

Chapter-3

Stereochemistry

It is the branch of Chemistry deals with the study of three dimensional Configuration of the atoms in a molecule.

Isomers :- Compounds which are having same molecular formula but different structural formula

Stereoisomers :- Isomers which have same structural formula but have different relative rearrangement of atoms or groups in space are called stereoisomers and phenomenon is called as stereoisomerism.

Stereo means - Three Dimensional
Also known as 3D Chemistry

Isomerism :- There are numerous chemical ~~reactions~~ compounds having same

molecular formula but having different physical and chemical properties. Such compounds are called isomers and the property is known as Isomerism

Difference in their structure is main reason for the compounds having different physical and chemical properties.

Types of Isomerism

- 1) Structural Isomerism ✓
- 2) Stereoisomerism ✓

1) Structural Isomerism:- It is due to different arrangement of atoms within the molecule

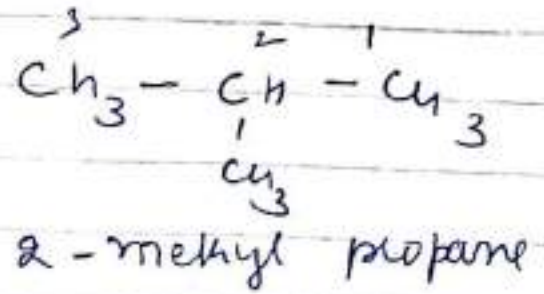
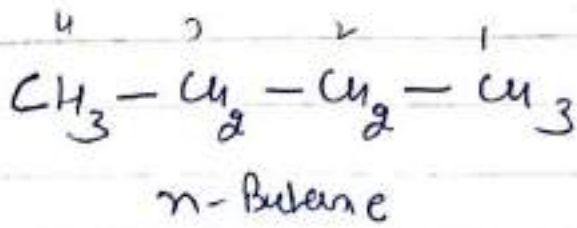
Types

a) Chain Isomerism:- Isomers which are having difference in the nature of carbon chains. (arrangement of carbon chains)

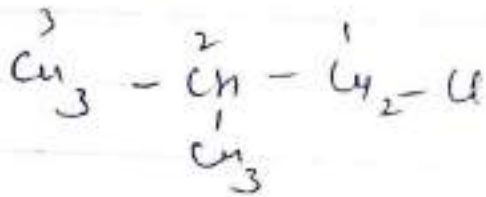
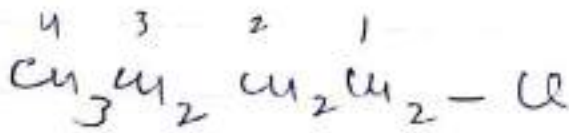
(i) Butane

n-butane

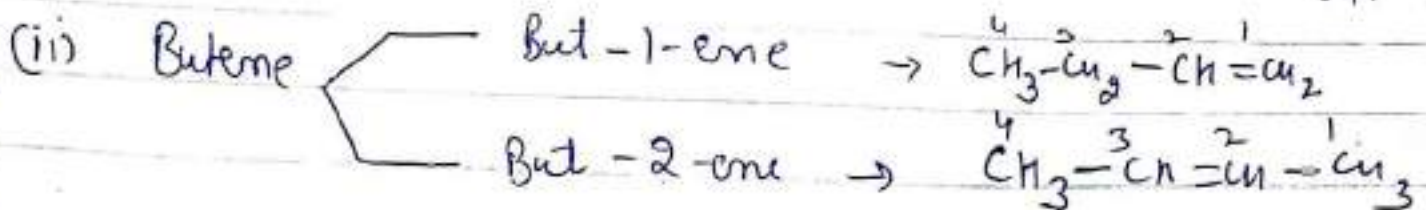
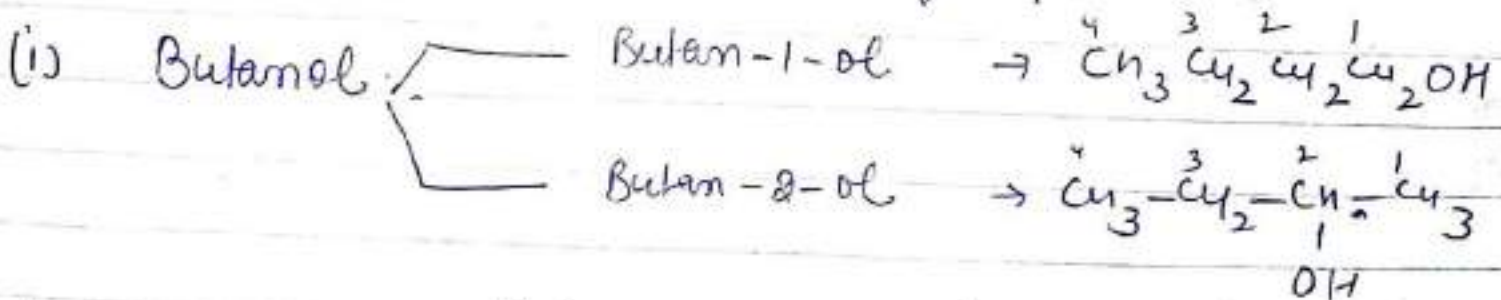
→ Iso-butane (2-methyl propane)



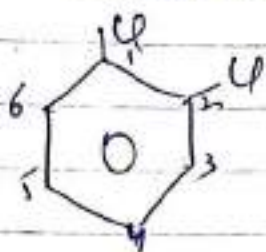
(ii) Butyl chloride $\begin{cases} \rightarrow \text{n-Butyl chloride} \\ \rightarrow \text{isobutyl chloride} \end{cases}$



(b) Position Isomerism :- which are having difference in position occupied by an atom or a function group.

