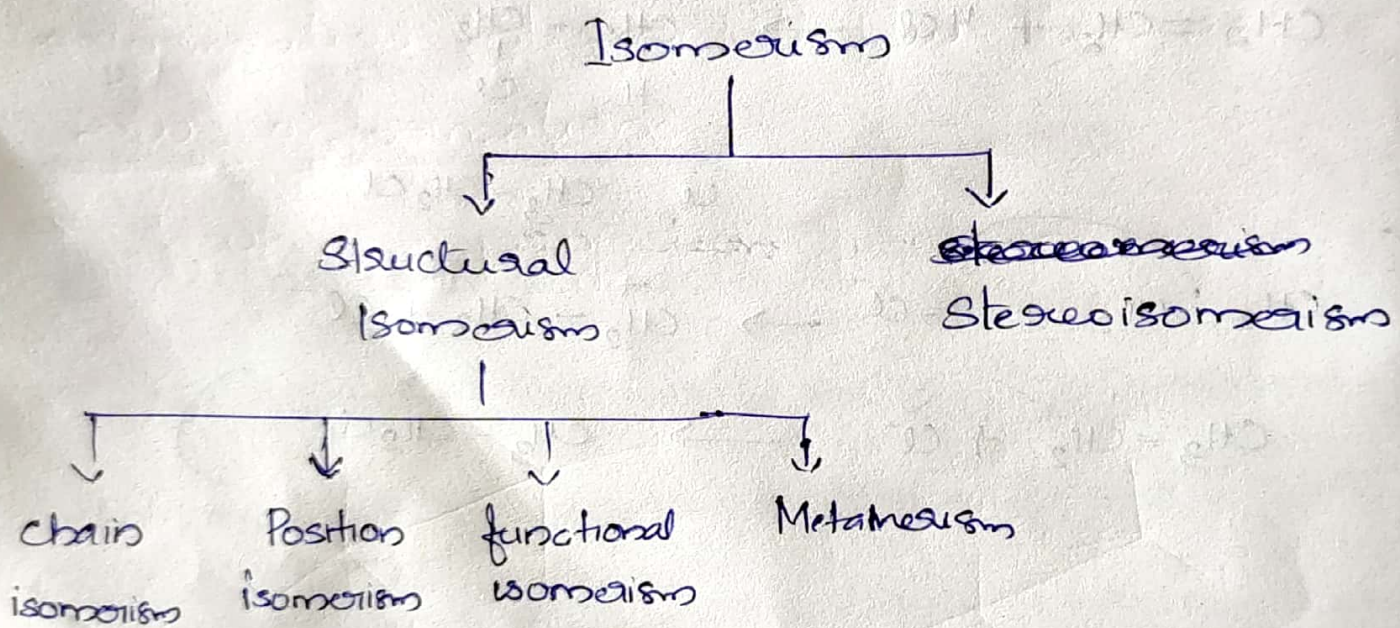


Stereochemistry

~~Stereoisomers~~ Compound with same molecular formula but differ in the arrangement of the constituent atoms ~~isomers~~ are called isomers.



Stereoisomerism

Isomers having the same structure but different spatial arrangements of atoms or groups are called stereoisomers. And the phenomenon is called stereoisomerism.

Stereoisomerism

Configurational

Conformational

(Due to free rotation about single bond)

Geometric Isomer

Optical Isomer

(Due to chirality)

(Due to restricted rotation about double bond)

Conformational Isomerism

The different spatial arrangements of atoms or groups in a molecule that arise from "free" rotation about a single bond are called conformations. Such isomers which are interconvertible merely by rotation about single bonds are called conformational isomers/rotamers.

Conformations of Ethane (CH_3-CH_3)

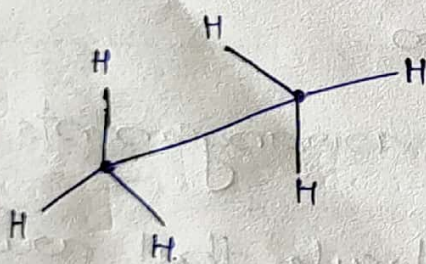
Free rotation about C-C σ bond gives rise to a infinite no. of spatial arrangement. The two extreme cases are

(1) Staggered conformation

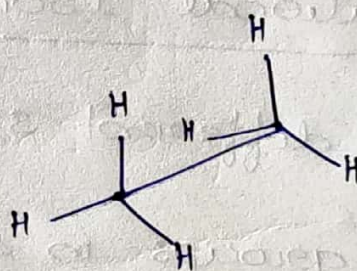
(2) Eclipsed conformation.

Conformation intermediate b/w them are called skew conformations

→ Sawhorse projection of ethane

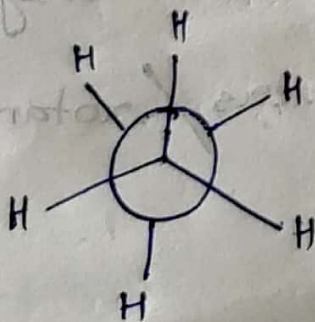


(a) Staggered form

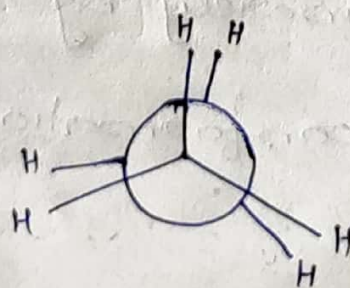


(b) Eclipsed form

→ Newman projection of ethane



(a) Staggered



(b) Eclipsed

Relative stabilities

Staggered is more than eclipsed.

