Isomerism:

Same molecular formula but diff. properties ⇒ Cpds are isomers

Classification of Isomers:

- Structural
  (Constitutional)
  dif. bonding seq. of atom
- Stereo
  (3D space)
  dif. in Orientation in space

Structural Isomers:

1. Chain - dif. carbon skeleton
2. position - dif. in position of multiple bond/func.grp
3. Functional - dif. in func. grp
4. Metamers - dif. in alkyl grp attached
5. Ring chain - ring and aliphatic chain
6. Tautomers - two or more readily interconvertible structure

Ex:

1. Chain isomers:

Pentane and 2-methyl butane

2,2-dimethyl propane

2. positional Isomers:

But-1-ene and but-2-ene

3. Functional Isomers:

propanone and proponal

$(-\overset{\overset{O}{\|}}{C}-)$ $(-CHO)$

4. Ring chain Isomers:

hexane and cyclohexane

5. Metamers:

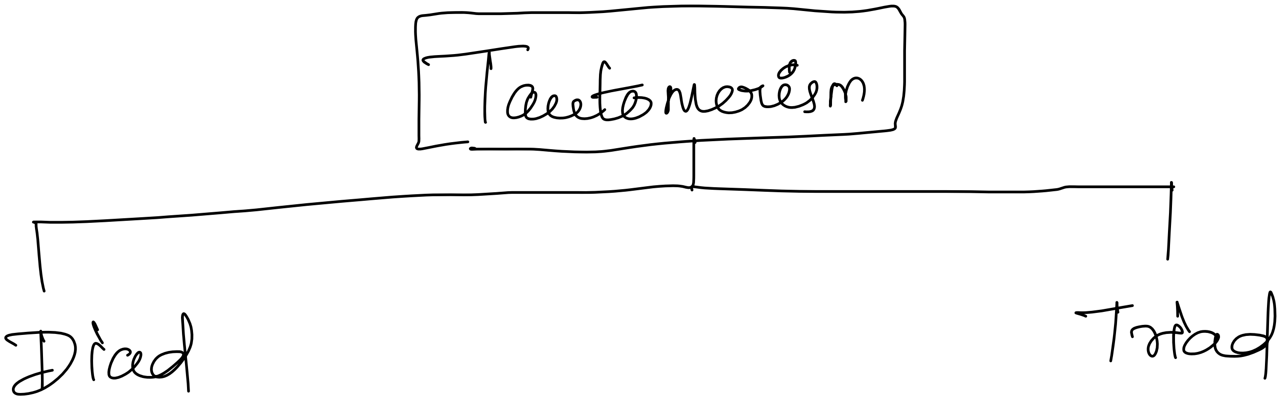
N-ethylethanamine and

N-methyl propanamine

Tautomerism:

Phenomenon by which a Single Cpd exist in two or more readily interconvertible Structure that differ in the relative positions of at least one atomic nucleus mostly hydrogen.

⇒ Isomers exhibiting this are "Metamers"



Diad -

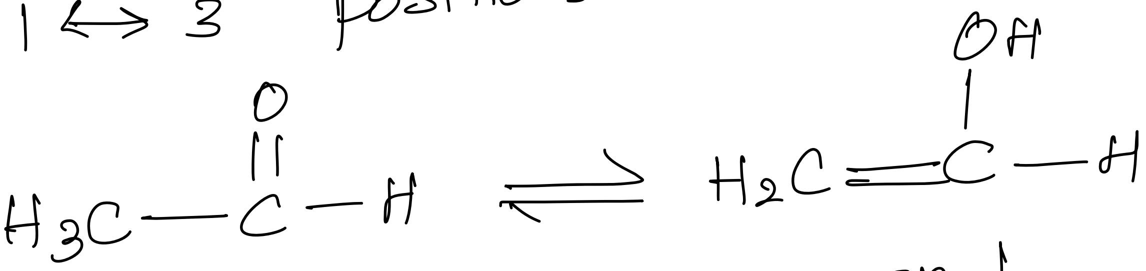
Movement of H-atom between $1 \leftrightarrow 2$ positions

$$\underbrace{H-C\equiv N \longleftrightarrow \overset{\ominus}{C}\equiv\overset{\oplus}{N}-H}_{\text{Tautomers}}$$

Triad Tautomerism:

movement of H atom between

1 ⟷ 3 positions.

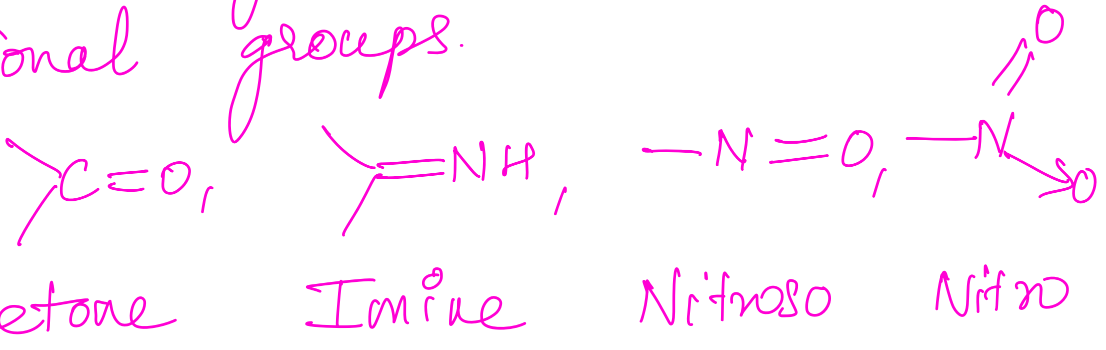


$$H_3C-\overset{O}{\overset{\|}{C}}-H \rightleftharpoons H_2C=\overset{OH}{\overset{|}{C}}-H$$