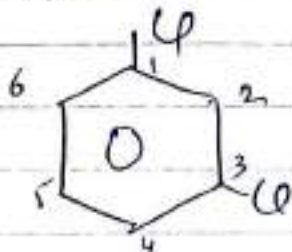


(iii) Dichloro Benzene



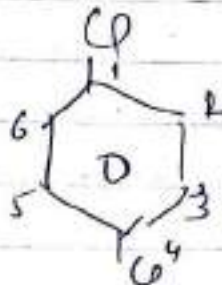
1,2 - Dichloro Benzene

o - Dichloro Benzene



1,3 Dichloro Benzene

meta or m - Dichloro Benzene



1,4 Dichloro Benzene

p - Dichloro Benzene

(c) Functional Isomerism

Compounds having same molecular formula but different functional groups are called functional isomers and the phenomenon is called as functional Isomerism.

(i) Alcohols and Ethers

Molecular formula C_2H_6O

Ethanol $\rightarrow CH_3CH_2OH$ (Ethyl Alcohol)

Methoxymethane $\rightarrow CH_3-O-CH_3$ (Dimethyl ether)

(ii) Carbonylic acids and ethers
molecular formula \rightarrow $C_2H_4O_2$

Ethanoic Acid - $CH_3 - \overset{O}{\parallel} C - OH$ - Acetic acid

Methyl methanoate - $H - \overset{O}{\parallel} C - OCH_3$ - Methyl formate

(iii) Cyanide and Isocyanide
molecular formula

~~C_2H_3N~~ C_2H_3N

Methyl Cyanide - $CH_3 - C \equiv N$ \rightarrow Ethanenitrile

Methyl Isocyanide - $CH_3 - N \equiv C$ \rightarrow Ethane isonitrile

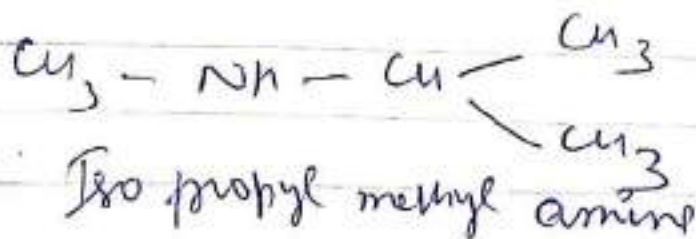
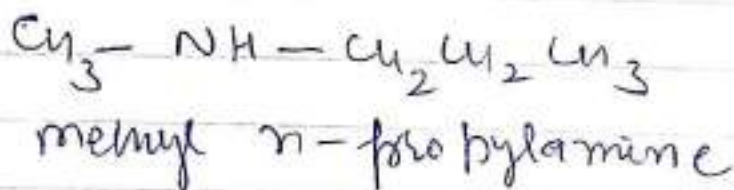
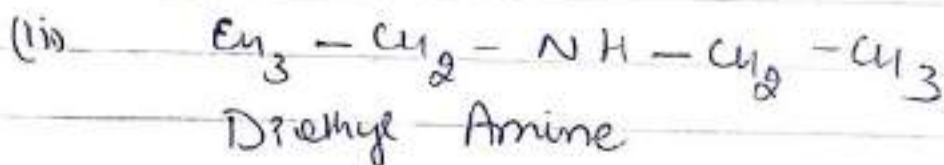
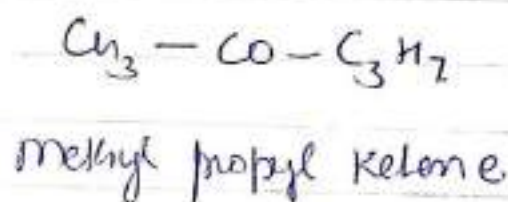
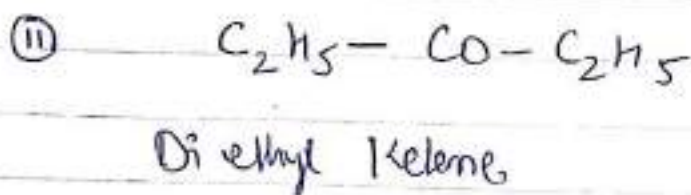
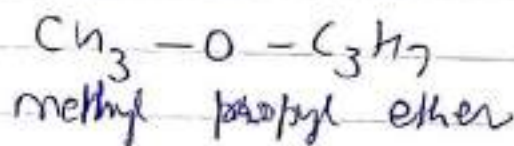
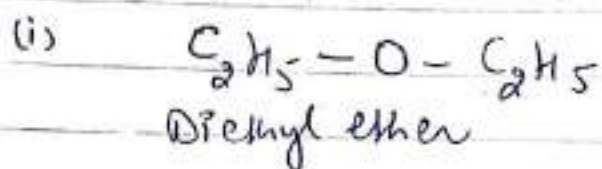
(iv) Aldehyde and Ketone
molecular formula