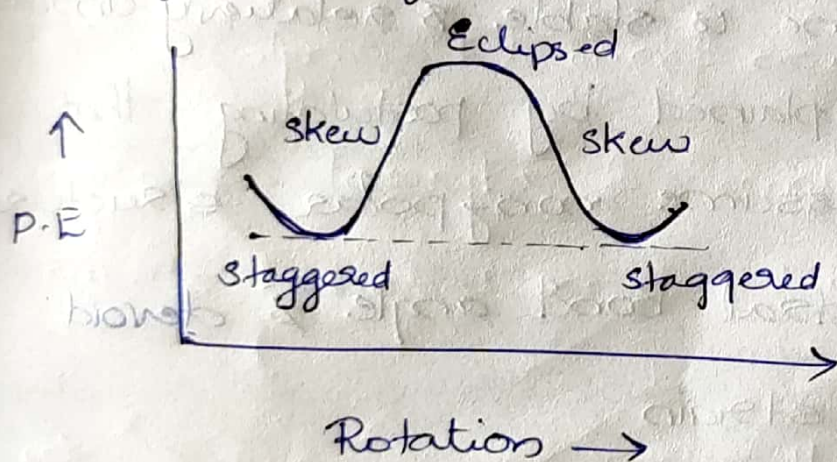
Explanation:

In staggered, H atoms on the two C atoms are situated at maximum possible distance apart.

While in eclipsed H atoms of two C atoms are close to each other, generating repulsion.

So ~~interactive~~ repulsive interactive force is less

for staggered form & hence it is stable.



Energy difference between staggered and the eclipsed form of ethane is 12.6 kJ mol^{-1} at 298 K & is referred to as torsion barrier

↓
This small energy diff is not sufficient to prevent rotation about C-C bond. So individual conformers can be isolated.

Conformation of cyclohexane (C₆H₁₂)

→ Have planar hexagonal ring.



→ C-C-C bond angle - 120° which is largely deviated from normal tetrahedral angle ~~109.5~~ 109.5° as expected for sp^3 .

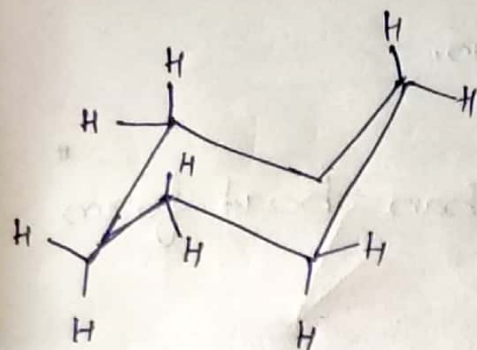
— This according to Baeyer's strain theory would produce considerable angle strain on the system making it unstable and reactive.

But cyclohexane is stable & relatively unreactive, this can be explained by postulating that cyclohexane assume non-planar structure having tetrahedral bond angle & devoid of any angle strain.

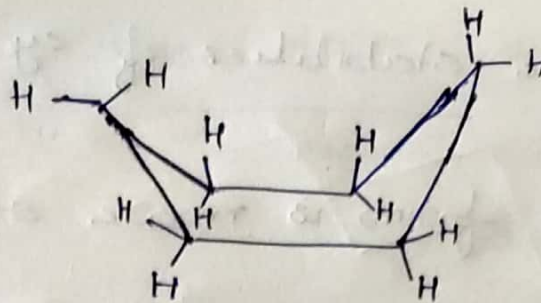
→ Cyclohexane has non-planar / puckered six-membered ring system in which normal tetrahedral bond angle of ~~109~~ 109.5° are maintained.

Two conformations are possible

- (1) Chair conformation
- (2) Boat conformation



(i) chair forms



(ii) boat form

Imp

Angle strain

Strain induced in a molecule when the bond angles are forced to deviate from the desired tetrahedral angle of 109.5°

Positional strain

Strain caused by the repulsive interactions between the σ -electrons of atoms/groups that take up eclipsed position.

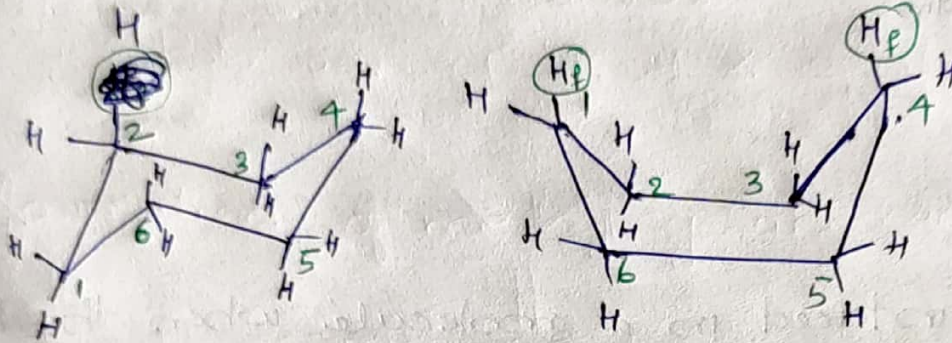
Steric strain

Strain caused by the steric crowding of atoms/groups which approach each other too closely in the structure.

Relative stabilities of cyclohexane

"Chair form is more stable than boat form"

Explanation:



→ Both forms are free from angle strain (bcz no deviation from 109° angle)

→ In chair - H atoms of adjacent C atoms are far apart so no torsional strain (staggered)

→ In boat form - H atoms on C^2 and C^3 & those on C^5 & C^6 are eclipsed. (~~due~~ repulsion due to σ electron clouds of C-H bonds) ~~and are close~~ so they ^{have} torsional strain

→ In boat - H atoms marked as H_p called ~~flagpole interaction~~ flagpole hydrogens on C^1 and C^4 point each other are close causing steric strain

ie

chair form

boat form

- No steric strains
- No torsional strains
- No angle strains

- Torsional strains
- Steric strains

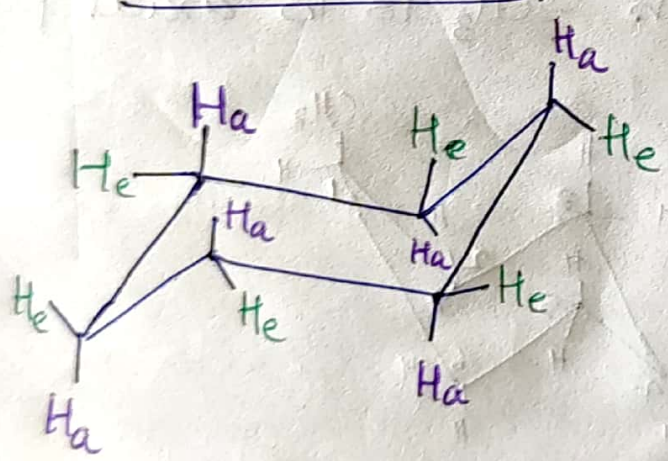
Free from angle strains



29 KJ/mol

This energy is not enough to overcome interconversion. So ~~can~~ this to cannot be separated.