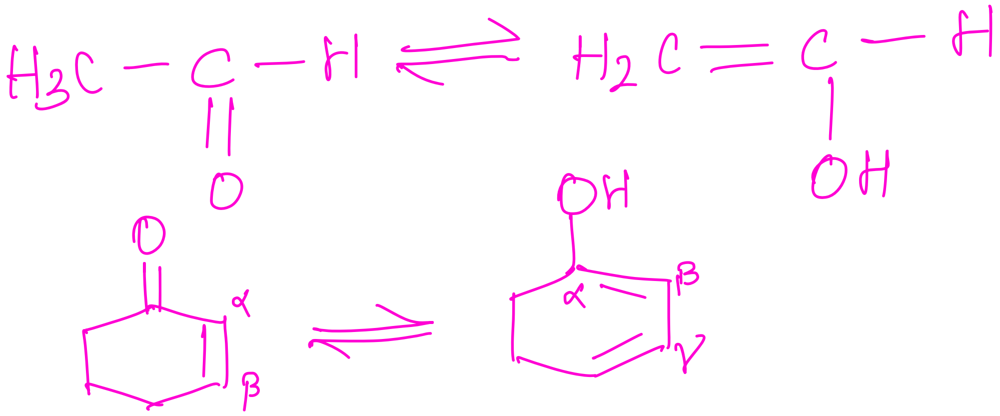
keto-enol tautomerism.

Conditions:

① Usually present in following functional groups.



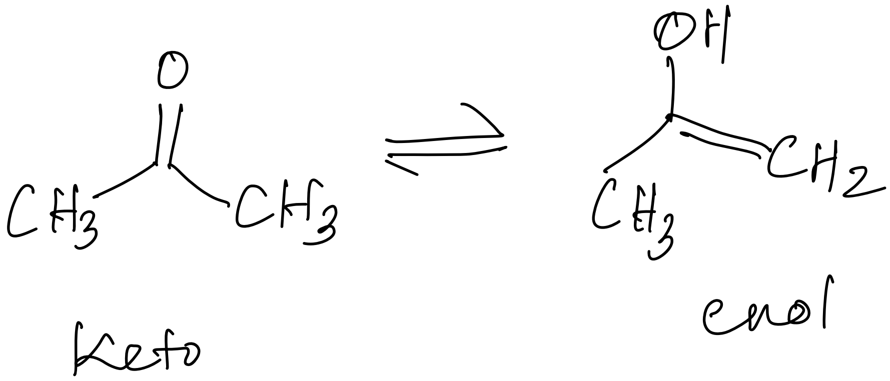
② At least one H-atom on the sp^3 hybridised α-C-atom



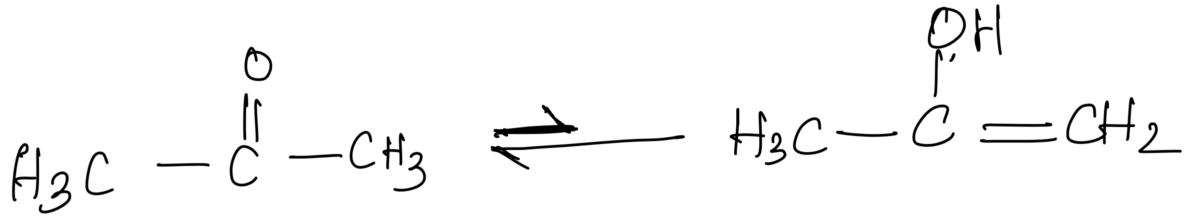
$$H_3C-\underset{\underset{O}{\|}}{C}-H \rightleftharpoons H_2C=\underset{\underset{OH}{|}}{C}-H$$

Keto-enol tautomerism

tautomerism between carbonyl Cpd containing α-H and its enol form



> Keto form of mono carbonyl cpd is more stable than its enol form



$$H_3C-\overset{\overset{O}{\|}}{C}-CH_3 \rightleftharpoons H_3C-\overset{\overset{OH}{|}}{C}=CH_2$$

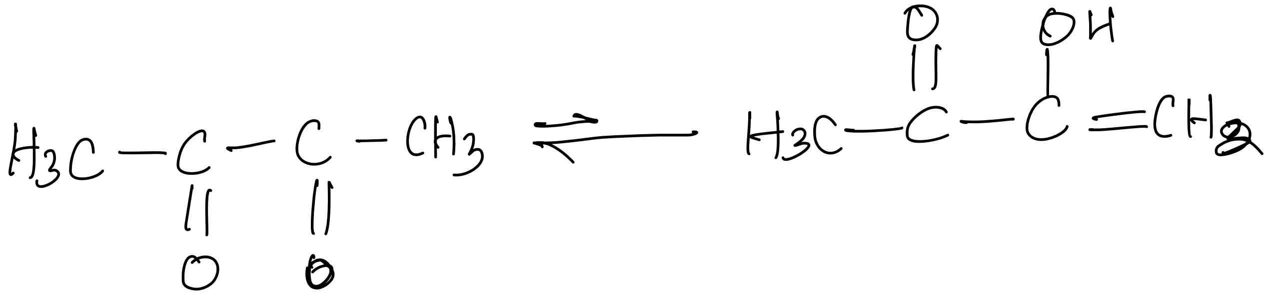
(>99% stable)

Stability of tautomers:

Keto form - ~1500 kJ/mol
(bond enthalpy)

