Unit-I

✶ Stereoisomerism ✶

Same compound

- Isomerism :-

  - The compounds which has same molecular formula but have different structures & different physical and chemical properties are called as isomers & the phenomenon is known as isomerism.

  - Isomerism is classified in two types which are
    ① Structural isomerism
    ② Stereoisomerism

✶ Classification :-

Isomerism

- Structural
  - → Chain
  - → Positional
  - → Functional
  - → Metamerism
  - → Tautomerism
  - → Ring-chain
- Stereo
  - → Geometric
  - → Optical

① Structural isomerism →

- Compounds with same molecular formula but different structures are called structural isomers & phenomenon is known as Structural isomerism

e.g.. Isopropane & n-butane

① Chain isomerism →

They have same molecular formula but differ in order in which Carbon atoms are bonded to each other.

e.g....

$CH_3-CH_2-CH_2-CH_2-CH_3$

pentane

$CH_3-CH(CH_3)-CH_2-CH_3$

Isopentane

(2-methylbutane)

② Positional isomerism →

They have same Carbon Skeleton but differ in position of functional group.

e.g....

$CH_3-CH_2-CH_2-Cl$ — 1-Chloropropane

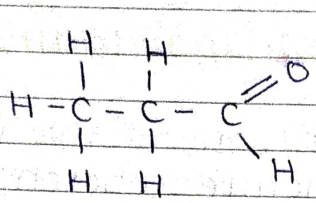
$CH_3-CH(Cl)-CH_3$ — 2-Chloropropane

e.g.. ether & ethanol

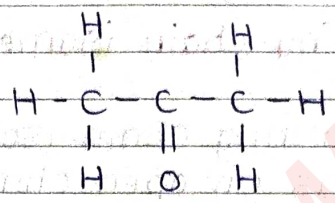
③ Functional isomerism →

- It is also known as Functional grp. isomerism
- As the name suggest, it refers to compounds that have same C.F but different functional groups attached to them.
- C_3H_6O

e.g....



Propanol



Propanone (acetone)

(iii) Metamerism →

This type of isomerism arises due to the presence of different alkyl chains on each sides of the functional group.

e.g....

$CH_3-CH_2-NH-CH_2-CH_3$

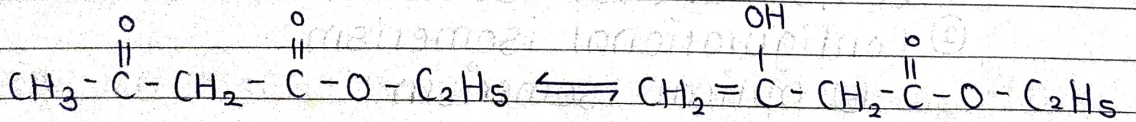
diethyl amine

(iv) Tautomerism →

- A tautomer of a compound refers to the isomer of the compound which only differs in the position of protons & electrons
- Typically, tautomers of compound exist in dynamic equillibrium & easily interchange.

e.g....

keto-enol Tautomerism

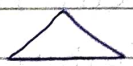


ethyl aceto-acetate (keto)

Ethyl aceto acetate (enol)

(vi) Ring chain isomerism →

- In ring chain isomerism, one of the isomers has an open chain structure whereas the other has a ring structure.
- They generally contain a different number of pi bonds.
- A great example of this type of isomerism can be observed in C_3H_6
  e.g....

$CH_3CH=CH$ and 

propene Cyclopropane

* Stereoisomerism →

Compounds having same m.F but different arrangement of atoms are called Stereoisomers & the phenomenon is known as Stereoisomerism.

