DEPTH OF BIOLOGY

STUDY MATERIAL

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Unit - Ist STEREOTSOMERTSM

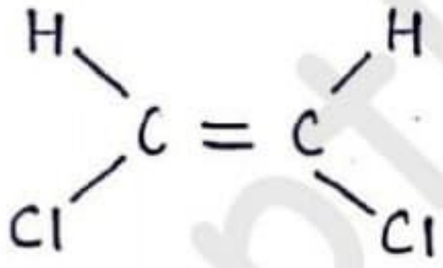
Isomers → These are those chemical substance which has same molecular formula but different structural formula and this phenomena is known as "Isomerism". [They have also different properties].

Example → $CH_3 - CH_2 - OH$ (ethyl alcohol) and $CH_3 - O - CH_3$ (Dimethyl ether)

- Isomerism
  - Structural Isomerism (same molecular formula but different in structure)
    - Chain isomerism
    - Position isomerism
    - Metamerism isomerism
    - Functional isomerism
    - Tautamerism isomerism
  - Stereoisomerism (same molecular and structural formula but different arrangement of atom in space due to rotation)
    - optical Isomerism
    - Geometrical Isomerism

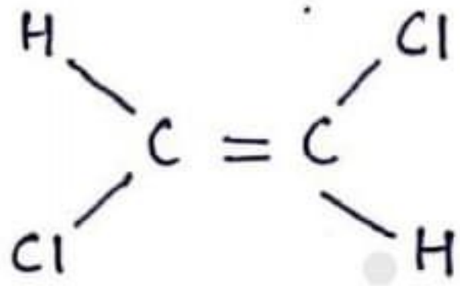
- **Stereoisomerism** → It is a form of isomerism in which molecule have the same molecular formula and same structural formula but different in arrangement of atoms/group in space.

Example → 1, 2 - dichloroethene



Cis - 1,2 - dichloroethene

OR

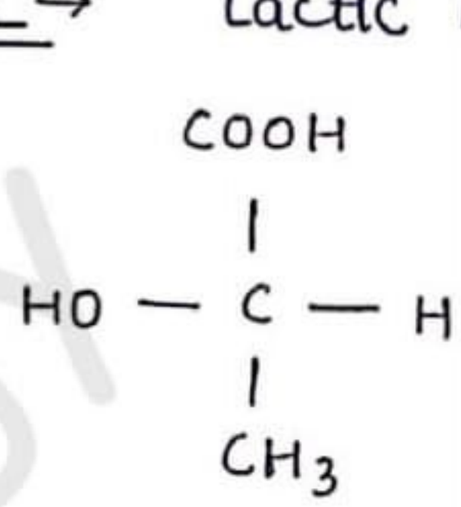


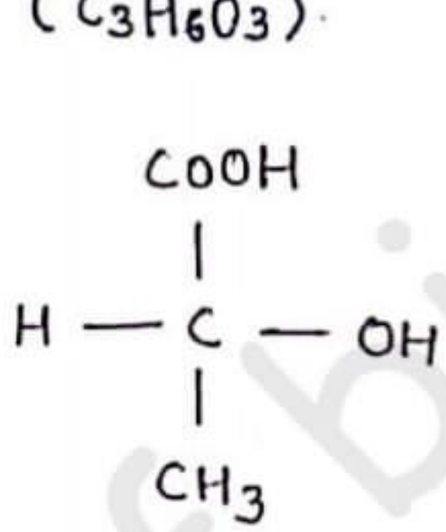
Trans - 1,2 - dichloroethene

- Optical isomerism → It is a type of stereoisomerism in which molecule have same molecular, structural formula and also have same physical properties, melting point, boiling point, density etc. But they differ in their behaviour toward light.

They also have same specific rotation of light but with opposite sign.

Example → Lactic Acid ($C_3H_6O_3$)





- Optical active compound (optical activity) → which has power to rotate the plane polarised light.

Optical Activity

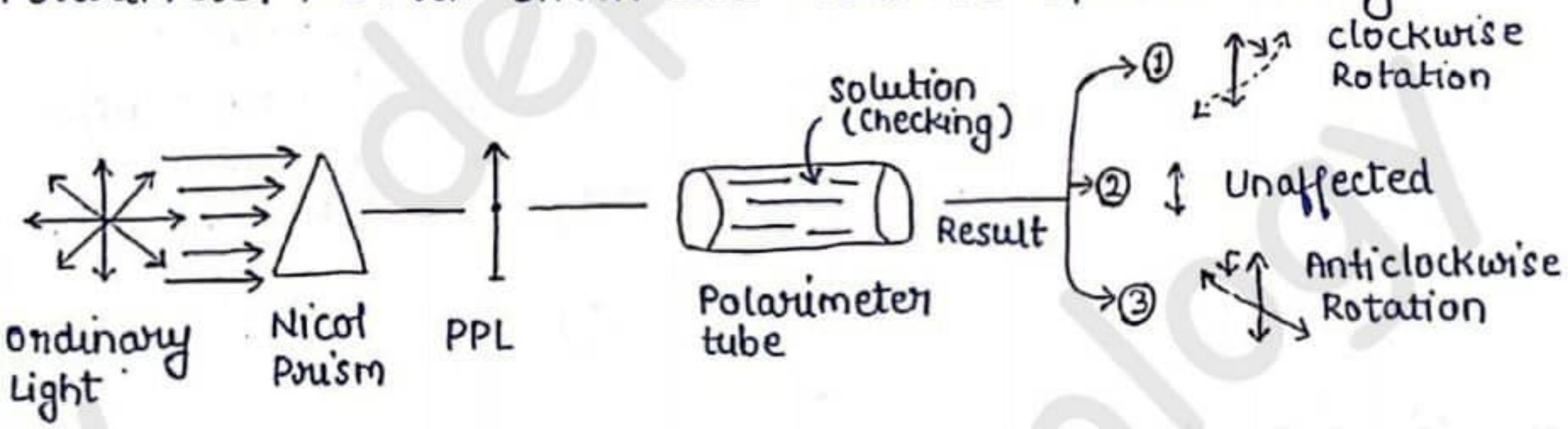
The power of any substance to rotate the plane Polarised light (PPL) from its axis to clockwise or anticlockwise direction is called "optical activity" and the substance is known as "optical active substance".

For Determination,

- Polarised (Nicol prism) – $CaCO_3$, which gathered ordinary light into one plane and make it PPL (Plane Polarised light).

[Ordinary light] [Nicol Prism] [Plane Polarised Light]

- Polarimeter, which check and measure optical activity.



- Firstly ordinary light passes through Nicol prism, make it PPL (Plane Polarised light), then pass this light from polarimeter tube in which we filled a 1% solution which we have to check optical activity.
- If the PPL goes unaffected then compound is "optically inactive" but if the PPL rotate then compound is "optically active".

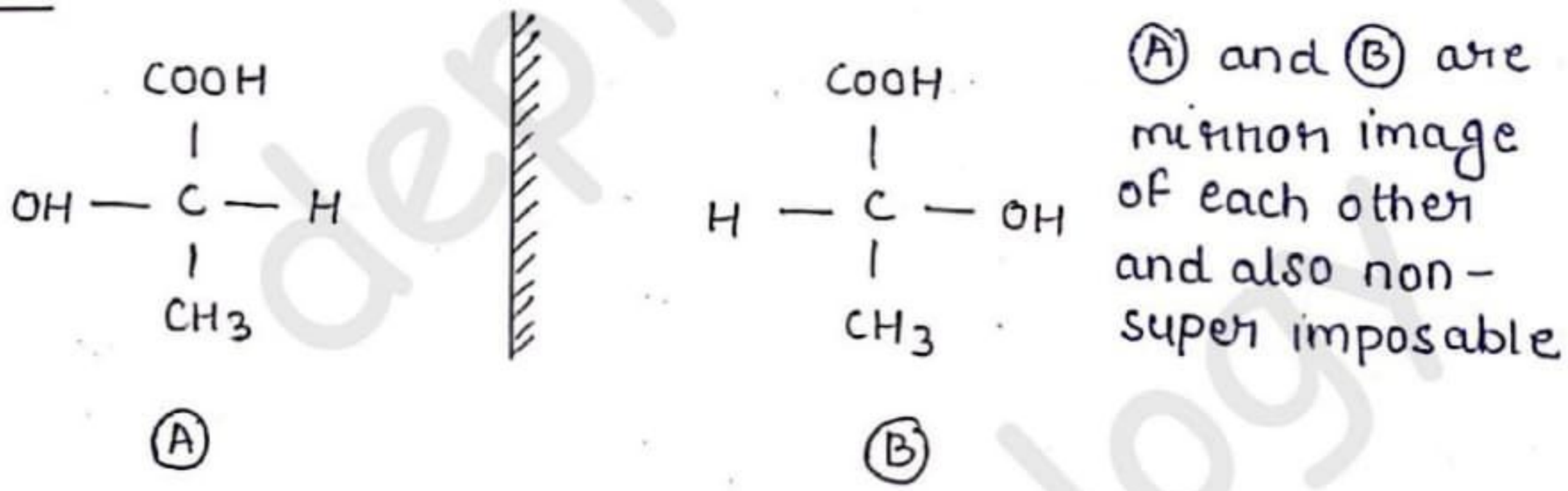
• Rotation is of 2 types :-

ⓐ If PPL rotates clockwise direction, the solution is "Dextro rotatory" denote as "D" or "+".