Enol form - ~1452 kJ/mol

→ More stable (thermodynamically)



$$H_3C-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-CH_3 \rightleftharpoons H_3C-\overset{\overset{O}{\|}}{C}-\overset{\overset{OH}{|}}{C}=CH_2$$

more stable

Stability of Enol form:

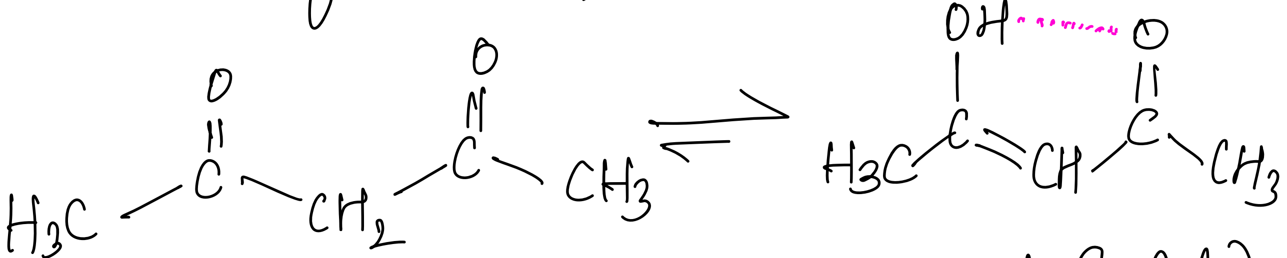
① − M Effect

② Resonance and hyperconjugation

③ Intramolecular H-bond.

$$\% \text{ Enol} \propto \frac{1}{\text{Polarity of Solvent}}$$

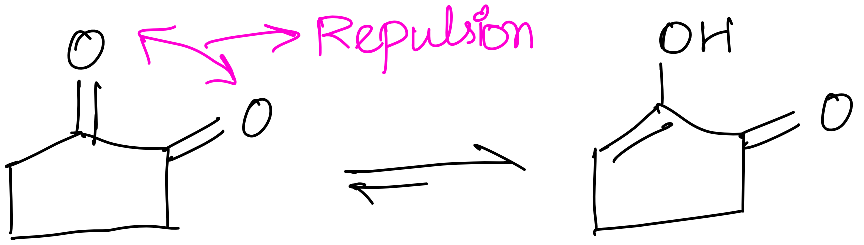
β-dicarbonyl cpds:



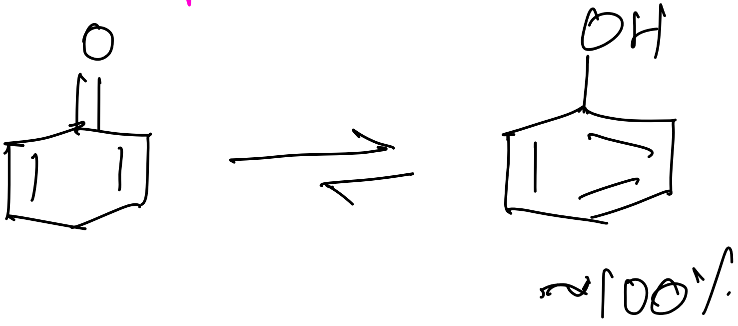
Enol (76%)

Stable due to H-bonding

Resonance Stabilised



Less stable due to repulsion



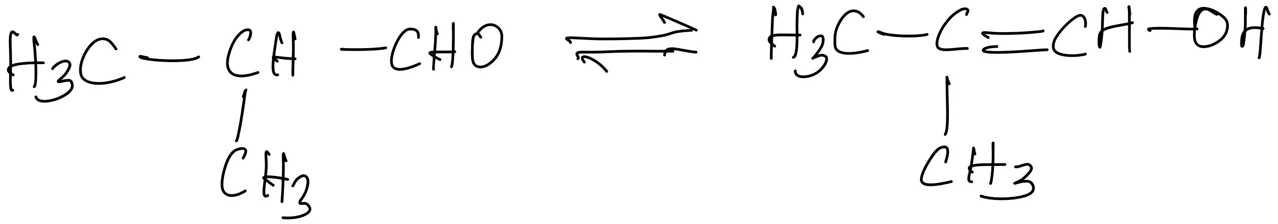
More stable due to aromaticity

Stability of alkene ↑

enol content ↑

$CH_3-CHO \rightleftharpoons H_2C=CH-OH$

$H_3C-CH_2-CHO \rightleftharpoons H_3C-HC=CH-OH$



$H_3C-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CHO \rightleftharpoons H_3C-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-OH$

% enol III > II > I

Order of % enol :

Aromatic > β-dicarbonyl > α-dicarbonyl > monocarbonyl

Examples of tautomers

$R_2\,CH-CR=NR \rightleftharpoons R_2C=CR-NH-R$

Imine Enamine

$CH_3-CH_2-NO \rightleftharpoons CH_3-CH=NOH$

Nitroso Oxime

$H_3C-CH_2-\overset{\oplus}{N}(=O)-O^{\ominus} \rightleftharpoons H_3C-CH=\overset{+}{N}(O^{\ominus})-OH$

Nitro Acinitro

Priority Order of Isomers

R > T > F > M > C > P

Ring Tauto Func. Met. Chain Posi

Degree of Unsaturation:

Sum of no. of π bonds & Rings in a cpd.