- It is of two types :-

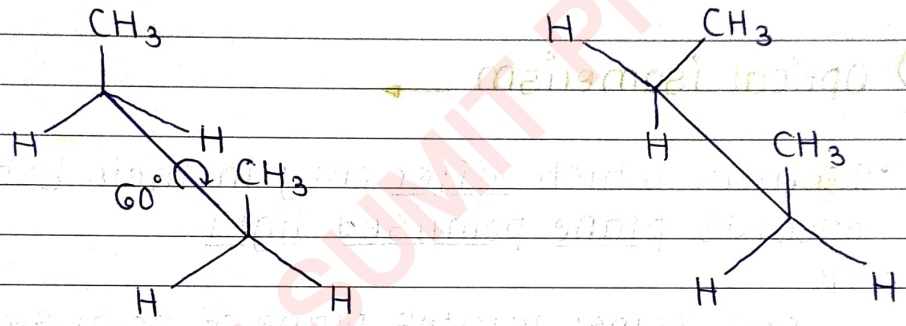
① Conformational isomerism
② Configurational isomerism
   ⓐ Optical isomerism
   ⓑ Geometrical isomerism

① Conformational isomerism →

° Isomers having the same bond connectivity sequence & can be interconverted by rotation around one or more single (σ) bond.

e.g...

Conformational isomerism in butane.



* Optical Activity →

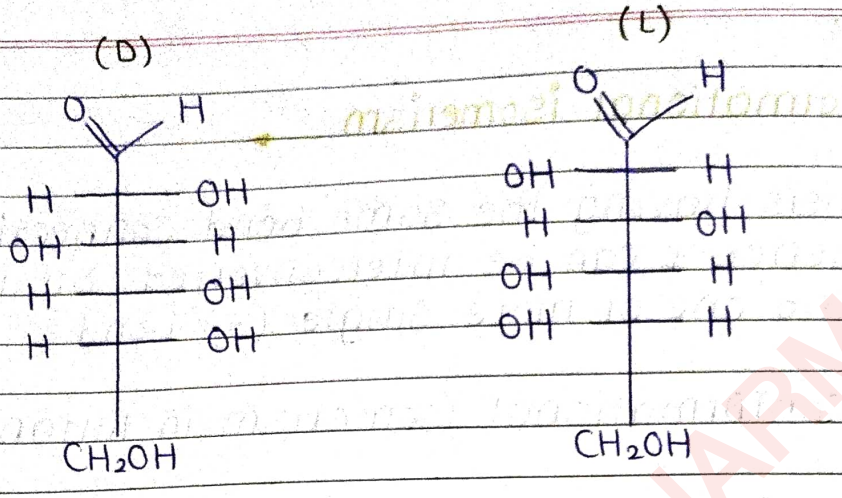
° Optical activity is the ability of a chiral molecule to rotate the plane - polarised light, measured using a polarimeter.

IMP

° If a compound rotates plane polarized light in the clockwise (+) direction, it is said to be dextrorotatory (d), while it is rotates light in the counterclockwise (-) direction it is a levoratatory (l).

Q. ~~e.g.~~.. An alkane which can exhibit optical activity is

→ 2, 3 dimethylbutane

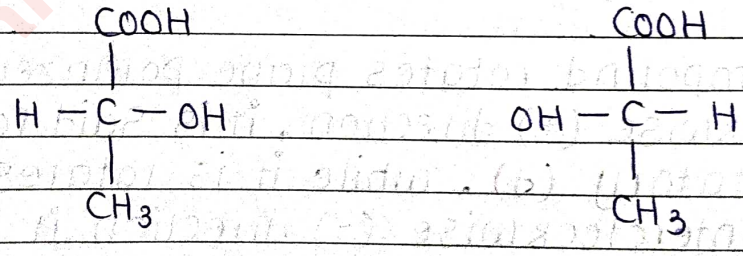


① Optical isomerism →

IMP
- Isomers which differ only in their behaviour towards plane polarised light
i.e.
one isomer rotates plane of polarised light towards right & other towards left.