C_3H_6O

Propanaldehyde - $CH_3 - CH_2 - CHO$ - Propenal

Acetone - $CH_3 - \overset{O}{\parallel} C - CH_3$ - Dimethyl ketone

(a) Metamerism:- Compounds having same molecular formula and even the same functional group, but the two alkyl groups attached to same functional group are different.



(e) Tautomerism :- Isomers which are special case of functional isomerism in which the isomers exist in dynamic equilibrium with each other.

It arises due to migration of a hydrogen atom from one carbon to another atom (oxygen or nitrogen) within the same molecule. The isomers thus obtained are called tautomers and phenomenon is called tautomerism.

Two types

(i) Dyad System

which involves 1,2-migration of a proton from one atom to another within the same molecule with necessary rearrangement of linkages.



Hydrogen Cyanide

Hydrogen Isocyanide

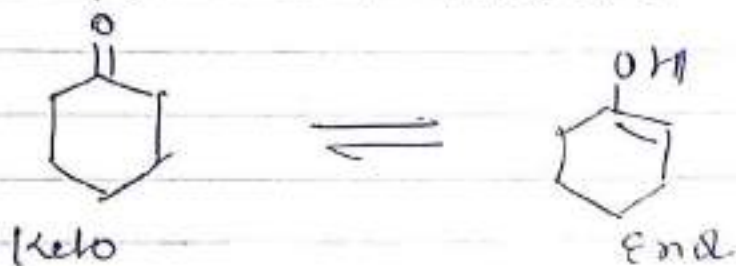
(11)

Triad System

Here 1,3 migration occurs



Keto-enol tautomerism



(12) Stereoisomerism :- Different arrangement of atoms around the Carbon atom in space. Stereoisomers have the same molecular as well as structural formula but possess different arrangement of atoms in space, i.e. Configuration.

Types:

- ✓ Geometrical or cis-trans
- ✓ Optical isomerism
- ✓ Conformational isomerism

Optical Isomerism :-

Optical isomers:- Such compounds which resemble one another in their physical and chemical properties but they differ in their behaviour towards the action of plane polarised light. Such compounds are called optically active and compounds possessing the property are called isomers (optical) and phenomenon is called optical isomerism.

Optical Activity :-

Optical Activity is the rotation of plane polarised light by certain compounds towards the right or left.

If the compounds rotate the plane polarised light towards the right side it is known as Dextro-Rotatory.

Representation d or (+) form

if the Compounds rotate the plane polarised light in ~~the~~ left side are called as Laevo-rotatory

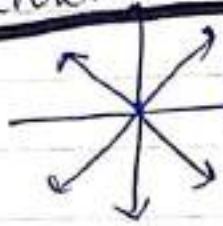
Represented by l or (-) form

The Compounds which show optical activity are known as optical active Compounds and such isomers are called as optical isomers and phenomenon of showing optical activity is called as optical isomerism.

✓ Plane

Polarised & light :-

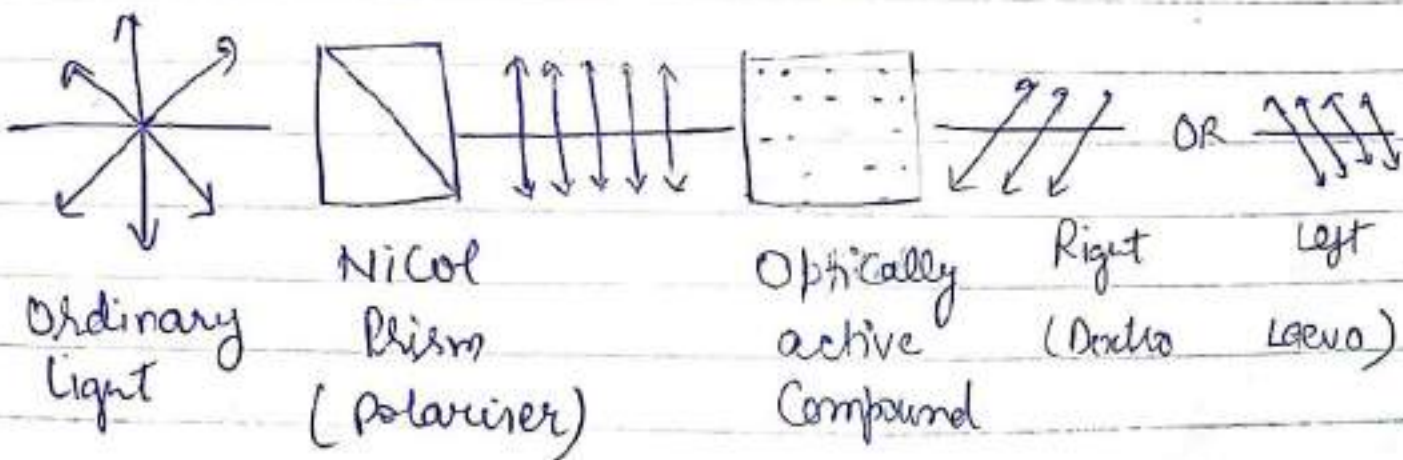
An ordinary light consists of electromagnetic waves and its vibrations taking place in all directions perpendicularly to the direction in which it travels!