ⓑ It PPL rotates anticlockwise direction, the solution is "levo rotatory" denote as "L" or "−".

• <u>Enantiomers</u> → The optical isomers which are non-super imposable mirror image of each other are called "enantiomers" and the process of formation of enantiomer by rotation of 180° is called "enantiomerism".

<u>Example</u> → Lactic Acid



• Enantiomers differ from one another in three dimensional spatial arrangement.

• They have same melting point, density, solubility, colour and reactivity toward acid and bases.

• They have different specific rotation of plane polarised light towards optical activity. Ⓐ → Levo [−]

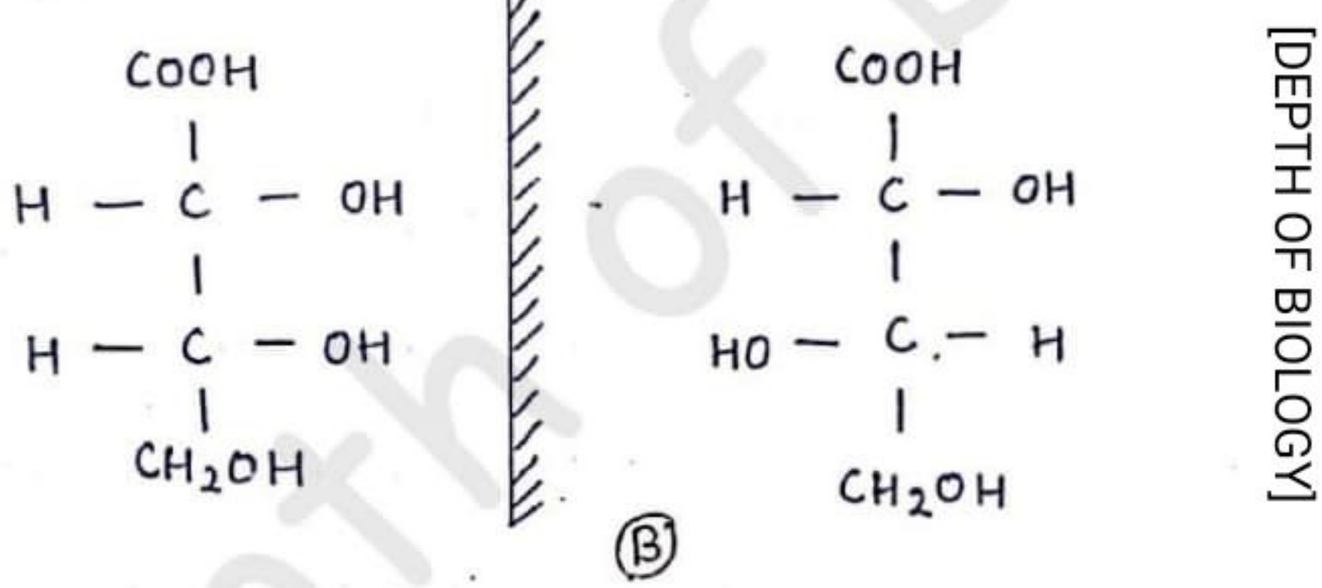
Ⓑ → Dextro [+]

• <u>Diastereoisomerism</u> :- The stereoisomer that are non-mirror images of each other and also non-super imposable of each other are called " diastereoisomers".

• They have atleast two stereocentres.

• Diastereoisomers have different properties such as melting point, boiling point etc.

<u>Example</u> :-



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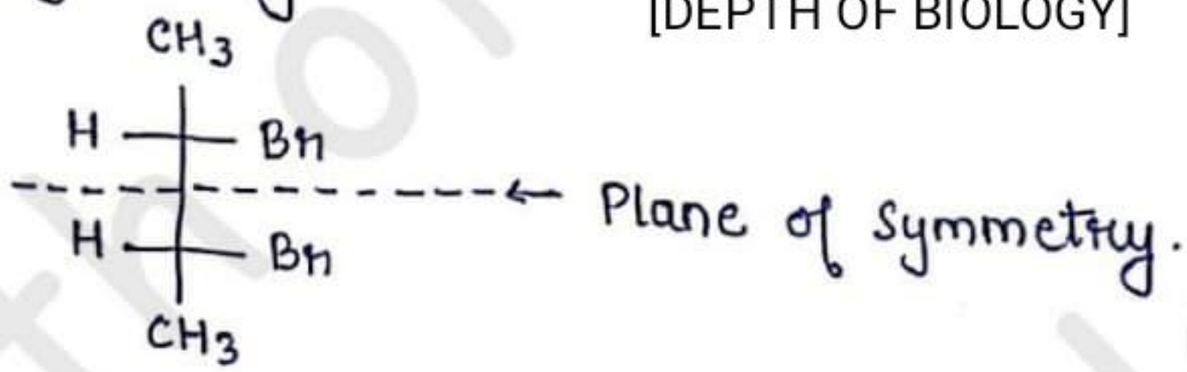
(A) and (B) are diastereoisomers.

• <u>Elements of Symmetry</u> :- Those compound which can be divided into an equal parts from any plane called " Symmetrical Compounds".

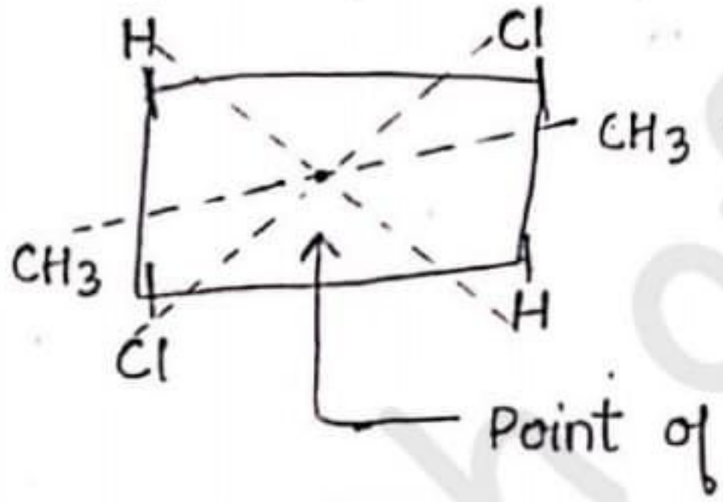
@ <u>Plane of Symmetry</u> → A plane which divides an object into two symmetrical halves is called plane of symmetry.