- Such pair of isomers are called optical isomers and the phenomenon is called as optical activity.

e.g.,

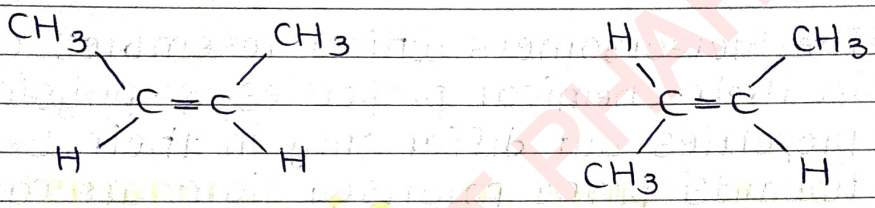


d- lactic acid l- lactic acid

② Geometrical isomerism →

These are isomers having same M.F and

S.F but differ in the special arrangement of atoms about the double bond are called geometrical isomers & the phenomenon is called as geometrical isomerism.
e.g....



IMP

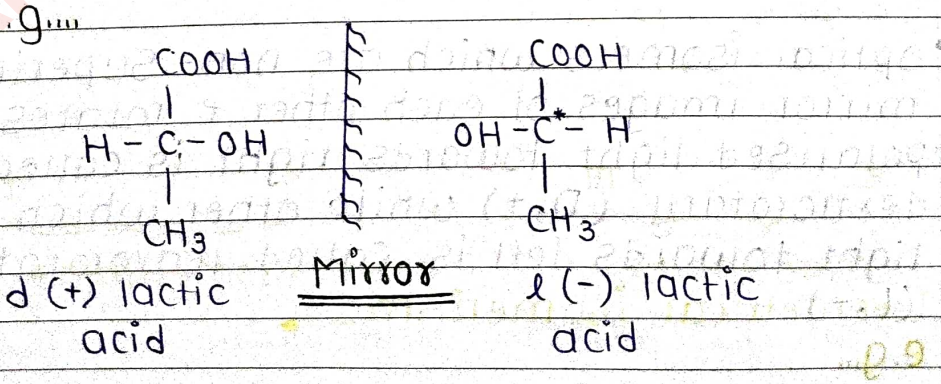
Cis But-2-ene

Trans But-2-ene

* Chirality of molecules →

- It is observed that molecular structure of all optically active compounds is chiral (disymmetric) in nature.
- A molecule is chiral only if it is non superimposable on its mirror image. This property of non-superimposibility is called chirality.

e.g....



d (+) lactic acid

Mirror

l (-) lactic acid

Q. Which of the following is not true of enantiomers ? They have same Specific Rotation

① BP ② MP ③ S.R ④ Density / ① B.P ② MP ③ S.R ④ Chemical reaction towards achiral reagent

- While a molecule which is Superimposable on its mirror image is called achiral or Symmetric molecule.

* Optical isomerism →

The Stereoisomers which resembles each other in their chemical properties & physical properties but differ only in their behaviour towards plane polarised light are called optical isomers & phenomenon is called as a optical isomerism.

- It is divided into three types :
  ① Enantiomers
  ② Diastereomers
  ③ Meso - Compounds.

① Enantiomers →

racemix mixture and

- It is also known as optical isomerism having one Chiral carbon.

- optical isomers which are non-Superimposible mirror images of each other & rotates plane polarised light towards right is called dextrorotary (D, +) while other which rotates light towards left is called leavorotatary (L, -)

e.g...
Lactic acid

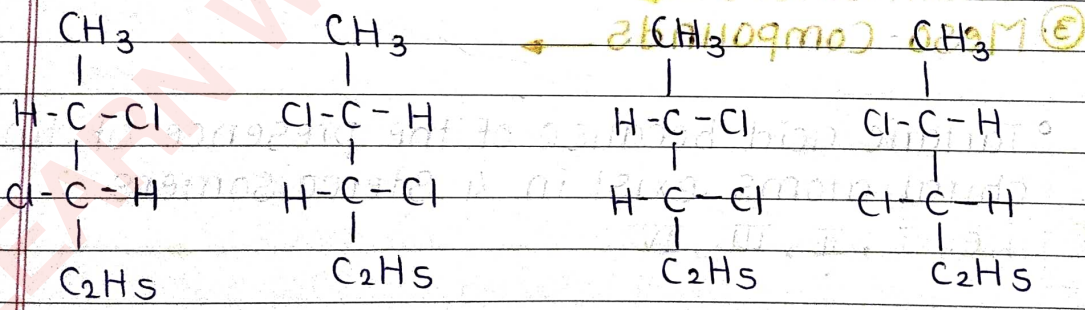
9.