^{Single}
Mono chromatic light is the one which consists of waves of one wavelength only.

 Direction in which it travels
 → But have vibrations in all planes

When a ray of monochromatic light is passed through a Nicol prism, the wave motion of light is in one direction only or in one plane.

Such a beam of light which has vibration in one plane only is called plane polarised light (PPL)

The Nicol prism used to obtain plane polarised light is called polariser.



Hence an optically active compound rotate the PPL through a certain angle.

The property by virtue of which the organic compounds can rotate the PPL is known as Optical Activity



Specific Rotation :-

The angle through which PPL is rotated by an optically active compound is known as Angle of Rotation.

Represented by (α) alpha

Instrument — Polarimeter

- 1) Nature of the compound
- 2) Nature of solvent
- 3) Concentration of solution
- 4) Length of the solution
- 5) Temperature
- 6) wavelength

Power to rotate plane polarised light by a solution is expressed as "Specific Rotation"

It is defined as angle of rotation (α) produced by one decimetre length of solution having one gram of the substance per millilitre.

Specific Rotation :- $100 \times \frac{\text{observed angle of rotation } \theta}{\text{Length of decimeters} \times \text{Gram of substance present in 100 ml of solution}}$

Length of decimeters \times Gram of substance present in 100 ml of solution.

D is D-line (wavelength for Na light)

$$[\alpha]_D^{T^\circ} = \frac{100 \times \theta}{l \times c}$$

$$[\alpha]_D^{20^\circ} = -20^\circ$$

means that a specific rotation of -20° is obtained at 20°C of temperature

Chirality :-

Chiral structures :- \rightarrow A structure or object is said to be chiral if it has no plane of symmetry and is not superimposable on its mirror image.

Exp - Human hand (non superimposable)

Achiral structures :- \rightarrow A structure or object is said to be Achiral if it has

a plane of symmetry and is superimposable on its mirror image.

Exp



Superimposable

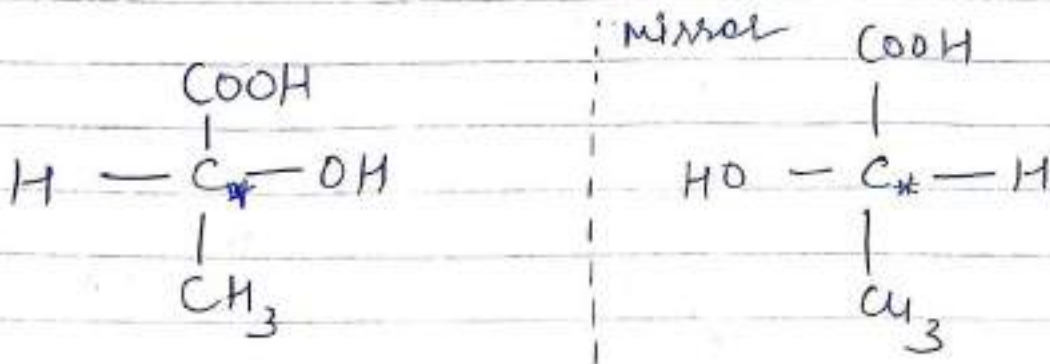
Chirality is the property of a chiral molecule to be non superimposable on its mirror image.

Chirality in Organic Compounds

Chirality means dissymmetry

• A carbon is one having all

Example Lactic Acid (no symmetry)

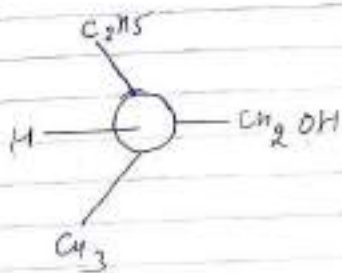
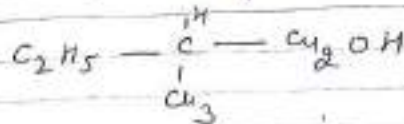


C^* = chiral carbon

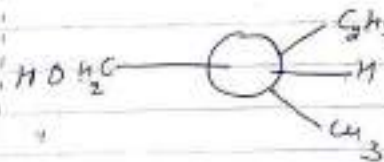
Types of Optical Isomers

- 1) Enantiomerism
- 2) Diastereomerism

Exp 2-methyl-1-butanol



Non Superimposable

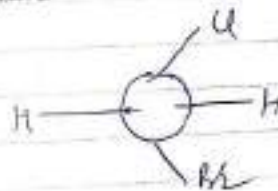
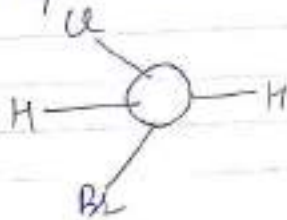


mirror

Enantiomeric forms

Question Is CH_2ClCH_3 show Enantiomerism?