<u>Example</u> :-



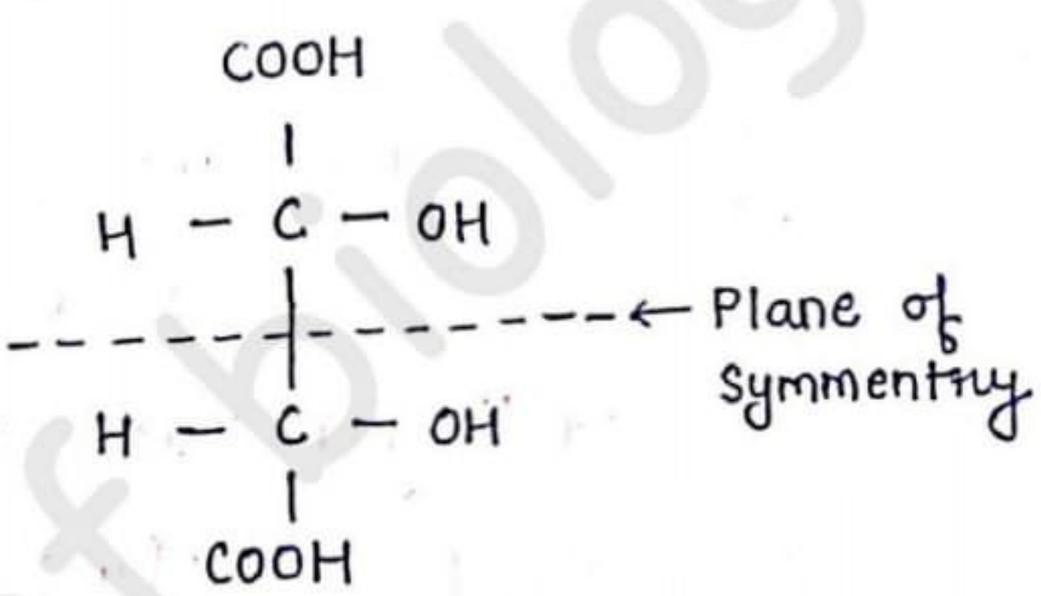
(b) Centre of Symmetry → Also known as "Point of Symmetry". If all straight line that can be drawn through the centre of the molecule meet identical atoms at equal distance from the centre.

Example :-



- Meso Compounds → A compound with two or more asymetric carbon atoms but also having a plane of symmetry, one half of the molecule is mirror image of other half.

Example → Tartaric Acid



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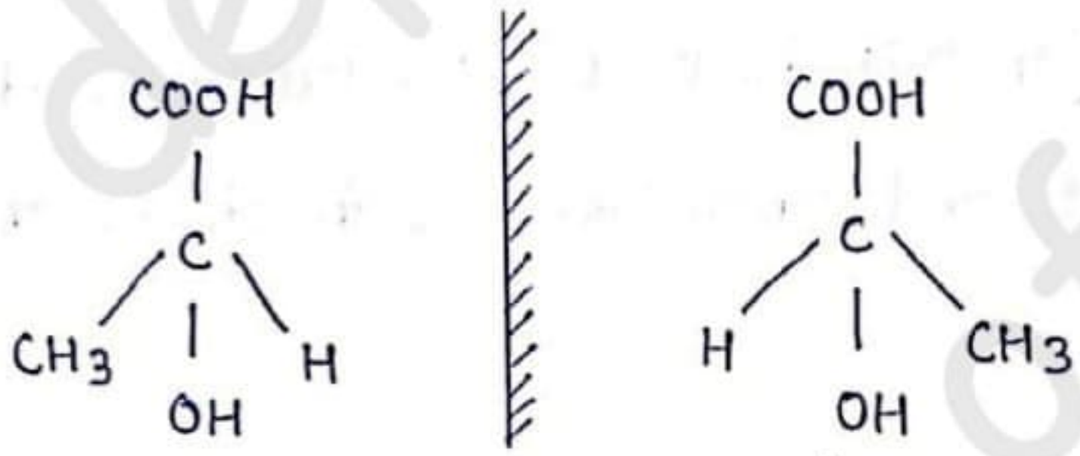
- These types of compound are optically inactive due to internal compansation.

• Chiral Molecules → Those molecules which cannot super-imposable on its mirror image. These molecule are optical active which rotate plane polarised light.

Example :- Lactic Acid



• Chiral molecule also have a 'chiral centre' or 'asymmetric carbon atom.'

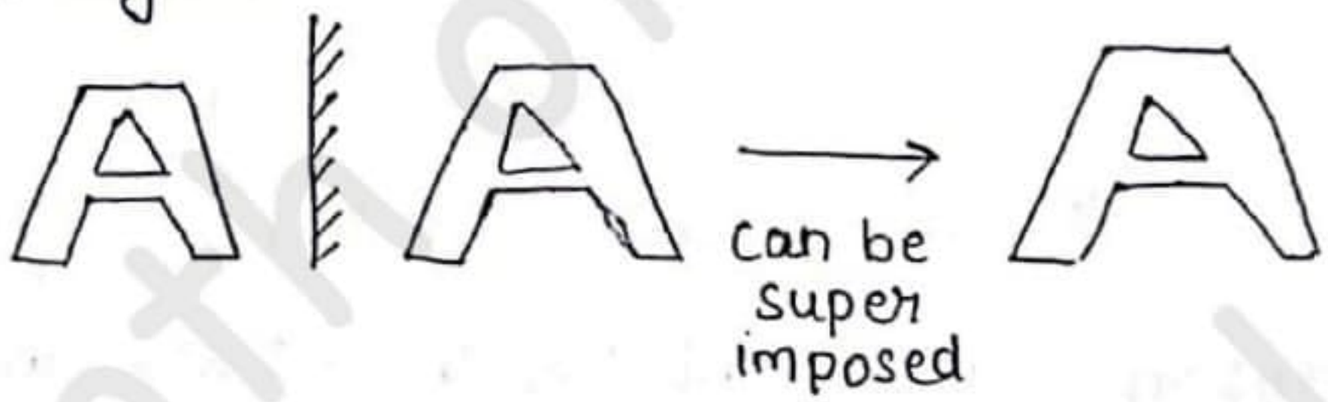
• Chiral Centre [Chiral Carbon atom] → A carbon atom which attached with 4 different atom / groups. eg → Lactic acid

Chiral carbon atom also known as asymmetric carbon atom.

Achiral Molecules → Those molecules which are super-imposable on its mirror images.

But these are optical inactive molecules which cannot rotate plane polarised light.