Axial & Equatorial bonds

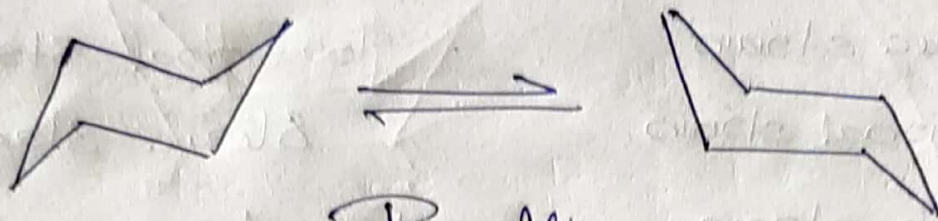


~~12 C-H bonds~~ in this form can be divided into 12 C-H bonds →

two, Axial bonds and equatorial bonds

→ C-H bond which are parallel to symmetry axis of the ring — Axial

→ C-H bond which lie in ~~the~~ a belt about the 'equator' of the ring — Equatorial



Ring flip

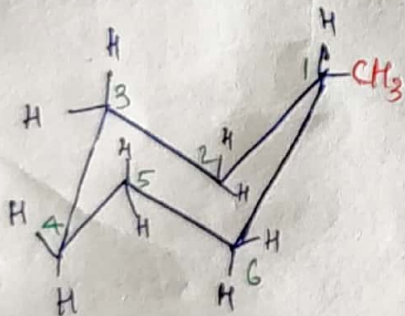
(Interconversion)

Both are identical & equal energy.

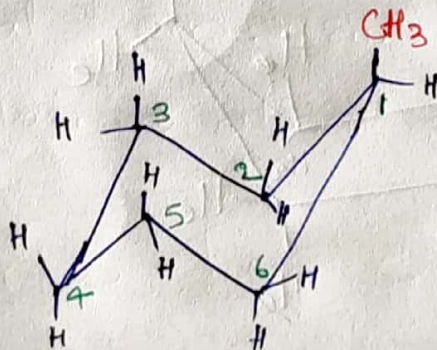
Conformations of methylcyclohexane ($C_6H_{11}-CH_3$)

→ Important forms are two chair forms,

one in which $-CH_3$ group is in equatorial position & the other in which $-CH_3$ is in axial position.



Equatorial methylcyclohexane



Axial methylcyclohexane

chair form in which CH_3 is in equatorial position is more stable than axial form.

In axial CH_3 - two axial H atoms on C^1 & C^5 approach CH_3 group on C^1 quite closely as these are on same side of the

gung are parallel to each other. — ie crowding
between 2 axial H atoms & CH₃ group resulting
in repulsion. Since these are 1,3 position
these steric interactions are called 1,3-diaxial

interaction
In equatorial CH₃ — there is no such
repulsion because the groups are
distant.

→ Energy difference between the two is
7.5 kJmol⁻¹ — This is too small to prevent
the interconversion & so ~~cannot~~ individual
components cannot be isolated.

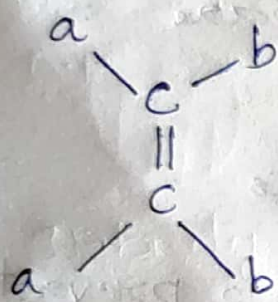
Geometrical Isomerism

Isomers which have the same structural
formula but differ in the spatial arrangements
of atoms/groups around a double bond due to
restricted rotation about the double bond are
called geometrical isomers.

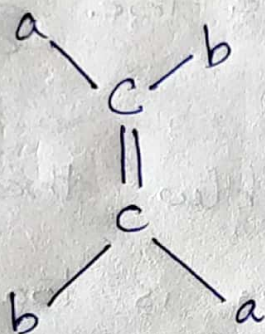
Cis & Trans isomers

Cis isomer \rightarrow Isomer with similar groups on the same side of double bond.

Trans isomer \rightarrow Isomer with one of the similar groups on opposite side of double bond.



Cis-isomer



Trans-isomer

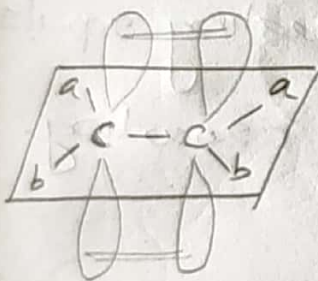
Cause of geometrical isomerism: Restricted rotation about double bonds

- \rightarrow A double bond plus two C atoms consist of a σ bond & a π bond. ~~atoms~~
- \rightarrow Strong σ bond formed by head-on-head overlap of sp^2 hybrid orbital of C atoms.
- \rightarrow Weak π bond formed by ~~side~~ ^{sideways} overlap of unhybridised P orbital standing \perp to sp^2 hybrid orbitals.

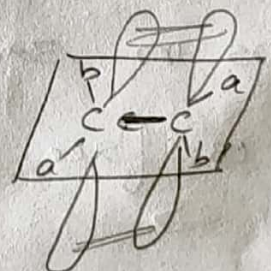
→ π bond locks the molecule in this position above & below the plane of the atoms.

→ Any attempt to distort the system from its planar arrangement of atoms by rotation about the double bond would tend to ~~use~~ break the sideways overlaps & break π bond. This is not favoured.

→ Thus presence of π bond restricts the rotation of molecule about a double bond. (making geometric isomerism)



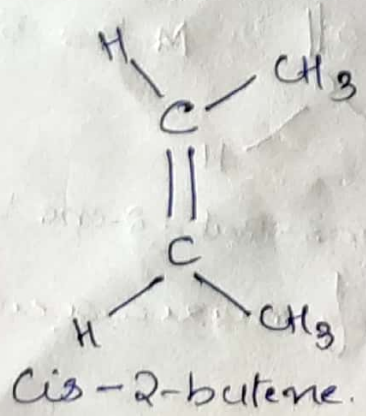
Cis isomer



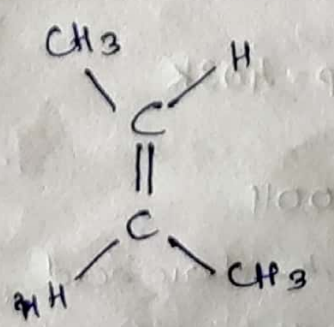
Trans isomer.