* Properties of Enantiomers →

1. They have mirror image relationship.
2. They have mostly one chiral centre.
3. They are always optically active in nature.
4. They have similar physical properties like MP, BP
5. They have identical chemical properties but have different rate of reaction.

② Diastereomers →

It is also known as optical isomerism in compound having two different chiral carbon atoms.
It means a compound which contain two or more chiral atoms exist in more than two Stereoisomeric forms.
e.g...
2,3 diachloropentane has 2 chiral atoms.



I II III IV

enantiomers enantiomers

(2S,3S)2,3 dichloroPenta (2S,3R)2,3- dichloropentane

(2R,3R)2,3 dichlo— (2R,3S)2,3 dichloro—

Q. Which is meso Compound ?

① (2R,3R)- 2,3 dibromobutane
② (2R,3S)- 2,3 ——"—— Pentane
③ (2R,4R)- 2,4 ——"——
④ (2R,4S)- 2,4 dibromo- Pentane

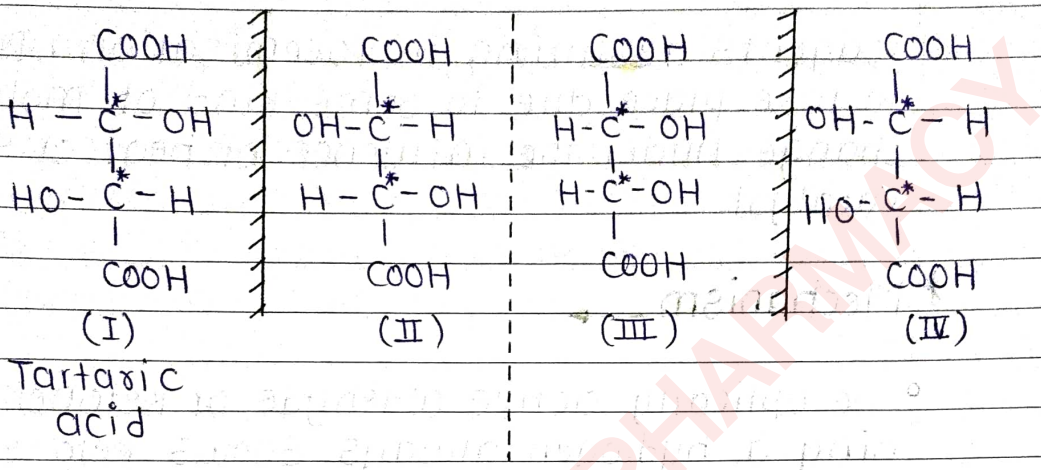
- 1 & 2 are Stereoisomers of 3 & 4
- 1 & 2 are also not mirror images of 3 & 4
- Therefore, 1 & 2 are diastereomers of 3 & 4
- Stereoisomers which are not mirror images of each other having two or more chiral carbon atoms are called as diastereomers.

* Properties of Diastereomers →

① They do not have any mirror image relationship
② They have 2 or more chiral carbon atoms
③ They can be optically active or inactive
④ Different physical properties like MP, B.P
⑤ They do not have identical chemical properties.
⑥ They can be Separated by Chromatography.

③ Meso-Compounds →

- Tartaric acid because of the presence of two chiral atoms exist in 4 Stereoisomers. i.e. I, II, III, IV
- I & II while III & IV are mirror images of each other, non-Superimposable & optically active.



Tartaric acid

If IV Structure is rotated, it gives superimposable compounds which are optically inactive having the plane of Symmetry.