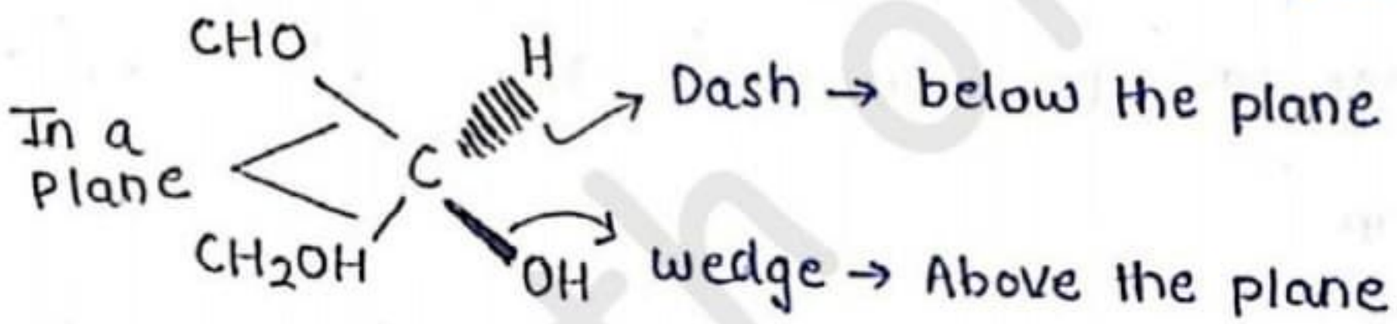
Example →



Representation of structure of Molecules

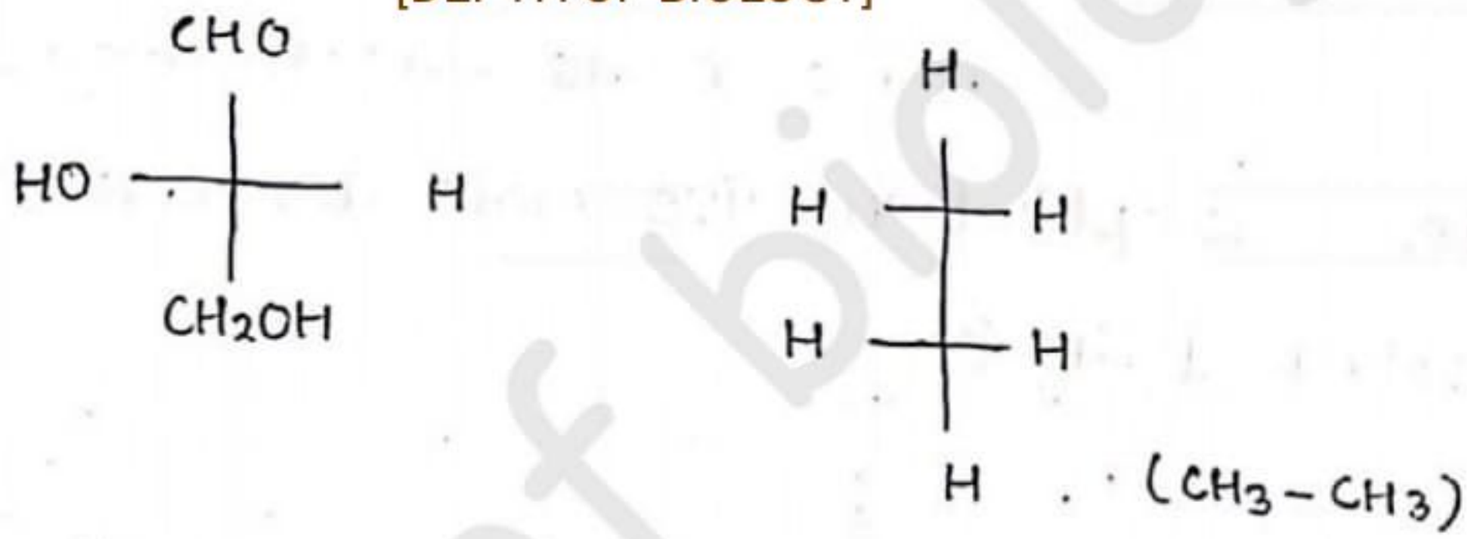
① **Wedge and Dash [flying wedge Projection]** → These are the "3D representation" of molecules. They are used for both chiral and achiral molecule. This projection is used for tetrahedral structure, in which two atom/group are in plane and other two are in above and below the plane.

Example :-



② **Fischer Projection** → It is the "2D Presentation" of molecules. In this method molecules are represented by cross line and the centre of line is assumed as carbon atom.

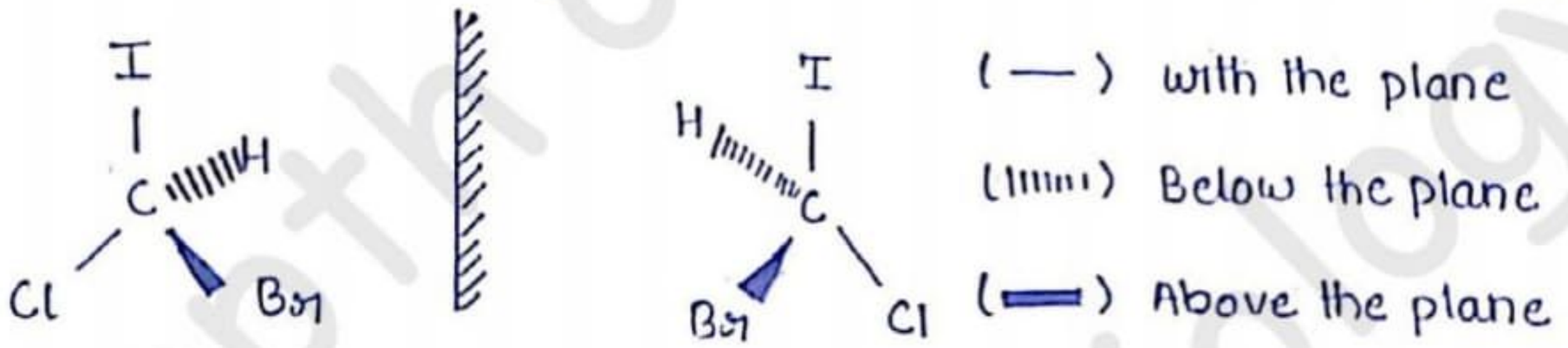
Example :-



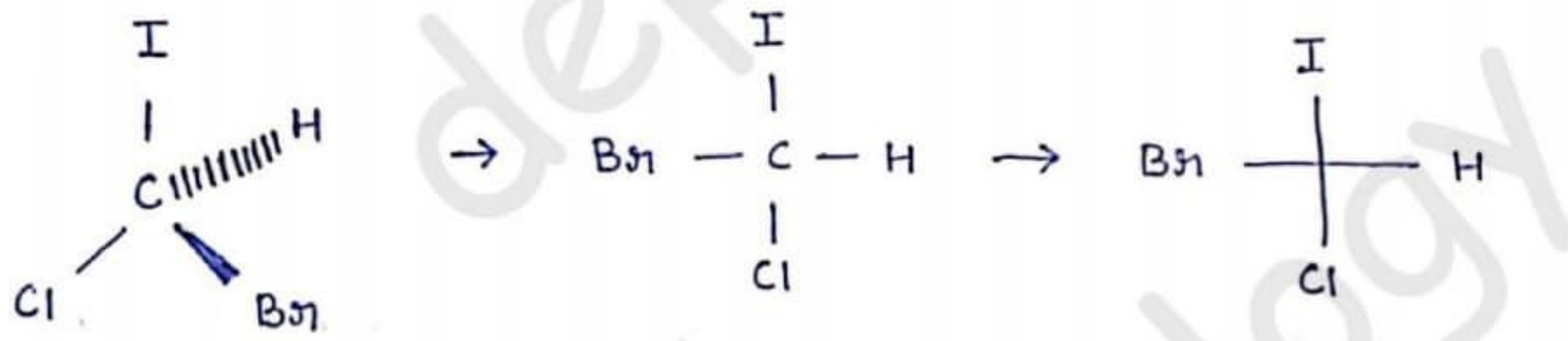
* How to convert "wedge-Dash Projection" to "fisher Projection"

- This conversion is important for the (D&L) and (R&S) configuration of molecules.

In this, 3D structure of molecules is convert into 2D structure.



- Those atoms / group which are on plane, represent on vertical line in fischer projection.
- Then watch wedge-dash structure from that side on which "above and below the plane" atoms / group attached.
- Then that atom/group which is in your left side, put it in left side and that atom/group which is in your right side in "fishcher projection".



"Wedge - Dash" "Fischer Projection"

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* Nomenclature of optical isomers

① DL System (Relative Configuration) → The D/L System was developed by fischer and Rosanoff in around 1900.

- This method is used for optical active compounds.

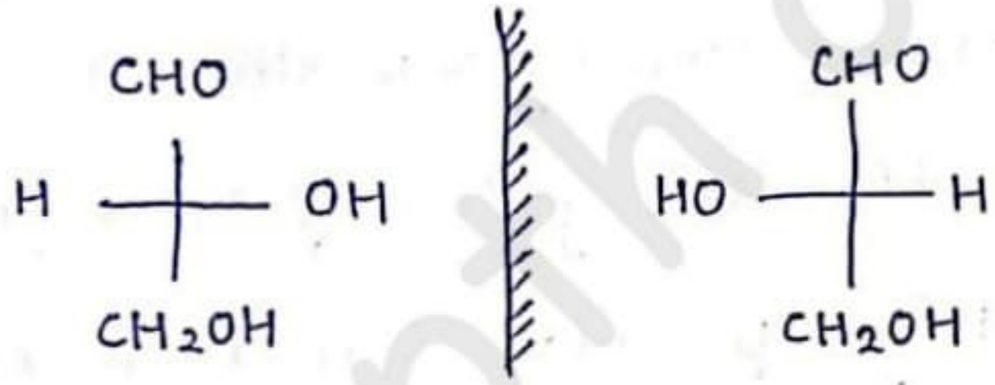
D → which has clockwise rotation on Right hand side (↻)

Represented as D (+) Dextronotatory.

L → which has anticlockwise rotation on left hand side (↺)

Represented as L(−) levonotatory.

• This D/L configuration is used for amino acid and Carbohydrate In this configuration, "Glyceraldehyde" is used as a reference compound.



(D - Glyceraldehyde) (L - Glyceraldehyde)

Rules :-

@ Draw proper fisher projection formula of molecules.