Let's take $C_aH_bX_cN_dO_e$

$$DOU = (a+1) - \left(\frac{b+c-d}{2}\right)$$

Ex:

C_6H_6O

$$DOU = (6+1) - \left(\frac{6+0-0}{2}\right)$$

$$= 7 - 3 = 4$$

C_6H_5I

$$DOU = 7 - 6/2 = 4$$

C_5H_9N

$$DOU = 6 - 8/2 = 2$$

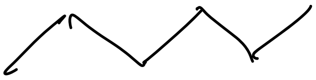
No. of Structural Isomers of

C_6H_{14}

DOU = 0

So, No ring or π bond only

Chain with no unsaturation.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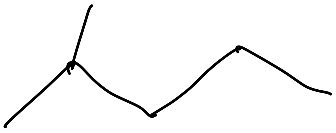
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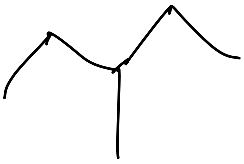

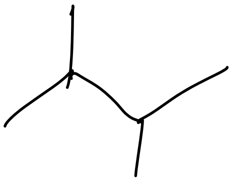
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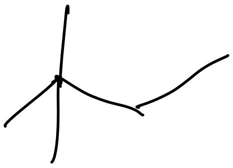
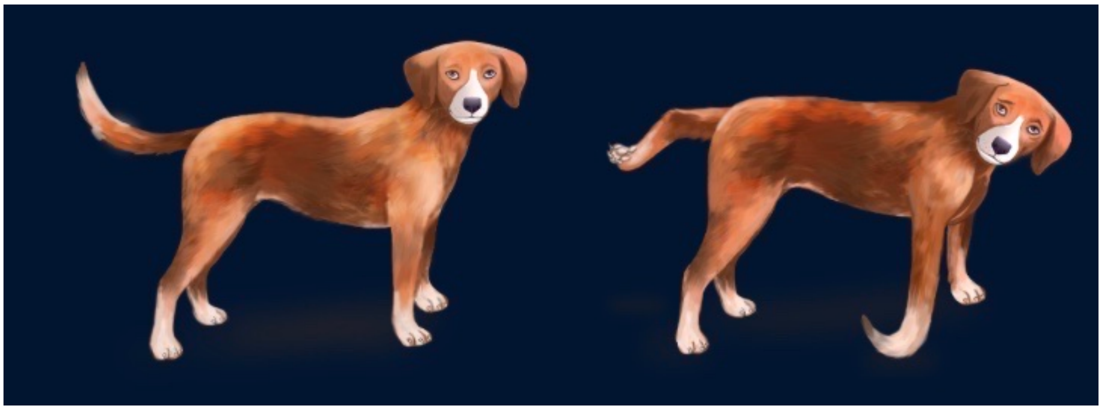


Stereoisomers:

Configurational Isomers:

> Spatial arrangement of atoms

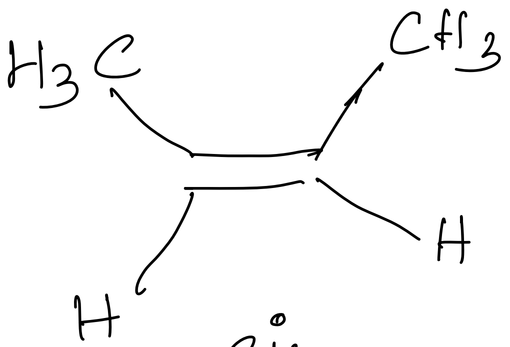
> Arises due to interconvertibility at R.T



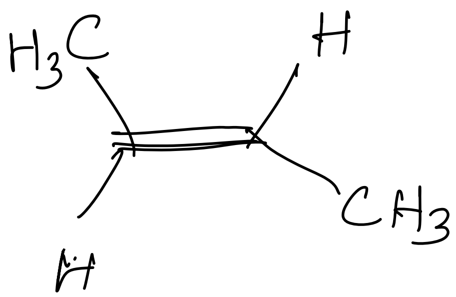
> Breaking & Making of bonds

Geometrical Isomerism!

Cis-trans Isomerison!



cis



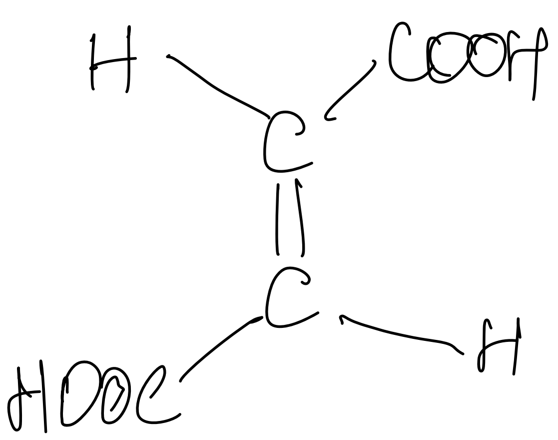
trans

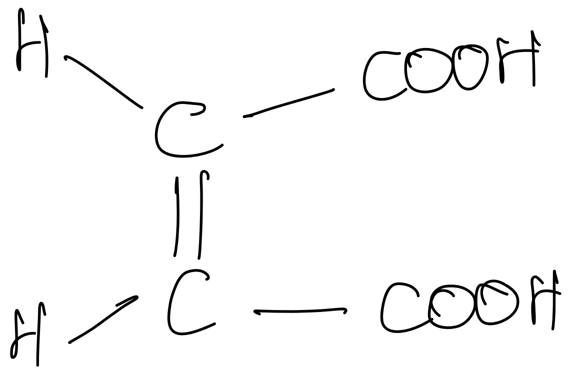
Same groups are on same side

⇒ cis

Same groups are on opposite side

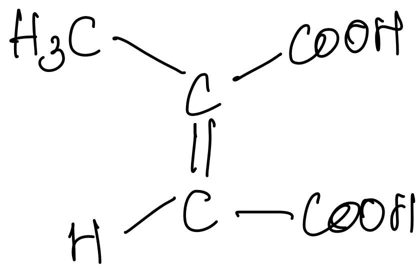
⇒ trans

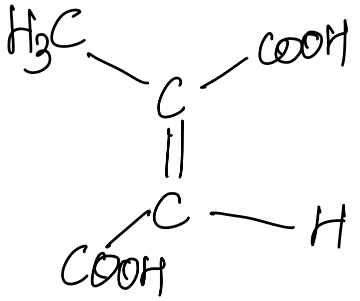




Fumaric acid (Trans)