Examples:

① 2-butene $\text{CH}_3\text{-CH=CH-CH}_3$



Cis-2-butene.



Trans-2-butene

Cis 2-butene

- Low M.P bcz low symmetry & fit into a crystal lattice more poorly than trans isomer

$$M.P = 134 K$$

$$B.P = 277 K \text{ due to high polarity}$$

Stability:

" Trans-2-butene is stable "

Can be explained by steric effect - Cis form has two bulky groups in same side creating repulsion whereas trans is free from steric crowding.

trans 2-butene

$$M.P = 167 K$$

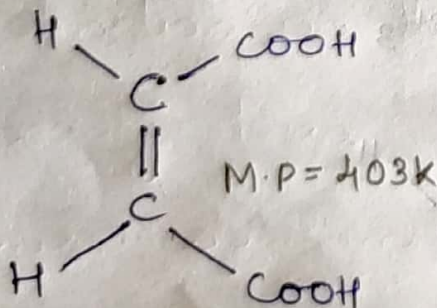
$$B.P = 274 K$$

(being symmetrical

it have zero dipole moment)

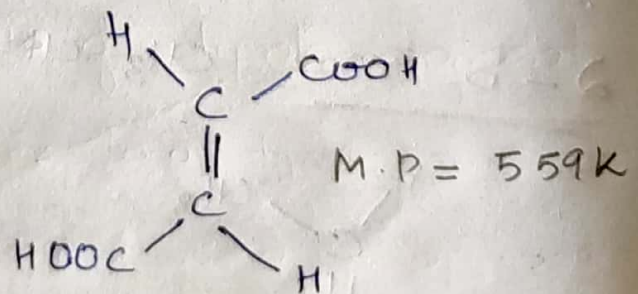
② but-2-ene-1,4-dioic acid ($\begin{matrix} \text{COOH} \\ | \\ \text{CH} = \text{CH} - \text{COOH} \end{matrix}$)

(Geometric isomerism) of maleic & fumaric acid



Cis-But-2-ene-1,4-dioic acid

Maleic acid



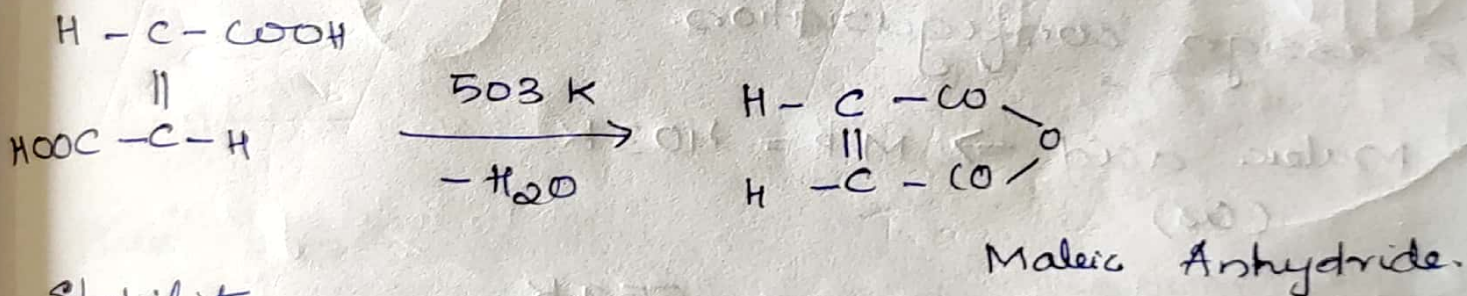
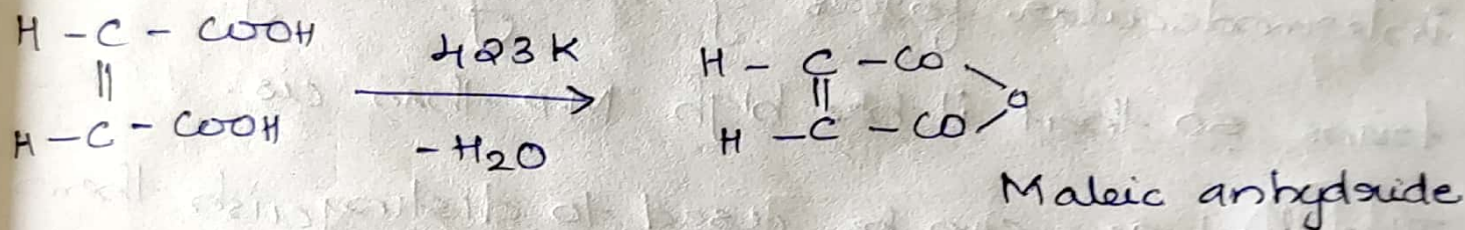
Trans-But-2-ene-1,4-dioic acid

fumaric acid

"Among geometrical isomers, the cis form has lower melting point & higher B.P., refractive index, dipole moment etc"

→ When heated above its M.P maleic acid readily yield maleic anhydride.

But fumaric does not yield its own hydride, instead, on strong heating it yield maleic anhydride.



Stability:

"Fumaric acid is more stable than maleic acid"

This can be explained by steric strain

H.W fill the explanation.

Methods of distinguishing geometrical isomers

(a) Distinction on the basis of M.P of isomers.

Cis isomer is less symmetrical as the two similar groups lie on the same side of the $C=C$ bond & hence does not pack well into the crystal lattice. As a result intermolecular forces generally strong in trans so that it has high M.P than cis.

This feature can be used to distinguish them & assign configuration.

Maleic acid \rightarrow M.P = 403 K
(Cis)

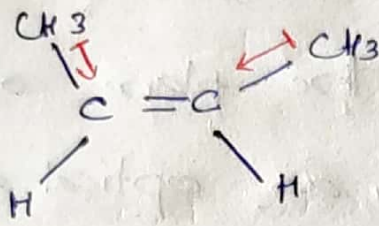
Fumaric acid \rightarrow M.P = 559 K
(Trans)

(b) Distinction on the basis of dipole moment

Generally trans form has low dipole moment because two similar group lie on the opposite side, the corresponding bond moments would get cancelled out to a great extent.