Ans: - NO, because all the four groups are not different



Superimposable

mirror image

Essential Condition for Enantiomerism

→ Chiral Carbon is required.

→ Isomers are non superimposable mirror images of each other.

→ No plane of symmetry

Characteristics of Enantiomers

① They have identical physical properties

Such as melting points, boiling points solubilities etc. The only difference lies in the direction of PPL

② They have identical chemical properties for ex-p (+) lactic acid have same property as that of (-) lactic acid the only difference lies in between the rates of reactions

③ They have different biological properties.

for Example

(+) Sugar plays important Role in animal metabolism

(-) Sugar is not metabolized.

(9) When equal quantities of Enantiomers are mixed together it results in the formation of an optically inactive form called "Racemic mixture"

Racemate
Represented by \pm

(+) Lactic acid and (-) Lactic acid are mixed

(\pm) Lactic acid [Inactive]

Diastereomerism:-

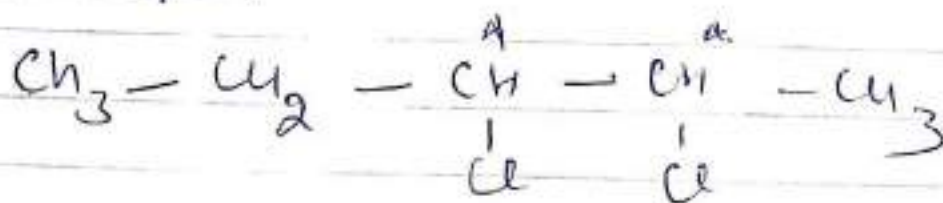
Diastereomers are the ^{stereoisomers} compounds ~~having~~ that are not the mirror images of one another and are not superimposable on each other.

Compounds containing more than one chiral centre exist in more than two stereoisomeric forms.

It is sometimes ^{difficult} to find out which isomers are diastereomers.

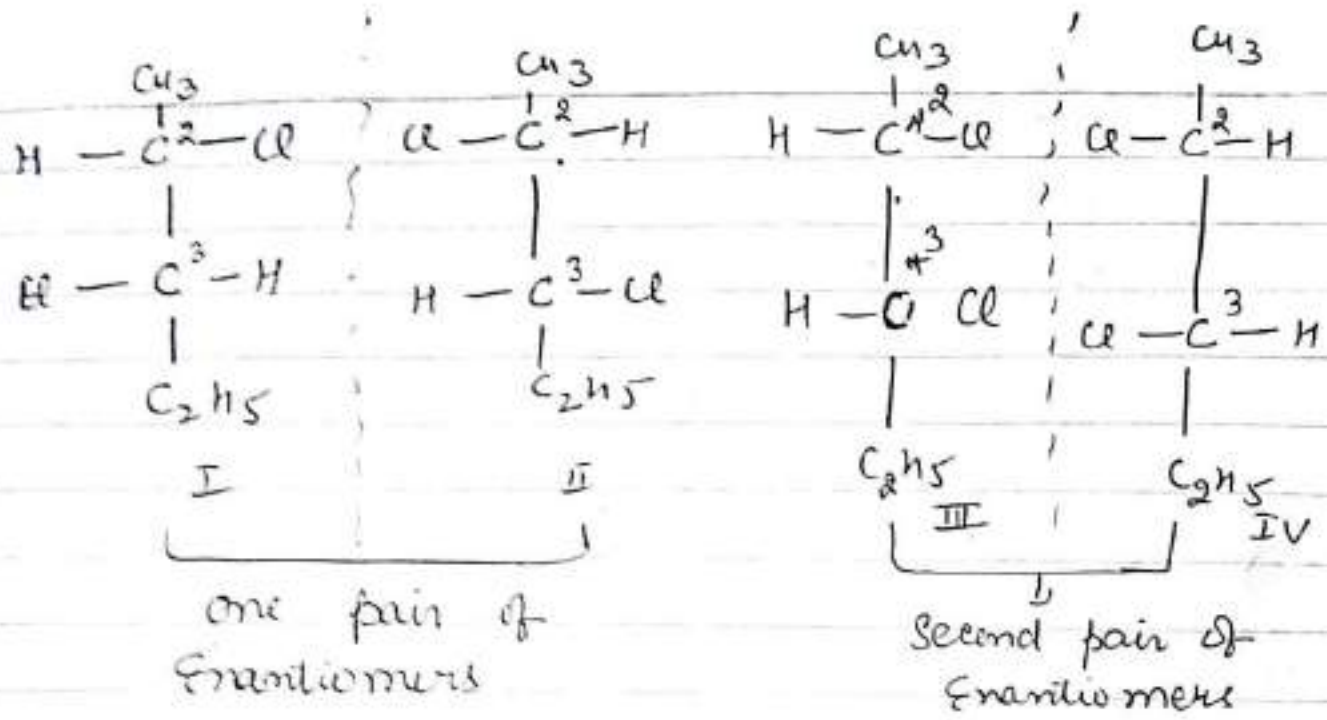
For a compound having more than two chiral centres we have a set of enantiomers (mirror images of each other) and a set of diastereoisomers (Not mirror image of each other)