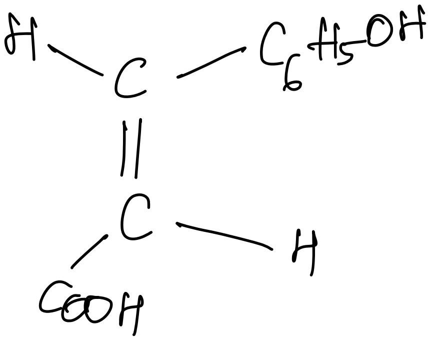
(maleic acid)
cis

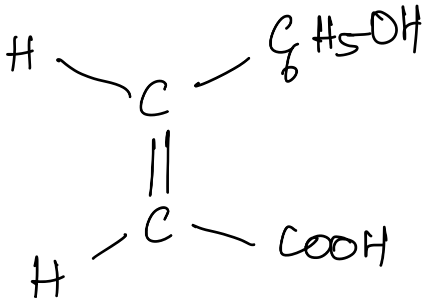




Citraconic acid

Mesaconic acid.

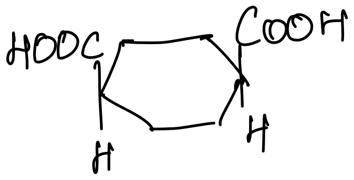




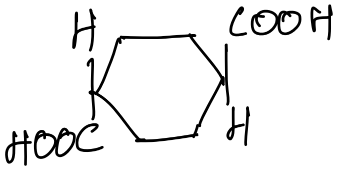
Coumaric acid

Coumarinic acid

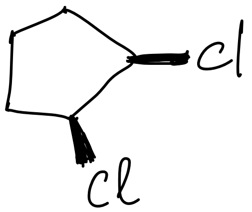
In Ring Systems :



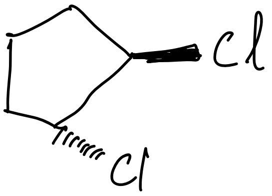
Cis



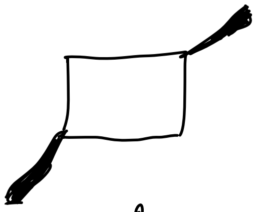
trans



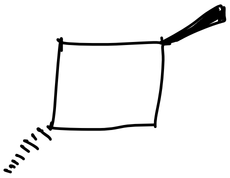
Cis



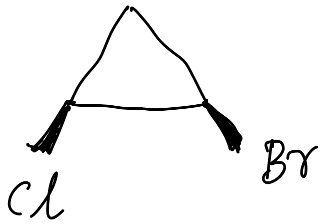
trans



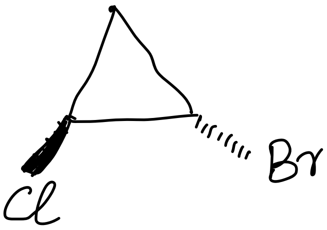
Cis



Trans

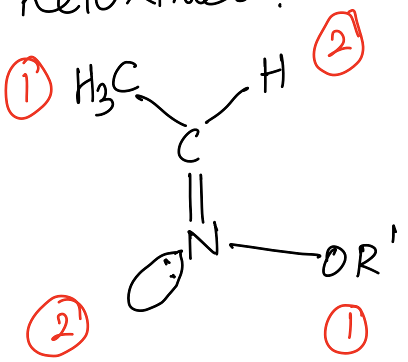


Cis

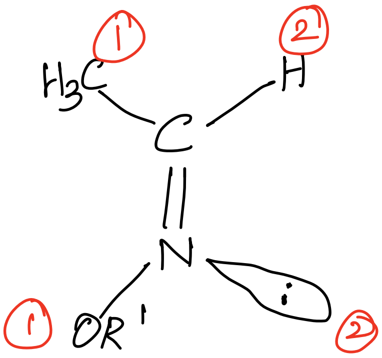


Trans

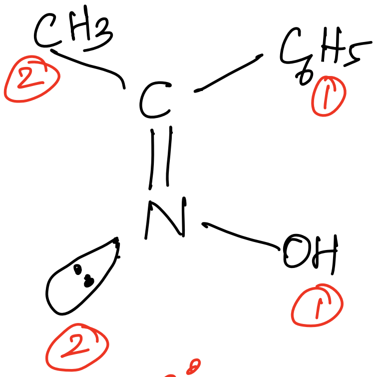
In Ketoxines :



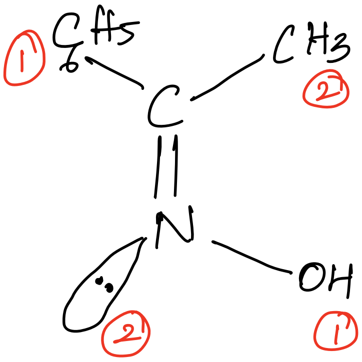
Trans (E)



cis (Z)