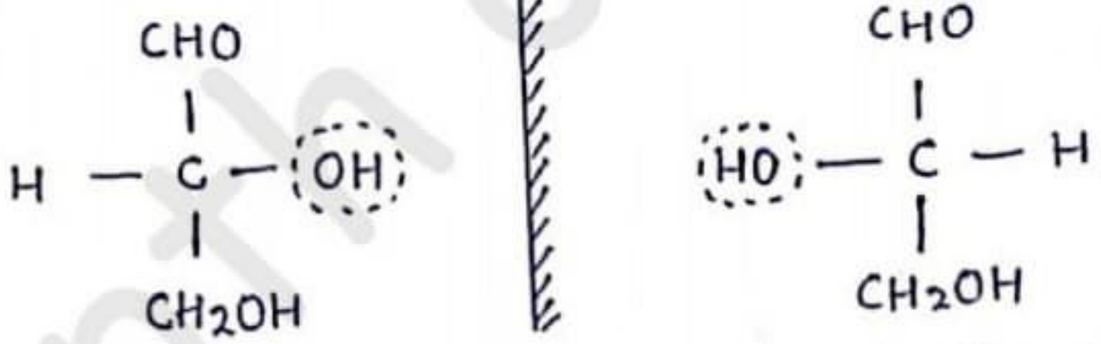
ⓑ Highly oxidised group must be on top. (if not then rearrange it)

ⓒ observe bottom most chiral (assymmetric) carbon, if it contain −OH/NH2 at right then 'D', if at left than 'L'.

ⓓ Longest chain is always on verticle line.

ⓔ If −OH and −NH2 both are present than D/L are dedicated decided by −NH2 group.

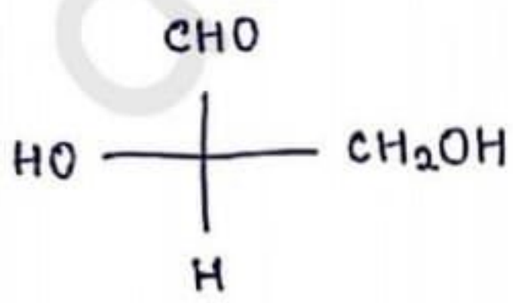
Example :-

① 

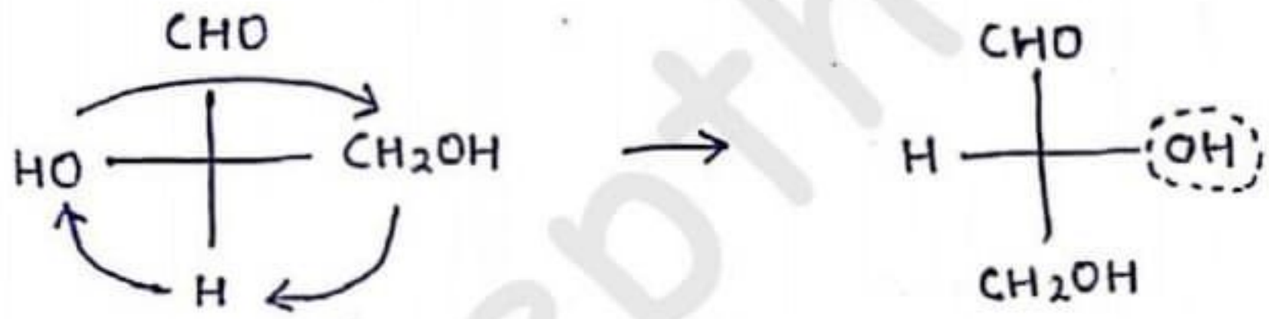
D(+), -OH Group is on right side

L(-), -OH Group is on left side.

② → the longest chain should be on vertical line,

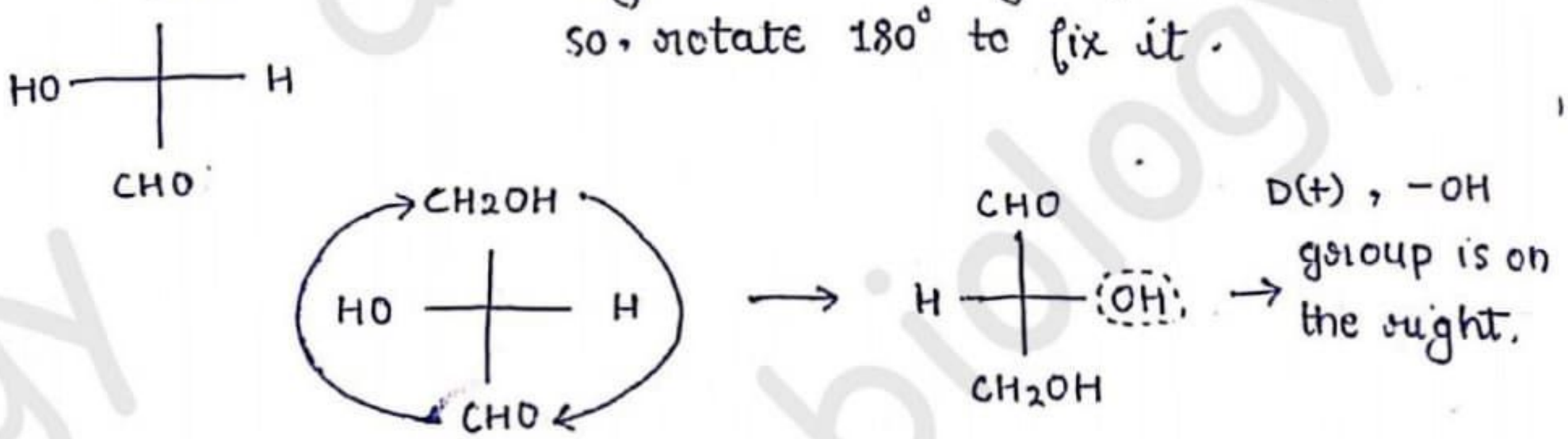


so, rotate clockwise (except top).

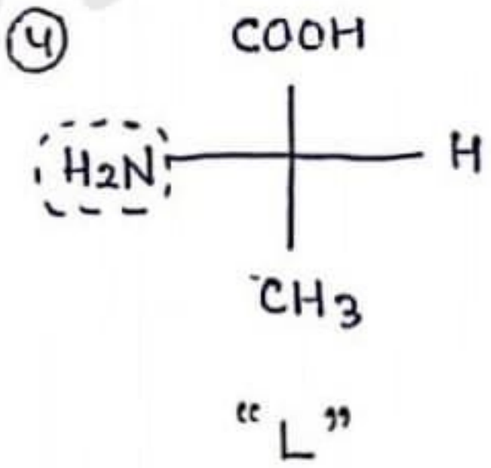


D(+)-, -OH group → is on right side.

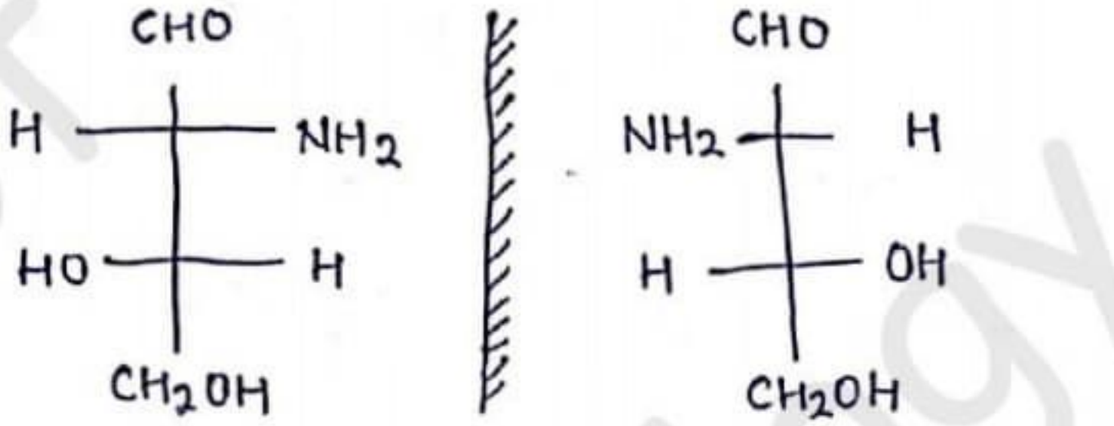
③ → Highest oxidized group must be on top.
so, rotate 180° to fix it.