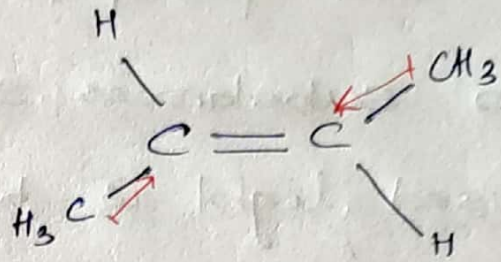
This feature is used to distinguish them and assign configuration.

Eq:



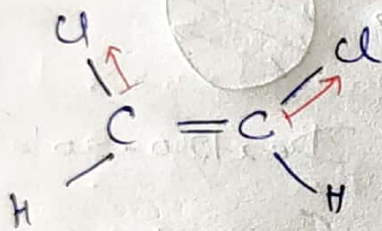
cis-2-butene

$\mu = 0.33D$



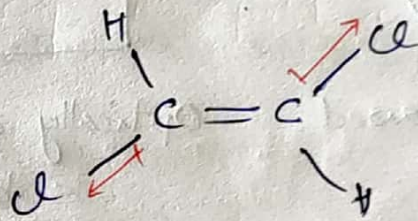
Trans-2-butene

$\mu = 0D$



cis-1,2-dichloroethene

$\mu = 1.85D$



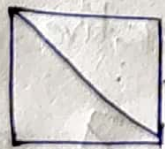
trans-1,2-dichloroethene

$\mu = 0D$

OPTICAL ISOMERISM

Plane polarised light

Polarisation



Ordinary monochromatic light

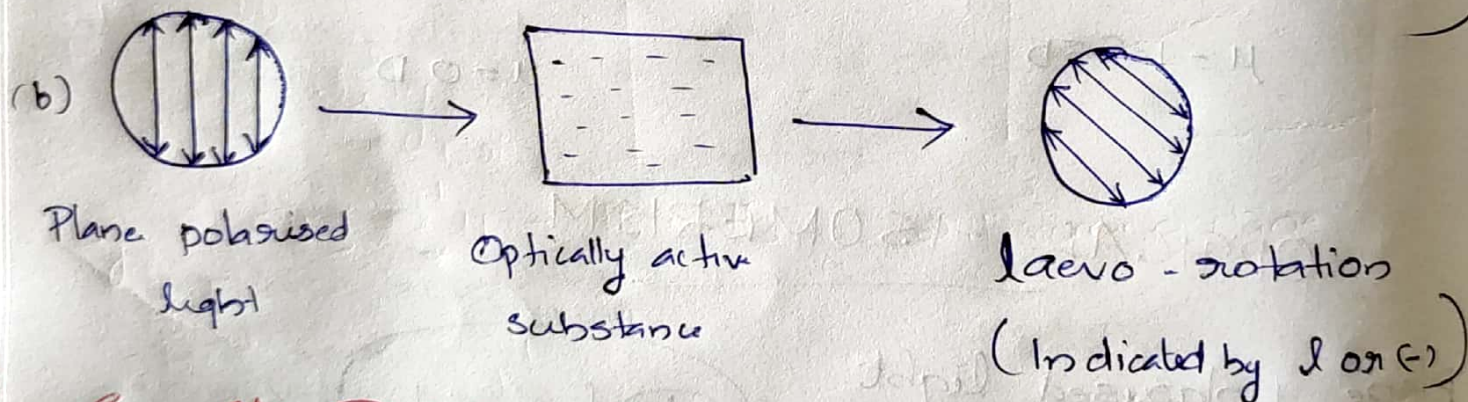
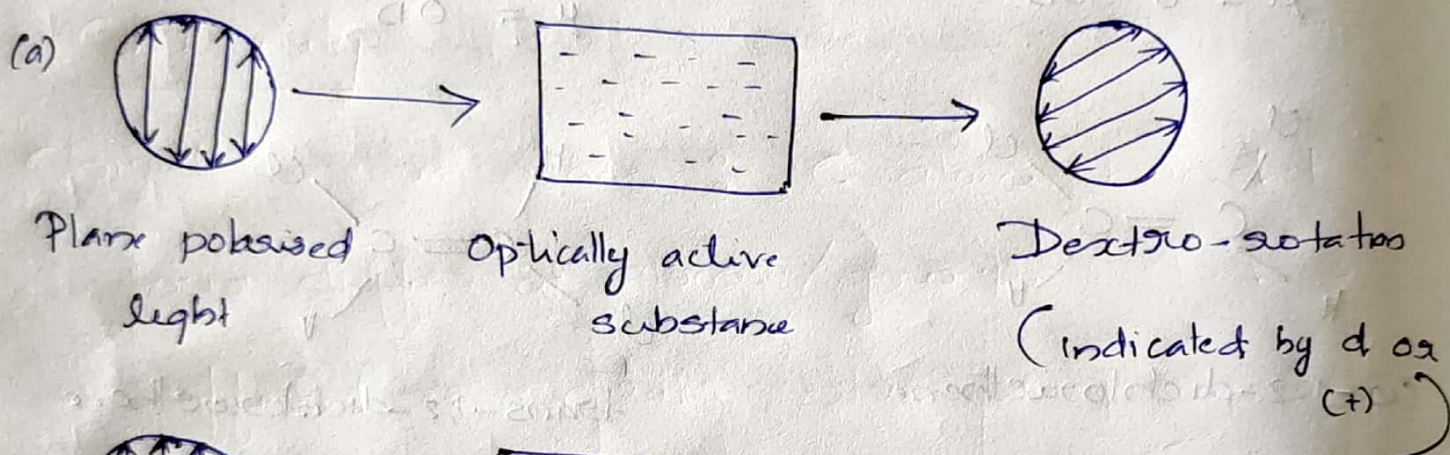
Nicol prisms

Plane polarised light

(Light whose vibrations occur in only one plane)

Optical Activity

The property by virtue of which certain substances rotate the plane of polarised light is known as optical activity & such substance called optically active.