Cis



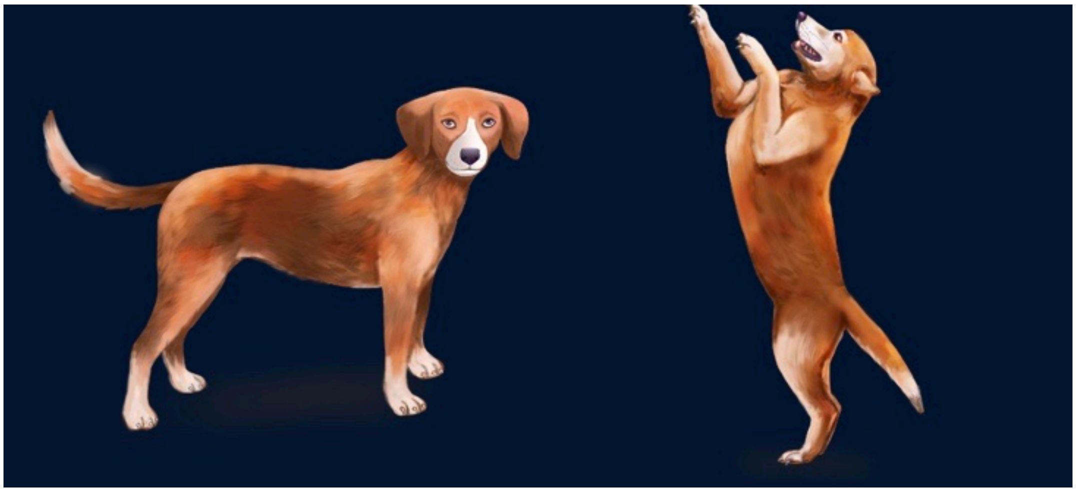
trans.

Conformational Isomers:

Infinite arrang. which arises due to the free rotn around C-C σ bond,

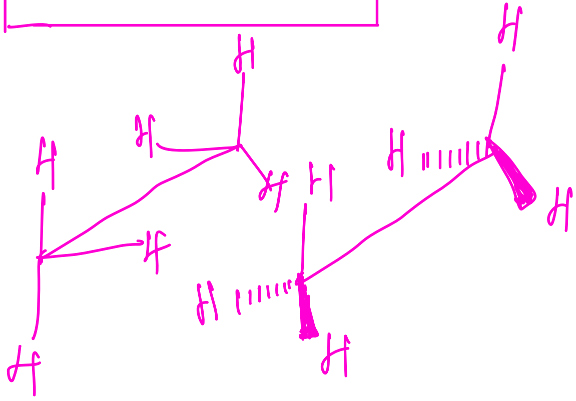
> Infinite Conformations are possible.

> Bond length and bond angle Same in all the Conformations.

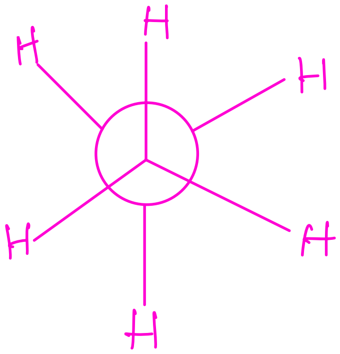


Projection formula:

Sawhorse

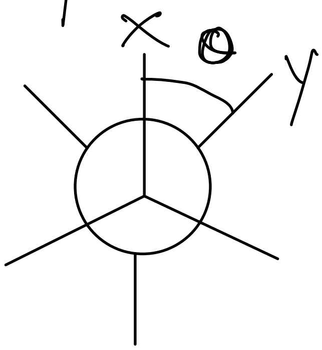


Newmann



Dihedral angle:

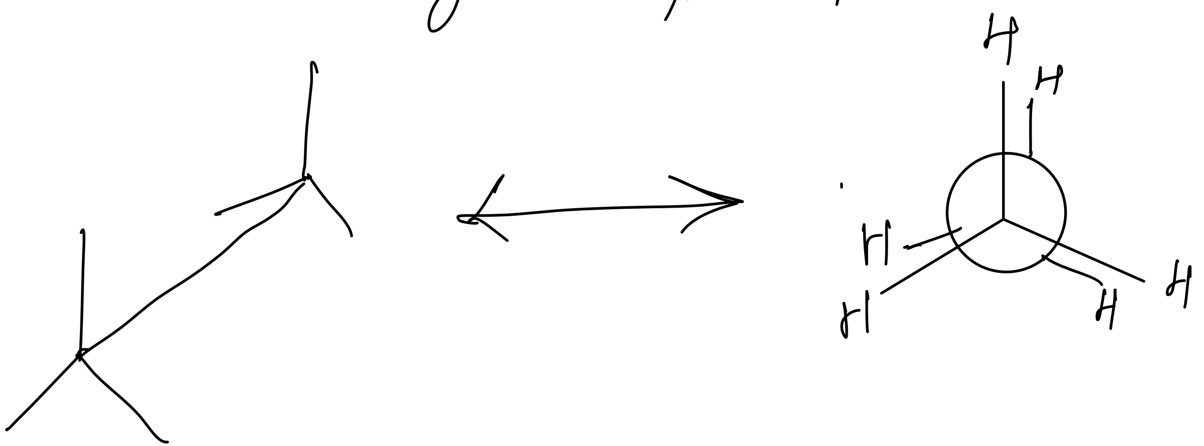
Angle between X C—C and Y C—C planes.