D(+), -OH group is on the right.

④ 

"L"

⑤ 

② RS System of Nomenclature of optical isomers

This is 'absolute configuration' which is used for 'optical active compound'.

- R → Rectus [Right], which rotate PPL clockwise
- S → Sinister [Left], which rotate PPL anti-clockwise

This configuration was given by three scienties (European) R.S. Cahn, C.K. Ingold and V. Prelog. So, it is known as "CIP System".

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* Sequence Rule (For RS configuration, it is necessary to know the sequence rule).

① Firstly identify all chiral centre, then decide priority of all attached atoms / group according to their "atomic number". i.e → higher atomic number with highe priority.

Example → S > F > O > N > C > H

② If the two or more atom / group attached to the chiral centre are same, then give priority according to their "next atom / group" and so on --

Example → −CHO, −COOH, −COOR | −COOR > −COOH > −CHO

③ The lowest priority atom / group must be on bottom and top of verticle line.

• <u>Some functional group with their priority order</u>

$-I > -Br > -Cl > -SH > -F > -OR > -OH > -NO_2 > -NH_2 > -CCl_3 >$

$-COCl > -COOR > -COOH > -CHO > -CH_2OH > -C\equiv C- > -C=C- >$

$C_2H_5 > -CH_3$ ——

* <u>Rules for RS Configuration</u>

① The atom / group attached with a chiral centre are assigned with a number according to "sequence rule".

② Now, If the lowest priority group is on vertical line, then,

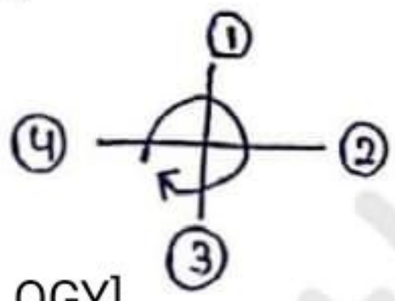
• Rotation of ① → ② → ③ is clockwise, configuration must be 'R' → Rectus

• Rotation of ① → ② → ③ is anticlockwise, configuration must be 'S' → sinister

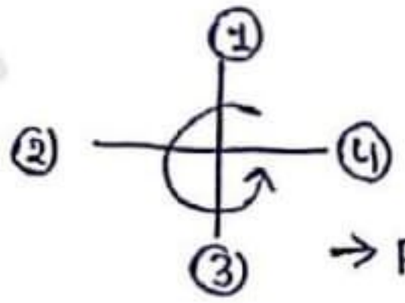
③ But, if the lowest priority group is on horizontal line, then,

• Rotation of ① → ② → ③ is clockwise, configuration is 'S'.

• Rotation of ① → ② → ③ is anticlockwise, configuration is 'R'

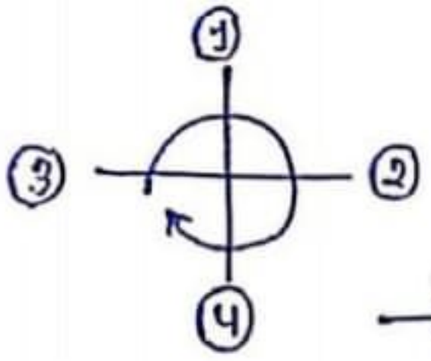


→ S

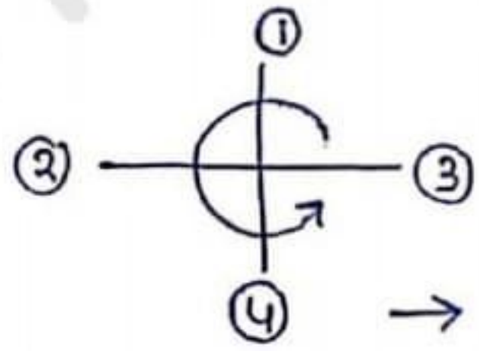


→ R

→ Lowest priority group is on horizontal line.



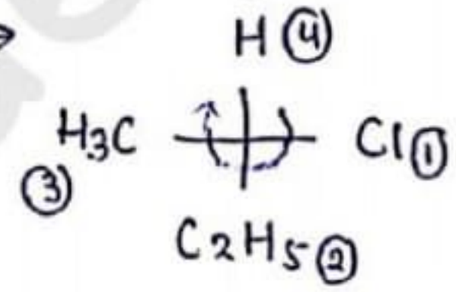
→ R



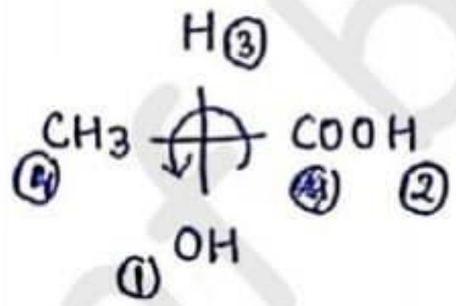
→ S

→ Lowest Priority group is on vertical line.

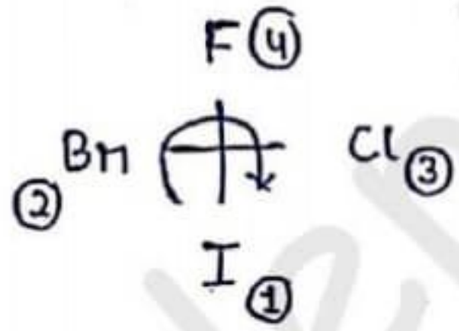
Example →



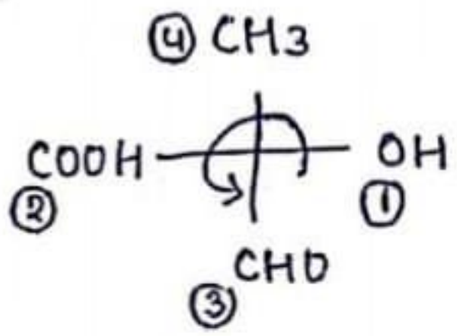
R - Configuration



S - Configuration



R - configuration



S - configuration

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* Reaction of Chiral Molecules

- **Chiral Molecule** → Those organic compound which has four different atom / group attached with Carbon.

- **Racemic mixture** → The equimolar mixture of Dextro (D)/(R) and Levo (L)/(S) substance is called Racemic mixture.

• Chiral Molecules show three types of reactions :-

ⓐ Inversion ⓑ Racemisation ⓒ Retention

ⓐ <u>Inversion</u> → These are those reaction in which chiral molecules change their nature after reaction, it convert :-

'R' [D] Dextro Compound ⟶ 'S' [L] Levo compound.

'S' [L] Levo Compound ⟶ 'R' [D] Dextro compound.

<u>Example</u> →

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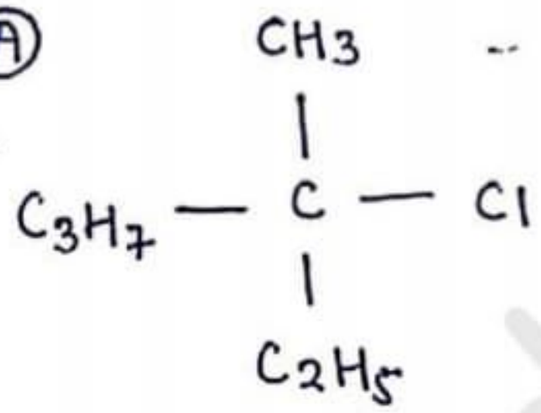
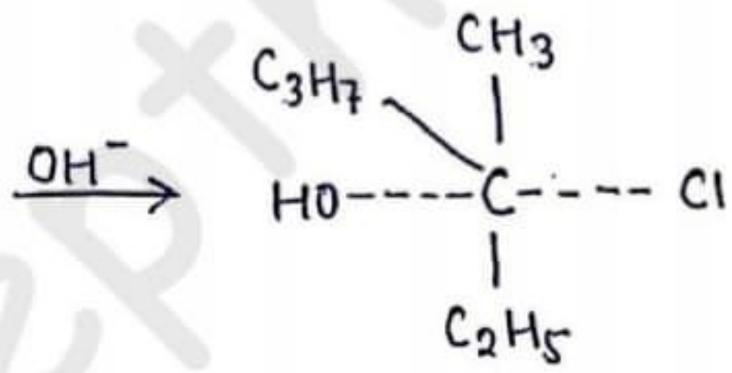
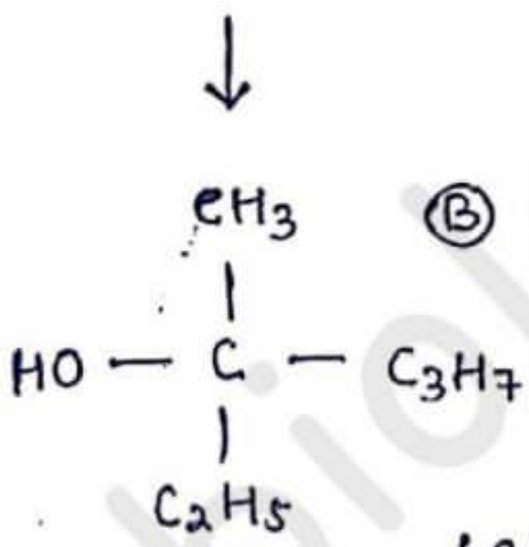
Ⓐ