Specific Rotation (α)

α of an optically active compound, at specific temp & for specified λ , is defined as observed rotation in degrees when plane-polarised light is passed through one decimeter of the solution of the substance having a concentration of one gram/ml.

$$[\alpha]_{\lambda}^T = \frac{\alpha_{\text{obs}}}{l \times c}$$

⑥ α depend on

- (1) Nature of substance
- (2) Temperature
- (3) λ of light used.
- (4) Conc of sample solution
- (5) length of polarimeter tube

Eg: $[\alpha]_D^{298K}$ → Specific rotation determined at 298 K using D-line of sodium light

→ $[\alpha]_D^{298K}$ of an aq. sucrose solution determined using D-line of sodium light is

$$[\alpha]_D^{298K} = +66.5^\circ \quad (\text{In water})$$

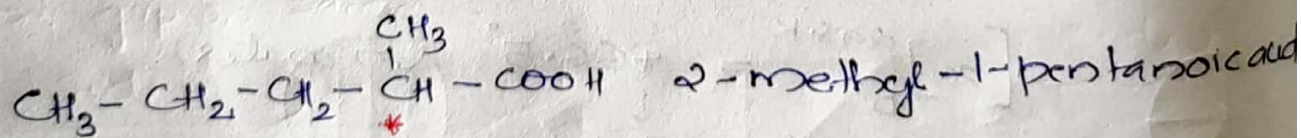
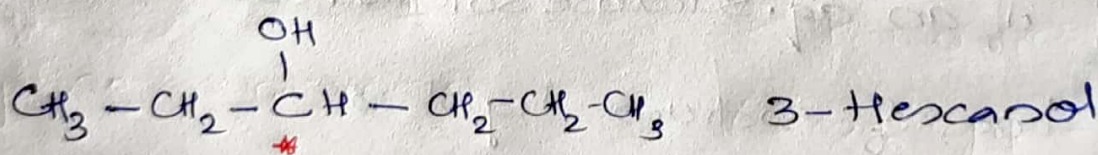
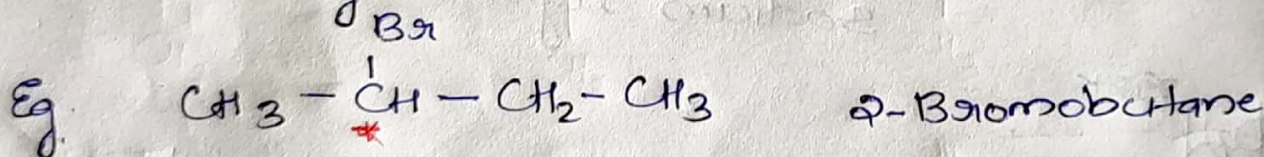
↓
(dextro)

Optical Isomerism

Stereoisomerism in which the isomers resemble in most of their properties but differ in their behaviour towards plane polarised light.

Chirality

Chiral Carbon atom: C atom bonded to four different atoms/groups. And is referred as chiral centre & property is chirality

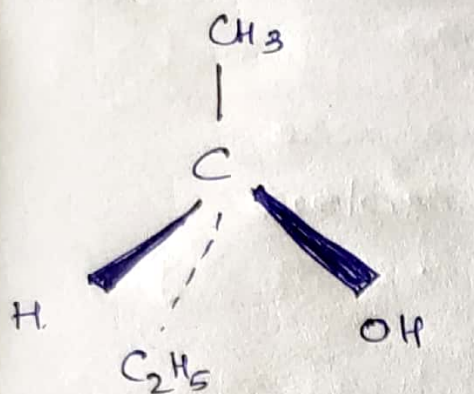


Enantiomers

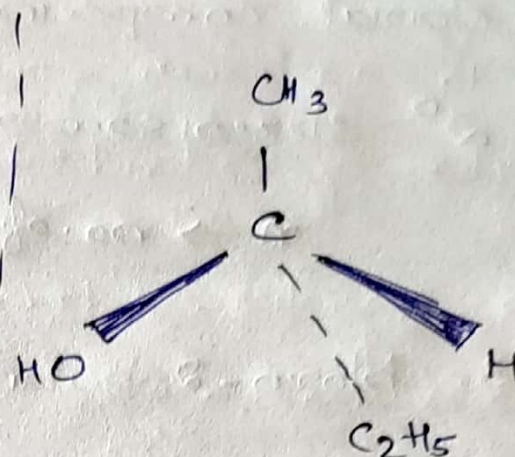
Stereoisomers which are non-superimposable mirror image & rotate the plane polarised light to equal extent, but in opposite directions

are called enantiomers.

Eg:-

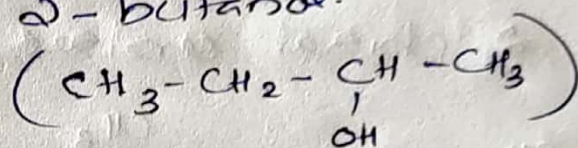


(+) or d-2-butanol



(-) or l-2-butanol

Enantiomers of 2-butanol.



* An equimolar mixture of two enantiomers of a substance is known as **racemic mixture** / **dl form** / **(±) form**.

→ Racemic mixture is optically inactive because optical rotation due to one enantiomer is exactly cancelled by the equal & opposite rotation due to the other.

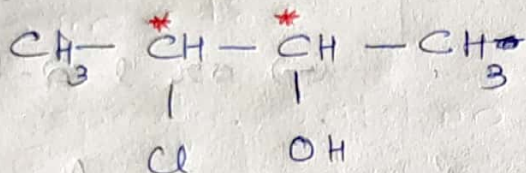
Diastereoisomerism

Stereoisomers which are not mirror images of each other are called diastereomers.