- Such an optically inactive compounds which are superimposible having plane of symmetry, are called as mesocompounds

- Thus tartaric acid exist in three forms i.e. D(+) tartaric acid, L(-) tartaric acid & meso tartaric acid.

* Racemization :-

- It is the process in which an optically active (d or l) compound is converted into a mixture of D & L forms with result that optical activity disappear & the observed rotation drops to 0.

- Optically active compound become inactive under the influence of heat, light or chemical

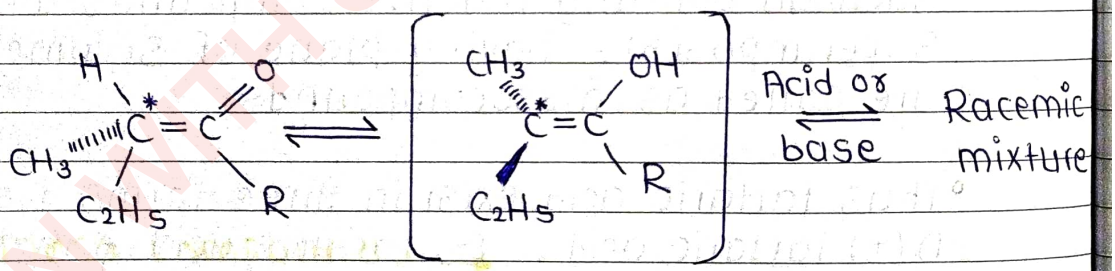
IMP Ratio of dextro & levo (d/l) compound present in racemic mixture is 50:50

reagents resulting in racemisation. It appear to take place due to some kind of molecular change under the influence of heat or some catalyst.

* Mechanism →

° The optically active aldehyde or ketone containing a hydrogen always shows keto-enol tautomerism, that form is responsible for racemization.

° It is optically inactive & it gives a racemic mixture by treating with an acid or base.



optically active aldehyde — Enol form

* Resolution of Racemic mixture →

° Racemic mixture contain equal amounts of optically active d & l isomers.

IMP ° The process of separation of racemic mixture into optically active d & l isomers is mixture is known as resolution.

Methods :-

1. Mechanical Separation method
2. Biochemical Separation method
3. Chemical Separation method
4. Chromatographic Separation method.

① Mechanical Separation method :-

- When Sodium & ammonium salt of racemic tartaric acid is allowed to crystalise slowly from the water solution. The crystals obtained are of two shapes which are mirror images of each other.
- These two types of crystals are sorted under microscope which contains dextro & leavorotatory form.

② Biochemical method :-

- These method was discovered by Pasteur.
- He found that the organisms such as bacteria, fungi or yeast are allowed to grow in a sol^n containing racemic compound, one of the enantiomers is destroyed by bacteria, fungi or yeast and other enantiomers gets separated.

e.g...

When penicillium galucum is allowed to grow in racemic tartaric acid, dextro form is separated in the sol^n.

③ Chemical method :-

① dl acid + l base → d acid - l base + l acid - l b

② dl base + l acid → d base - l acid + l base - l acid

° This is most important method developed by Pasteur. It is based on when a racemic acid is allowed to react with an optically active base, it gives two pairs having different physical properties and can be separated by psiyal method like crystallization.

④ Chromatographic Method :-

When a racemic mixture solution is passes through an optically active adsorbent, the two enantiomers can be separated.

* DL System of Nomenclature →
(Relative configuration)

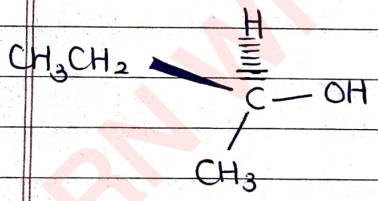
° The two enantiomers are denoted by D & L Symbols. The Compound which rotates the plane of polarised light towards right side is called as dextroisomer having (+) Symbol.

° The compound which rotates the plane of polarised light towards left side is called as leavoisomer having (-) Symbol.