For example



2, 3 - Dichloropentane

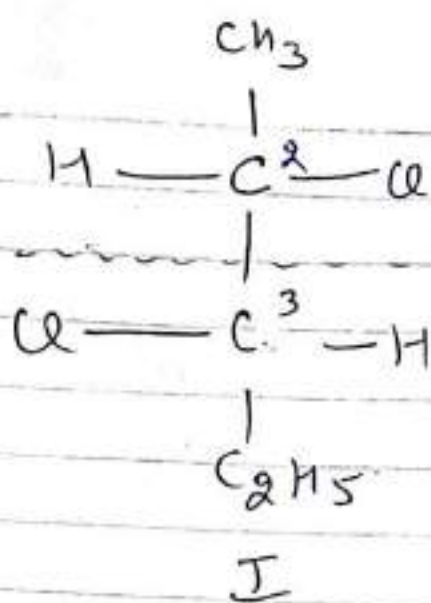
- It is having two chiral centres
- Four different groups attached to one chiral centre ~~are~~ are not same as those attached to other



→ Fig. I and II are the non-superimposable mirror images of each other.

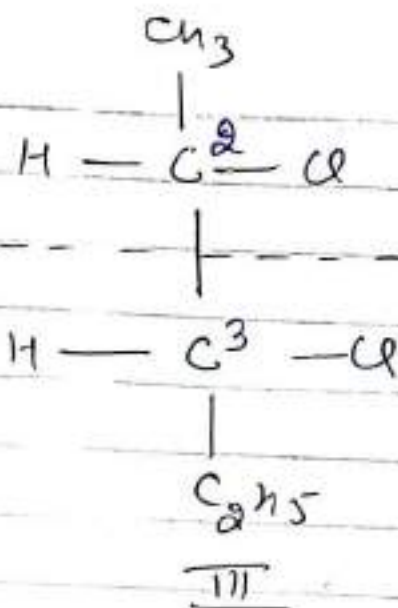
→ Similarly Fig III and IV are also non-superimposable mirror images of each other. So these are pair of Enantiomers.

Now Comparison of Fig I and III



Same
Configuration

mirror
images



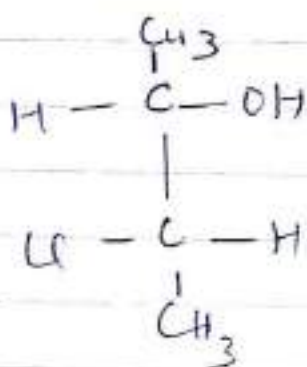
Horizontally chiral Carbon 2 and
I and chiral Carbon 2 of (II) are
identical Configurations.
But mirror images around
chiral Carbon 3.

Hence the two forms are neither
identical or not mirror images
of each other. Such a pair of
stereoisomer of a compound which
are not mirror images are
known as Diastereoisomers.

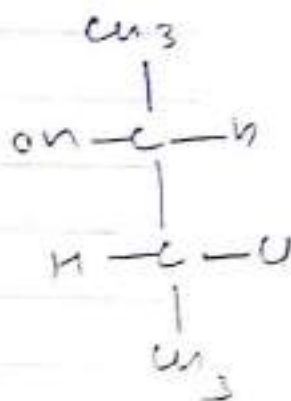
Similarly I and IV
II and III

II and IV are also pair of Diastereoisomers

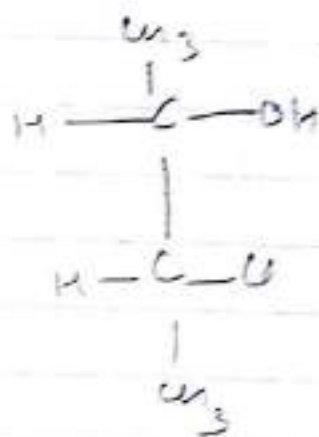
Q. Draw Diastereoisomers of 3-chloro-2-butanol?



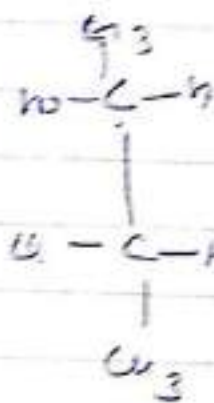
I



II



III



IV

Similarly

I and II, I and IV, II and III
and II and IV are pair of Diastereoisomers.

Characteristics of Diastereomers

① They show similar, but non identical, chemical properties.

Rate of reactions of two Diastereoisomers with a reagent are different.

2) They have different physical properties like melting pt., boiling pt. etc.

3) Due to diff. physical properties they can be easily separated by fractional distillations.