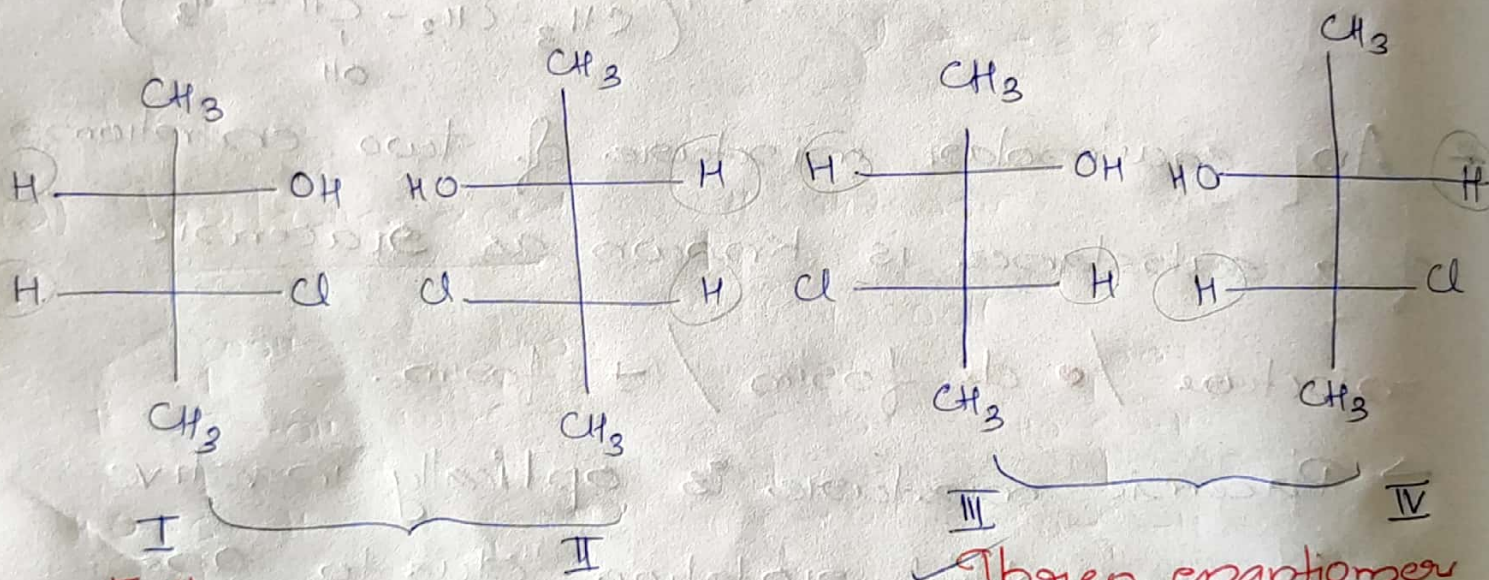
→ A chiral compound can have a maximum of 2^n stereoisomers

$n \rightarrow$ no. of chiral centres

Eg: 3-chloro-2-butanol.



2 chiral centres.



Erythro enantiomers
(Same grp on same side)

Threo enantiomers
(Same grp on diff side)

I & II → Non-Superimposable mirror image
III & IV → so enantiomers

I & III → Not mirror images of each other and are called diastereomers

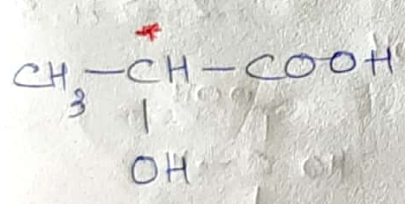
I & II and I & IV } diastereomers.
 II & III and II and IV }

→ Diastereomers differ in physical properties such as melting point, B.P., densities, refractive index etc & in their specific rotation.

Note down the table

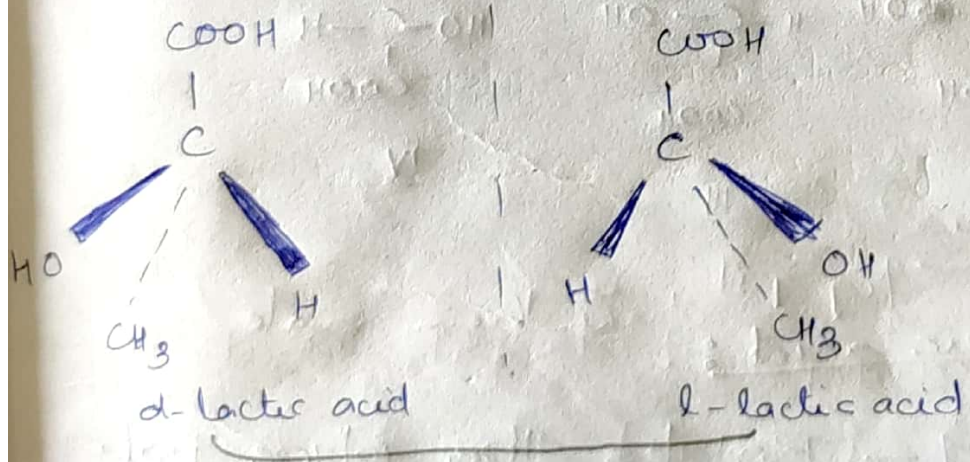
Optical Isomerism of :

(i) Lactic acid (2-hydroxypropanoic acid)

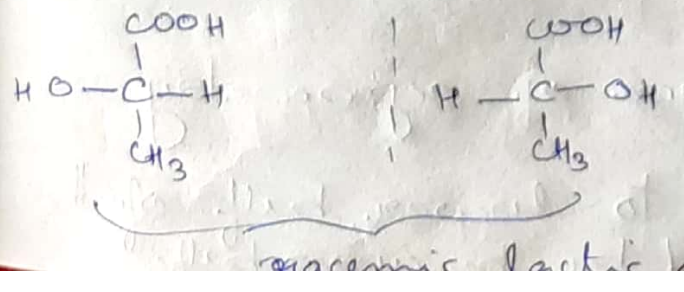


chiral carbon = 1

$2^n \Rightarrow 2^1 = 2$ stereoisomers.