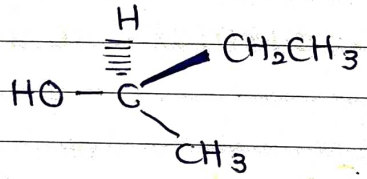
e.g.
Lactic acid

* R.S System of Nomenclature → absolute configuration.

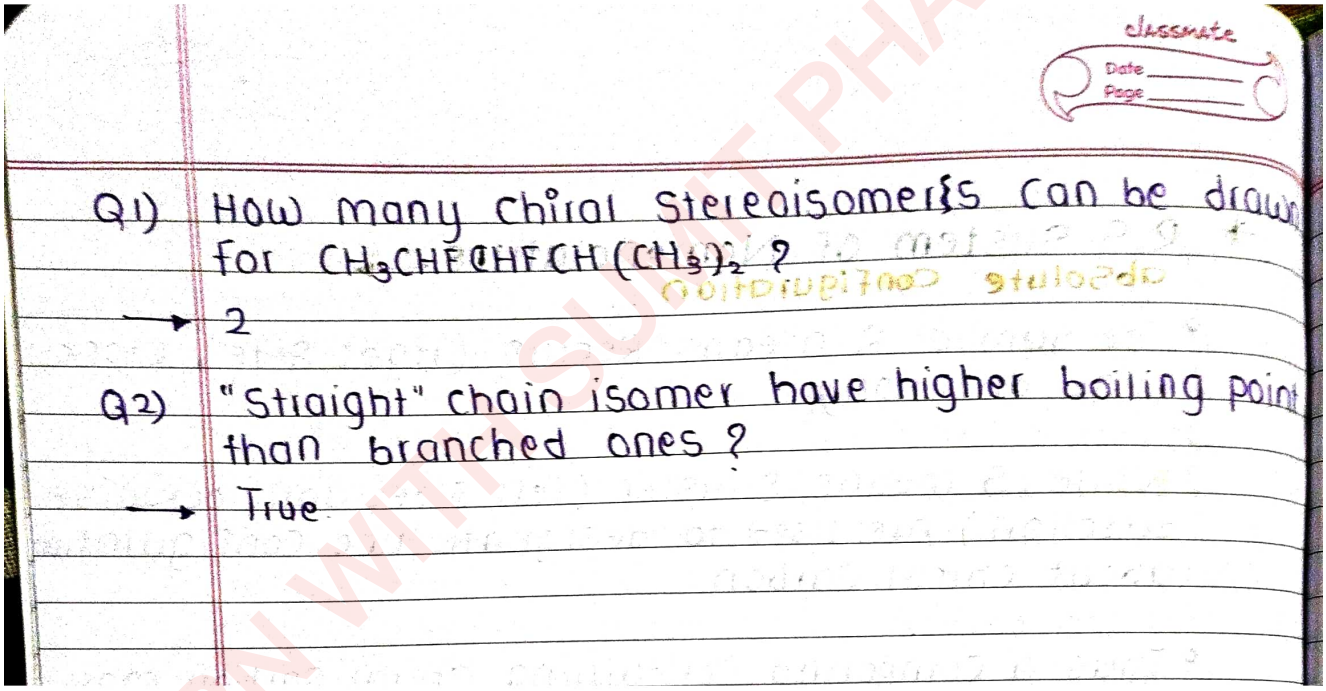
- The symbol R means Rectus (right side, clockwise direction)
- While, S means Sinister (left side, anticlockwise direction) are used to designate two configuration about chiral carbon.
- Thus a compound containing chiral carbon may have either 'R' configuration or 'S' configuration This System does not provide the sign of optical rotation
  i.e. +Ve or -Ve
  e.g.. 2-butanol.



(S)-2-butanol



(R)-2-butanol.



Q1) How many chiral Stereoisomers can be drawn for $CH_3CHFCHFCH(CH_3)_2$?

→ 2

Q2) "Straight" chain isomer have higher boiling point than branched ones ?

→ True