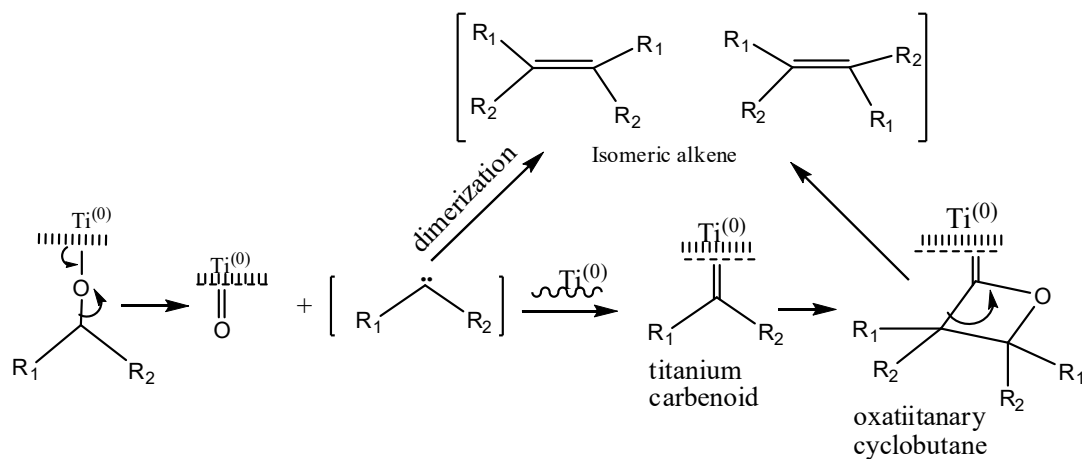
The mechanism of McMurry coupling is composed of two distinct steps.

- Pinacol formation
- deoxygenation to the alkene.

Extensive research showed that the low valent titanium is most likely a mixture of $(Ti)^{II}$ and $(Ti)^0$ and the ratio of these species depends on the method of preparation of (solvent, temperature, reducing agent etc.)

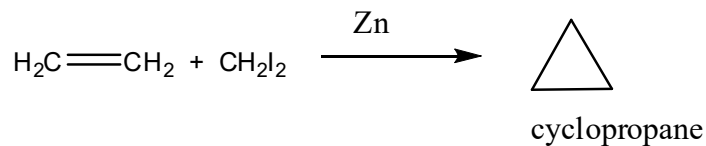


Mechanism involving carbene intermediate:



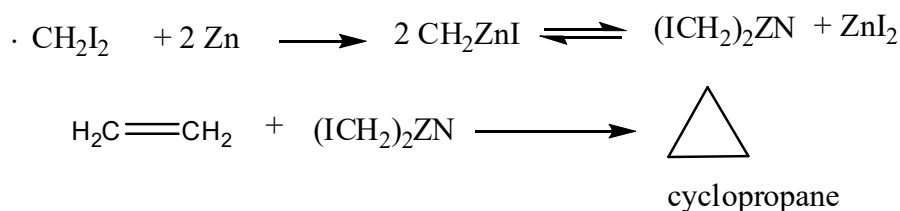
10] Simmons-Smith Reaction:

This reaction affords the cyclopropanation of olefins.



Mechanism:

Ultrasonication improve the rate of formation of these organozinc compounds, as with many organometallic reaction occurring at



The mechanism has not been fully clarified, but pure carbenes can be excluded and metal carbenoid is likely to be involved. The following result results may be interpreted to indicate the possible complexation of the active species by hydroxy group leading to reaction on the same face as this substituent. This would be possible only if an organozinc reagent present.

Synthetic Application

The Simmons-Smith reaction is the stereospecific conversion of alkenes into cyclopropanes using a zinc carbenoid intermediate (typically formed from diiodomethane and a zinc-copper couple or diethylzinc). It is prized in organic synthesis for its high functional group tolerance and ability to retain the alkene's stereochemistry without hazardous reagents.

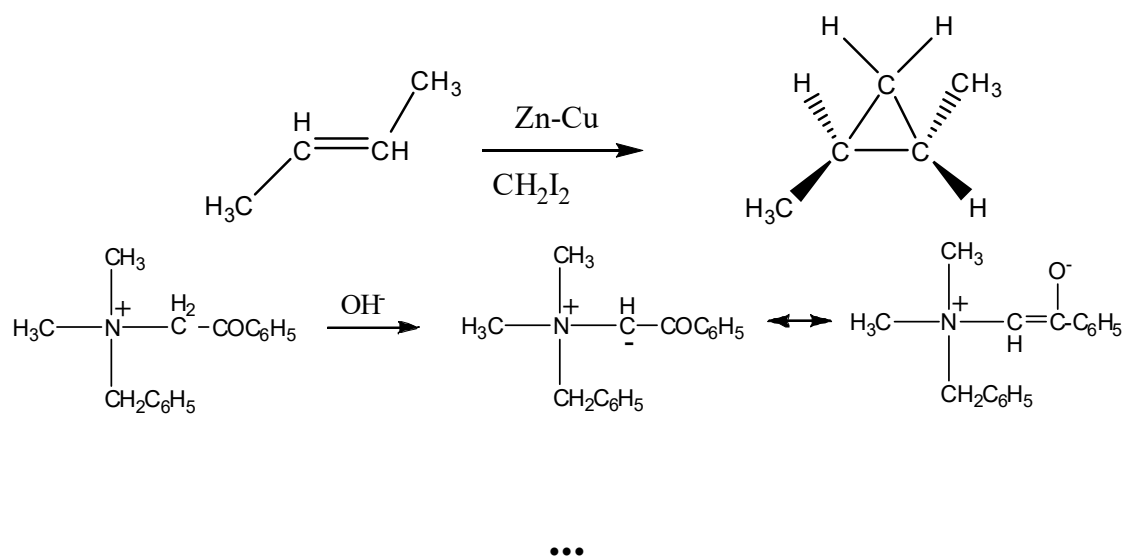
Total Synthesis of Natural Products: The cyclopropane motif is a core structural unit in many complex natural products, including terpenoids, alkaloids, and fatty acids. The Furukawa modification (using $(\text{Et})_2\text{Zn}$ and $(\text{CH}_2\text{I})_2$) is frequently used as a key step in total synthesis campaigns targeting bioactive natural compounds.

Pharmaceutical Development: The reaction is a critical step in the manufacturing of several key pharmaceuticals, including the antidiabetic drug Saxagliptin (Onglyza), the respiratory drug Ropivacaine, and investigational agents like GSK1360707F.

Biososteric Replacement: Medicinal chemists utilize the reaction to introduce cyclopropanes as rigid, metabolically stable surrogates for bulky groups like tert-butyl or isopropyl groups in drug design.

Synthesis of Constrained Amino Acids: By applying the Simmons-Smith reaction to allylic substrates, chemists synthesize conformationally constrained amino acid derivatives (such as methano-prolines), which are vital for studying protein structure and function.

Stereospecific Transformation: The reaction retains the geometry of the starting olefin; cis-alkenes yield cis-cyclopropanes, and trans-alkenes yield trans-cyclopropanes. The Simmons-Smith reagent transfers a CH_2 unit to the alkene in a stereospecific reaction. For example, *trans*-2-butene reacts with the Simmons-Smith reagent to give only *trans*-1,2-dimethylcyclopropane.



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