Difference b/w Enantiomers and Diastereoisomers

Enantiomers

- 1) They are mirror images of each other
- 2) They have similar physical properties
- 3) They cannot be separated by the methods
- 4) They have optical rotation in opposite

Diastereoisomers

They do not have mirror images
They have different physical properties
They can be separated by the fractional distillation and chromatography.
They have optical rotation in same

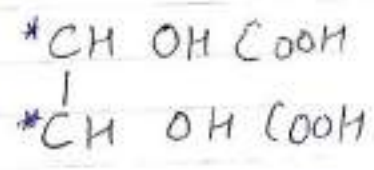
direction but to same extent
5) They have identical chemical properties except with other optically active compounds

Or different direction but to different extent
They have identical chemical properties but differ in the rate of reaction with optically active compounds.

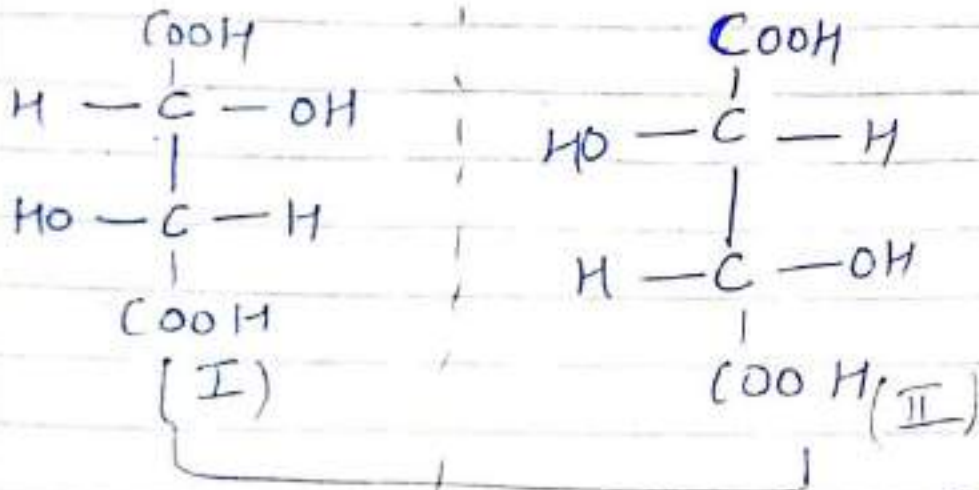
Meso Compounds

These are optically inactive compounds whose molecules are not chiral even though they contain 2 chiral centres. These are known as meso compounds.
For Example

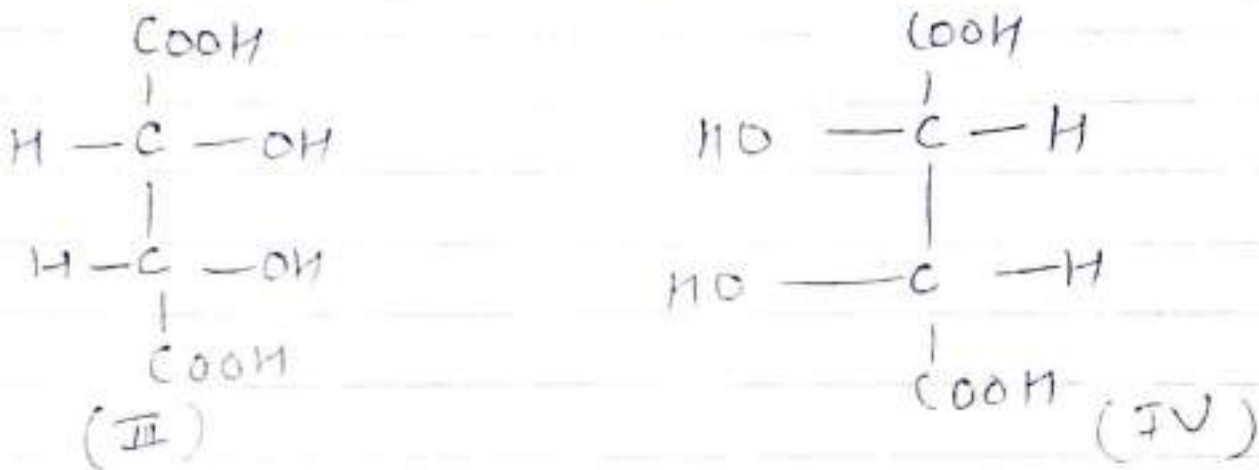
Tartaric acid (Containing two similar centres)



Four stereoisomers of Tartaric acid



Pair of Enantiomers (non superimposable mirror images)



Superimposable mirror images (III and IV)

One of the these structure is superimposed on the other just by rotating it through 180°

Despite of two chiral centre the molecule

Planar Representation of 3D Formula (FISCHER PROJECTION FORMULAE)

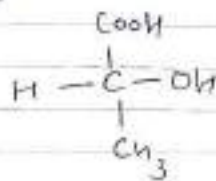
To represent the formulae of Stereo-Isomer Compounds a simple method was introduced by Emil Fischer (1891). The planar representations are called Fischer projection formulae.