'R' / 'S'



Transition State



'S' / 'R'

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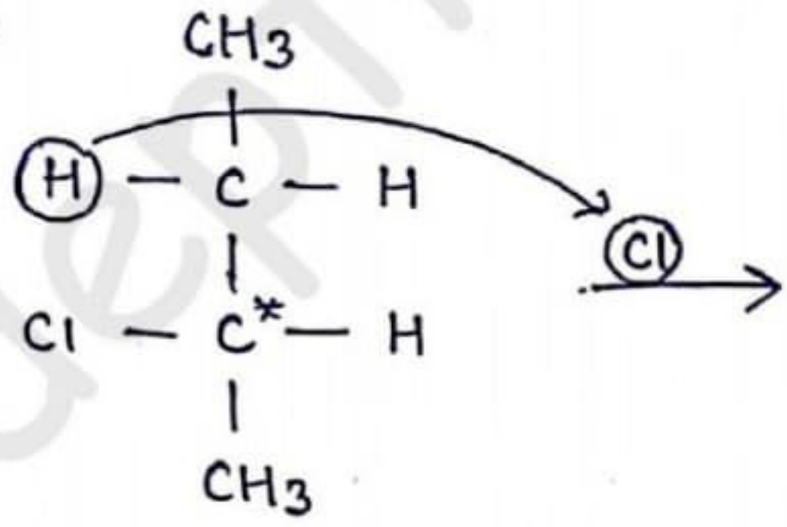
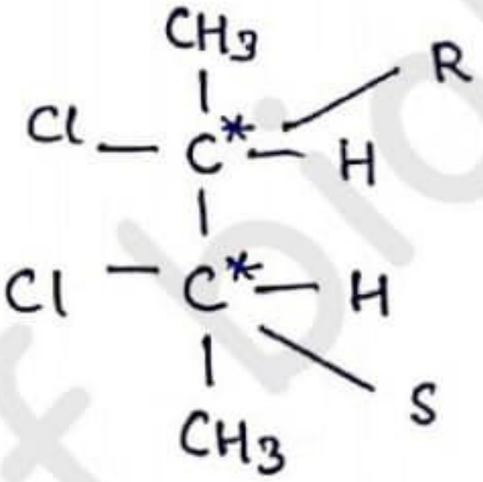
ⓑ <u>Racemisation</u> → In this reaction, optical active compound is converted into optically inactive compound after the reaction.

Example :-



'S' 2- chlonobutane

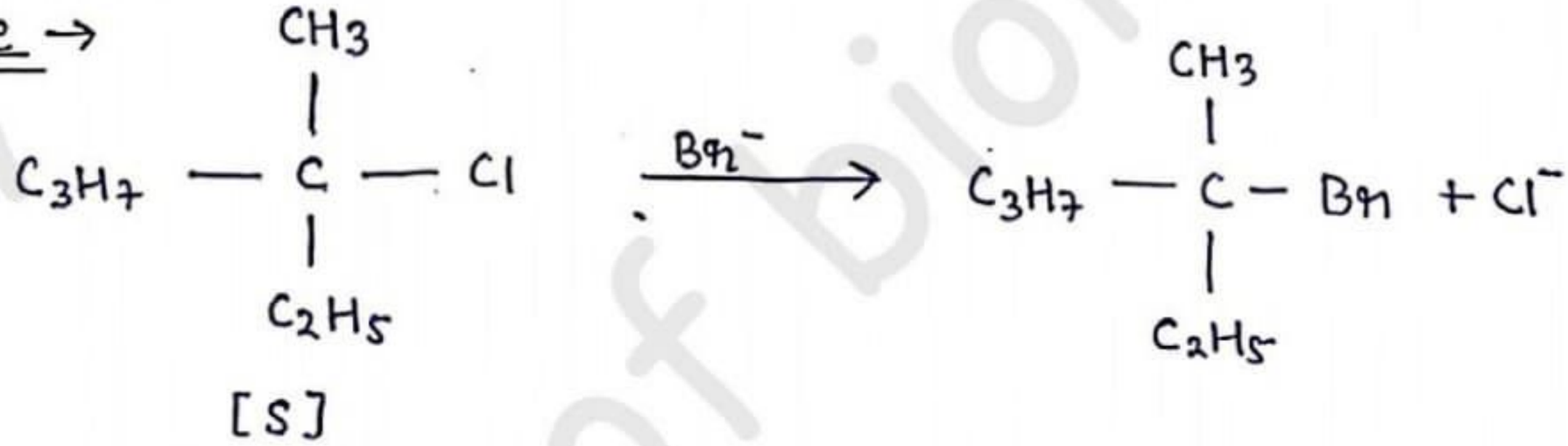


'R''S' – optically inactive
[Meso Compound]

- In this reaction, 'Cl' replace 'H' and form a meso compound, which is optically inactive.

© Retention → In this reaction, chiral molecules / compound remain constant (same configuration) after reaction.

Example →

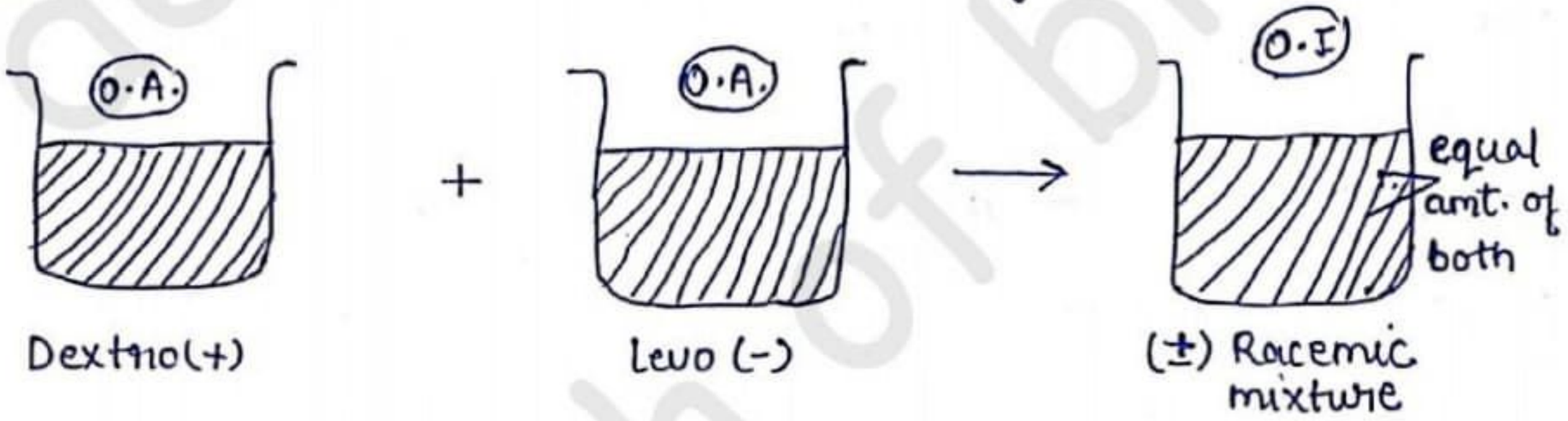


[S]

* Racemic Modification and Resolution of racemic mixture

• **Racemic Modification** → Also known as Racemic mixture represented as (DL , RS , ± , dl).