Conformations:

Eclipsed – directly opposite to each other

Dihedral angle 0°, 120°, 180°

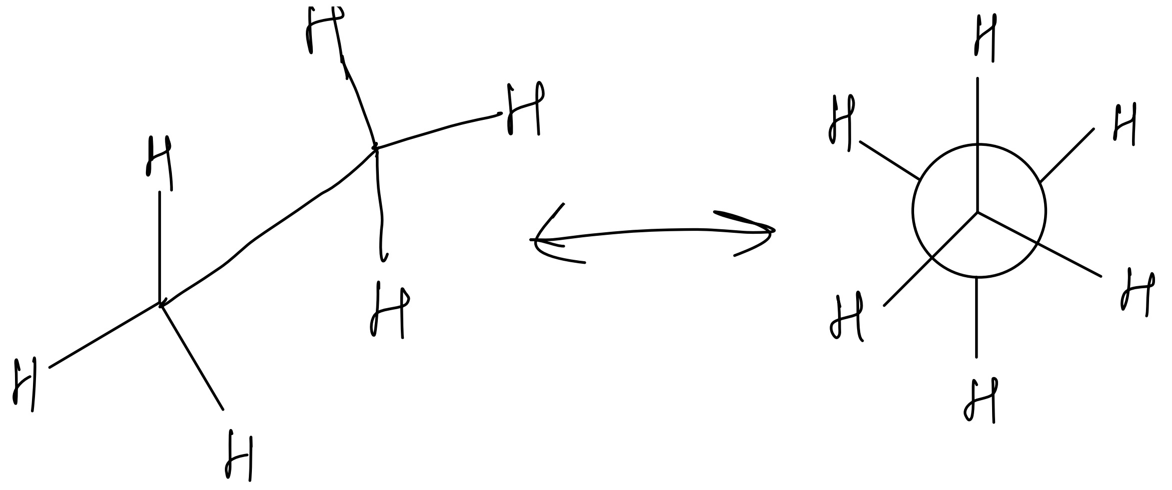


Sawhorse

Newmann

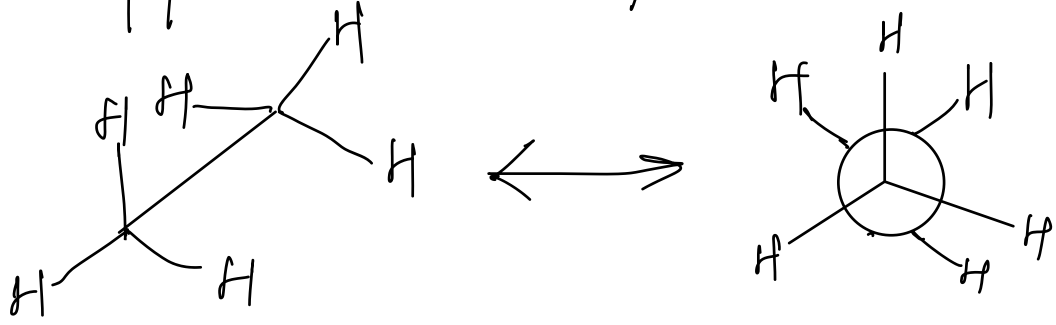
Staggered:

Dihedral angle between the bonds is 60°, 180°, 300°



Skew :

Conformn other than stagg. and eclipsed are skew.



Factors Affecting Stability of Conformers:

> <u>Angle strain</u>:

deviation from normal bond angles. only in cyclic structure

> <u>Torsional strain</u>:

1) Any deviation from staggered conformn

2) Also called 'pitzer strain' or Eclipsing strain.

3) Max. ~~for~~ for Eclipsed
Min for staggered.

<u>Vanderwaals Strain:</u>

> Non-bonded atom/groups that just touch each other ⇒ as far apart as the sum of their Vanderwaals radii

> If brought any closer they repel eachother

> Such crowding is accompanied by Vander waals Strain.

Conformational Energy:

> P.E dif. between most stable conformn and least stable conformn.