Racemic lactic acid (Equimolar mixture of the two)



→ dl-form of lactic acid is optically inactive due to external compensation of optical rotation of individual enantiomers

→ Both enantiomers have identical property

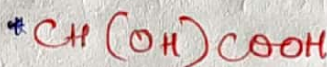
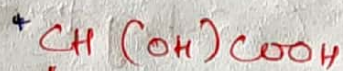
• Both m.p = 26°C

dl-form = 18°C

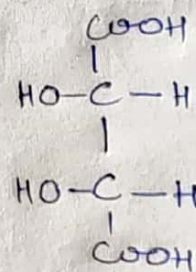
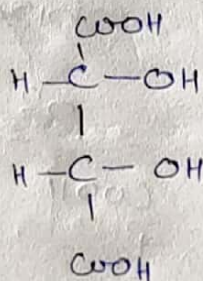
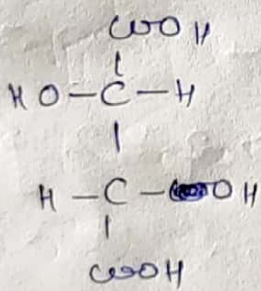
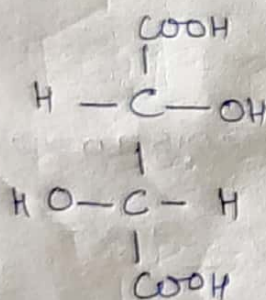
• Both specific rotation, $\alpha = 3.82^{\circ}$

dl-form = 0 (since d $\rightarrow +3.82$
l $\rightarrow -3.82$)

(2) Tartaric acid



$2^n \Rightarrow 4$ stereoisomers



I

II

III

IV

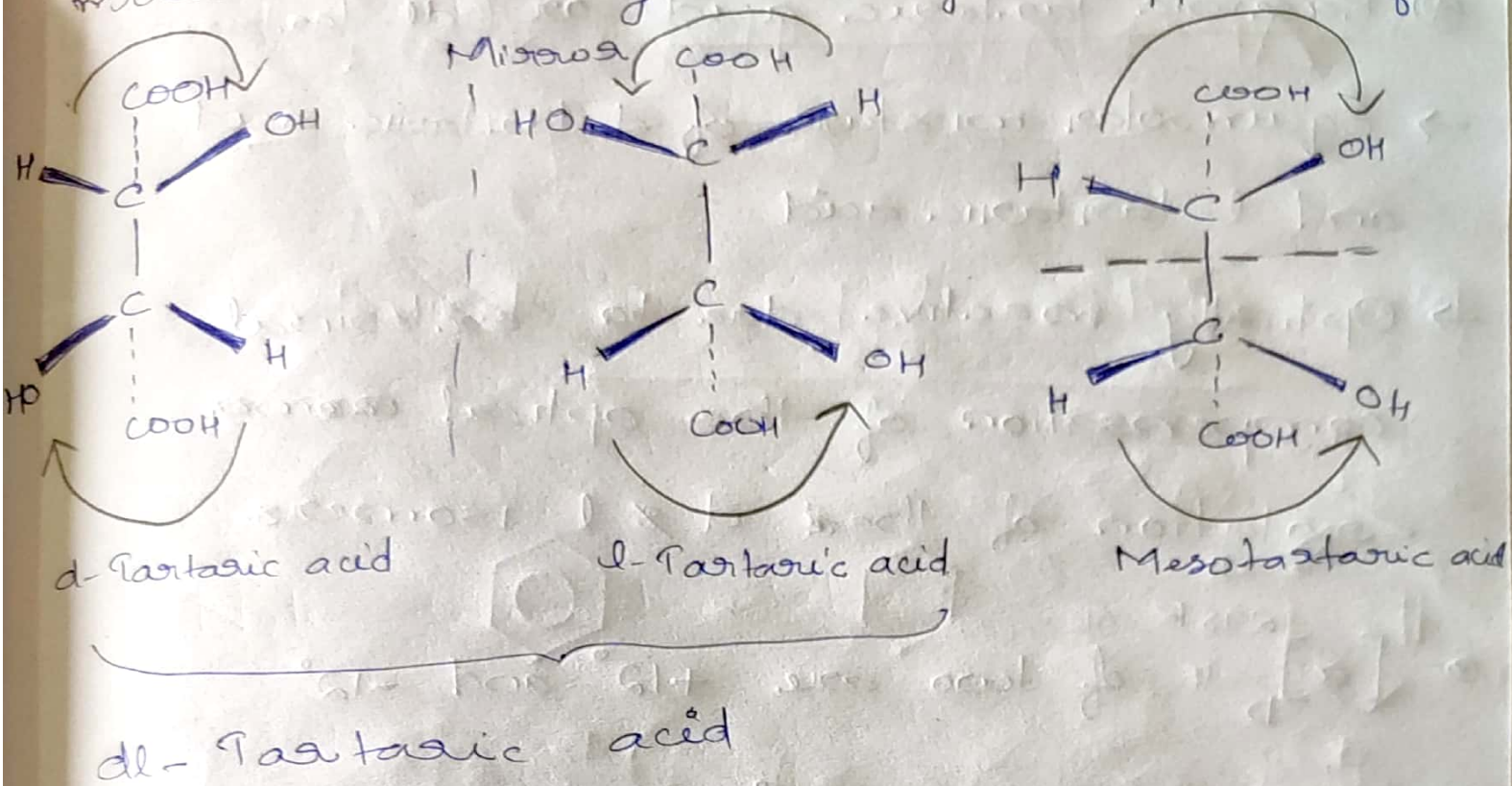
① Dextro-tartaric acid:

→ d-tartaric acid - Rotates the plane polarised light to the right,

→ Molecule has no plane of symmetry

→ Optical rotation due to lower half of the molecule is strengthened by the upper half.

molecule is strengthened by the upper half.



② Laevo-tartaric acid

- Rotate the plane polarised light to left
- No plane of symmetry
- Optical rotation ~~to~~ due to lower half is strengthened by upper half.

③ Meso-tartaric acid

- Contains plane of symmetry
- Optically inactive due to ~~and~~ internal compensations (i.e. optical rotation due to lower half is ~~cancelled~~ compensated ~~also~~ by the upper half)

Ⓐ Racemic tartaric acid or (dl-tartaric acid)

→ Equimolar mixture of d-tartaric acid and l-tartaric acid

→ Optically inactive due to external compensation of the optical ~~rotation~~ rotation of these d & l isomers.

• $[\alpha]_D^{298K}$ of two are $+12^\circ$ and -12°

• M.P of both -170°C

• Meso-tartaric acid is not a mirror image of d or l-tartaric acid & hence called diastereomer.

M.P = 140°C

Meso compounds

If a compound, despite the presence of two / more chiral centres in ~~the~~ ^{its} molecule is achiral due to the presence of a plane of symmetry and these are optically inactive due to internal compensation.

Eg: Meso-tartaric acid