– The equal amount of levo (-) and dextro (+) forms optically inactive mixture known as racemic modification.



* Resolution of Racemic mixture :-

It is the process of separation of a racemic modification into its enantiomers constituents.

– Also in this process , optically inactive compound is converted into optical active compound.

• **Methods used for resolution** :-

ⓐ Mechanically method [Crystallization Method]

ⓑ Chromatography

ⓒ Biological Method

ⓓ Chemical Method

ⓐ **Mechanical Method** → In this method , finstly crystallized the both enantiomers in racemic mixture.

- Now both have different shapes from each other. So, they ~~have different shapes from each other~~. are separated by magnifying lens and forceps.
- It is a mechanical separation (manual) given by Louis Pasteur in 1848.
- This method is applicable only to <u>racemic conglomerates</u>. (If the molecules of the substance have greater affinity for some enantiomers than for the opposite one)
- This method is economic but time consuming.

(b) <u>Chromatography</u> → Optically active substance can be resolved by chromatography.

In this process, the racemic mixture is run through a column, which is filled with a optically active adsorbant. (a chiral substance).

The enantiomers will interacts differently with the chiral substance and remove from different routes.

- In this, optically active substance are selectively adsorbed by optically active absorbent on the basis of their affinity.

<u>Example</u> → Amines resolved via acylation by optically active acid chlorides.

[DEPTH OF BIOLOGY]
[DEPTH OF BIOLOGY]

© Biological Method → In this method, certain microorganism (bacteria, fungi, enzymes etc) are allow to grow in racemic mixture.

- They destroy one of the less important enantiomers at faster rate compare to other.
- Hence, the unchanged (other) enantiomers retain and can be isolated by fractional crystallization or chromatography.
- It is developed by pasteur in 1958.

• Drawback → one enantiomers is sacrificed and if mixture is toxic than kill the microorganism.

Example → Penicillin can be used to remove D-ammonium tartarate from the mixture of racemic ammonium tartarate.

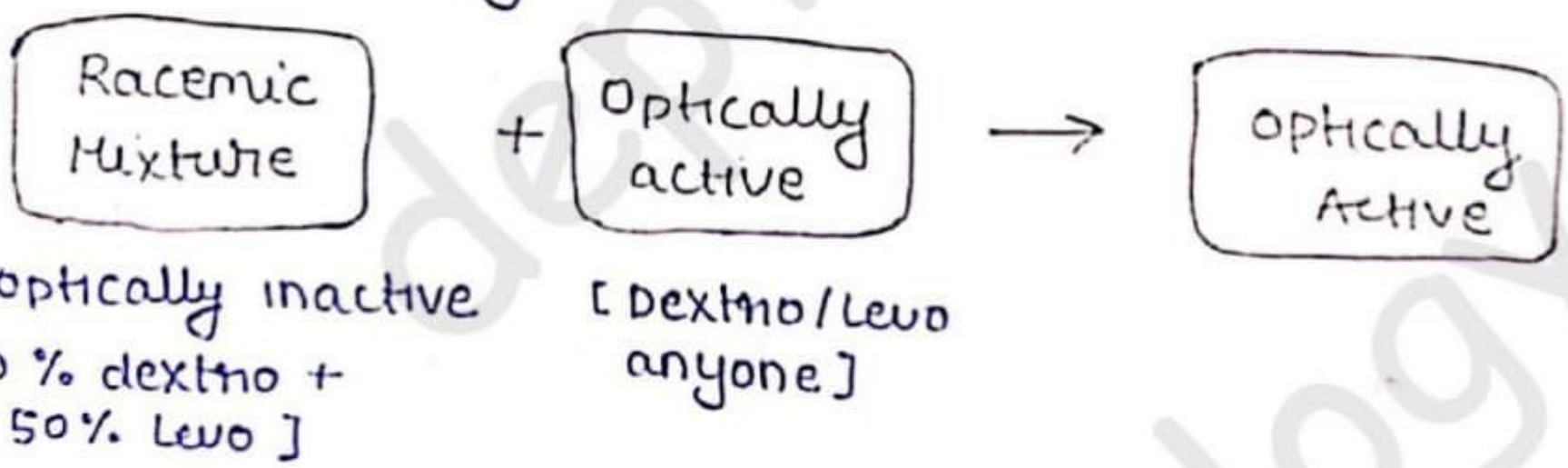
(d) Chemical Method → In this method, a racemic modification is converted into a mixture of diastereomers of another compounds.

→ The separation of enantiomers is difficult because of same physical properties. So, enantiomers reacted with optically active compound to form diastereomers.

- then, these diastereomers can be separated due to difference in their physical properties and after separation, they are reconverted into enantiomers by adding mineral acid (H^+)

Example → Acid-Base reaction are often used for resolution of racemic alkaloids like quinone, morphine etc...

- Asymmetric Synthesis → In this method, optically active compound is directly prepared from an optically inactive compounds under the influence of some other optically active substance. [DEPTH OF BIOLOGY]



OR, we can say that symmetric molecules (inactive) is directly converted into assymetric molecules (active).

- It is of two types :-

ⓐ Partial A-symmetric synthesis [DEPTH OF BIOLOGY]

ⓑ Absolute Asymmetric synthesis

① Partial Asymmetric synthesis :- In this synthesis, Both (+) and (−) enantiomers are formed but one of these is obtained in large amount.

So, Both are not in equal amount and act as a optically active compound and pass the plane polarised light. eg → Glucose

50 % (+)	50 % (−)

Racemic Mixture

$\xrightarrow{\text{Optically active substance}}$

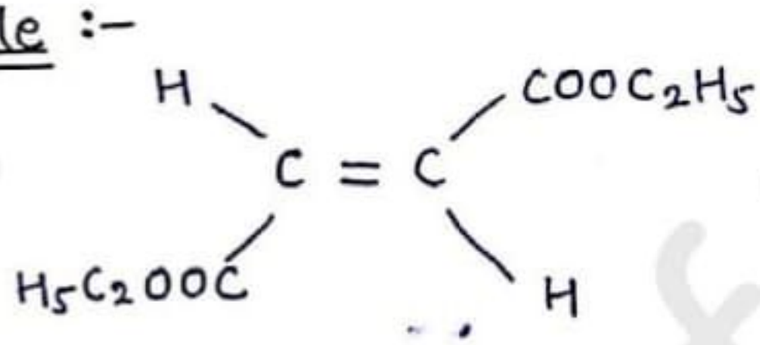
70% (+)	30% (−)

Optically active

② Absolute Asymmetric synthesis :- In this synthesis, Racemic mixture (symmetric molecules) is completely convert into optically active compounds [Dextro or Levo] any one. [DEPTH OF BIOLOGY]

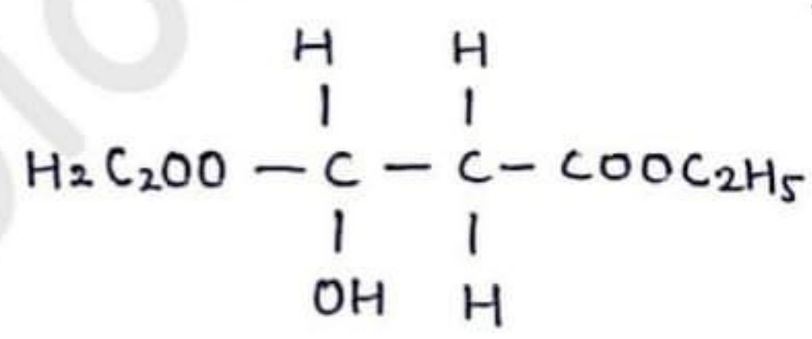
- In this, only one enantiomers can be formed completely.
- In this, any physical agent is used.

Example :-



[Ethyl fumurate]

$\xrightarrow{H_2O_2}$



[D-diethyl tartaric acid]

- Ethyl fumerate and H_2O_2 under influence of dextrorotatory light give (+) diethyl tartaric acid.