Steps

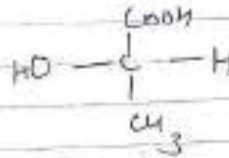
- (i) The chiral molecule is held in such a way that the two groups attached to Chiral Carbon lie horizontally and point towards the observer and other two groups lie vertically away from the observer.
- (ii) The various groups attached to the Carbon are then projected on the plane of the paper.
- (iii) The vertical part of the projection formula should represent so far as possible, the longest chain of Carbon atoms in the molecule with C to be represented by 1.

according to IUPAC system

Exp Two Enantiomers of lactic acid

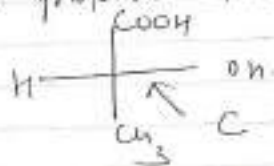


(R) - lactic acid



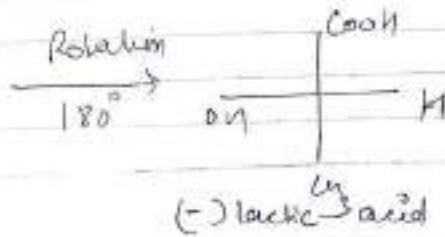
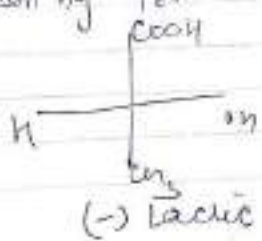
(S) - lactic acid

(iv) Chiral carbon is not written while writing the projection formulae

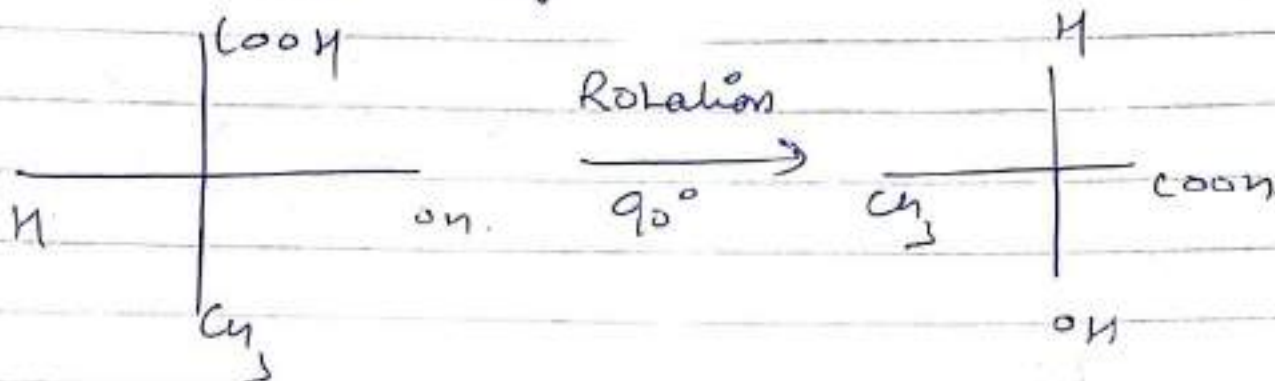


(v) if necessary planar formulae may be imagined to be rotated from end to end without lifting on the paper

Rotation by 180°



Rotation by 90° or 270° leads to the Inversion of Configuration



Configuration On the basis of

R and S Notations (Absolute Configuration)

Cahn, Ingold and Prelog suggested a very simple procedure to specify a Configuration in terms of R or S

R \rightarrow Rectus

S \rightarrow Sinister

Steps Involved

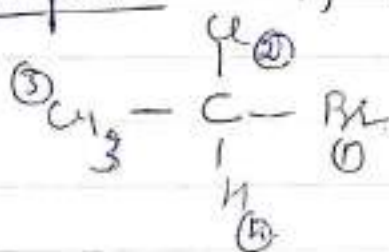
1) Step - 1

The four atom or groups bonded to Chiral Carbon are assigned a

sequence of priorities in accordance with the set of rules known as sequence rules

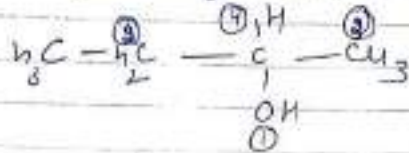
a) If all the four atoms bonded to the carbon are different then priority is selected on the basis of ~~atomic~~ atomic number. The atom with highest ~~atomic~~ atomic number gets the highest priority and lowest atomic number comes last in the order

For example 1, - Bromo 1 - Chloro Ethane



b) If two or more groups are having same atomic number then priority is decided by the next atom in the group. If it is again same then decided by the next and so on

Ex-1 Sec butyl alcohol

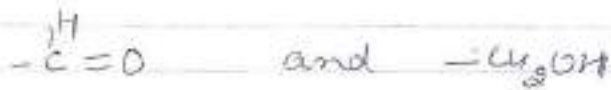


As OH highest atomic number



c) If a group has an atom X linked to some other by double or triple bond, X is considered to be equivalent to two or three such atoms

Ex-2



highest
priority



lowest
priority