> $\boxed{G-CH_2-CH_2-G}$

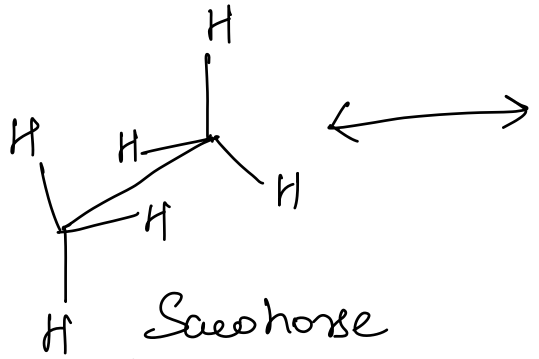
Size of G ↑ , Conformn. Energy ↑

Ethane - 12.5 KJ/mol

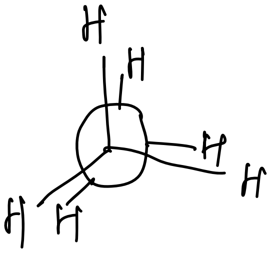
propane - 14.5 KJ/mol

Butane - 19 KJ/mol

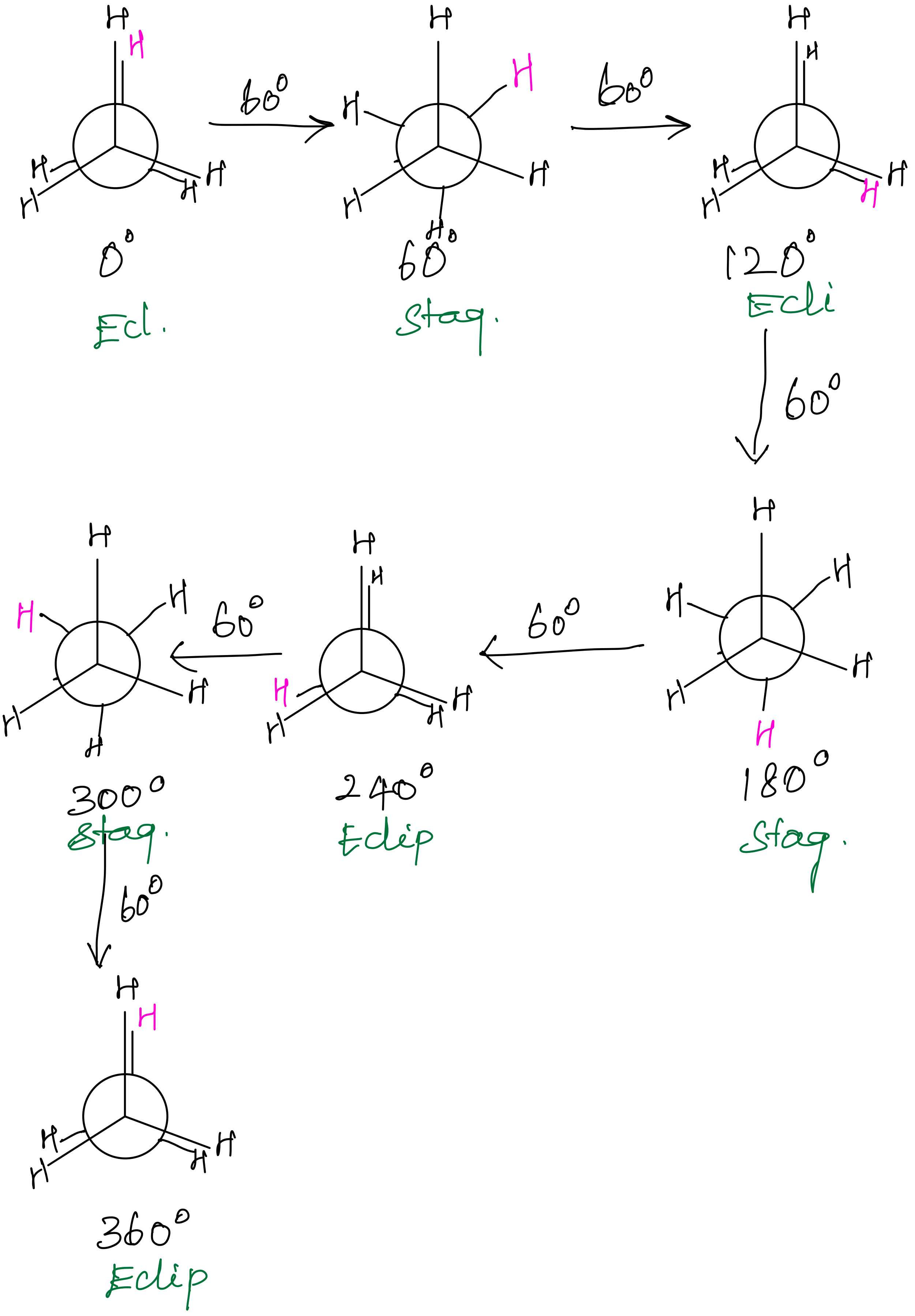
Ethane:

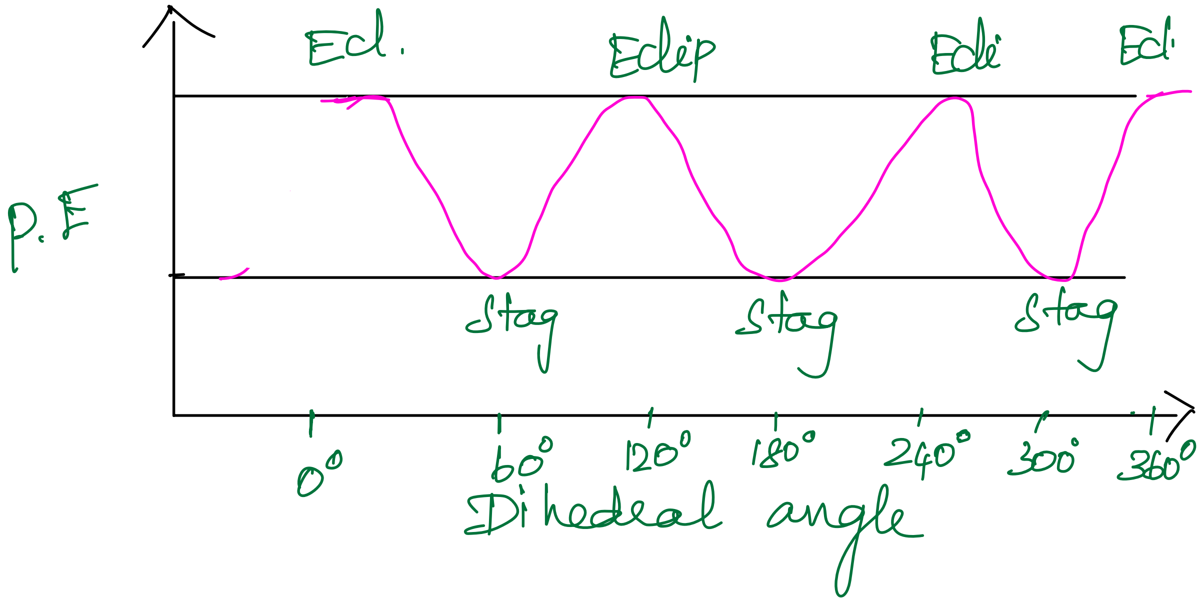


Sawhorse (Newmann)

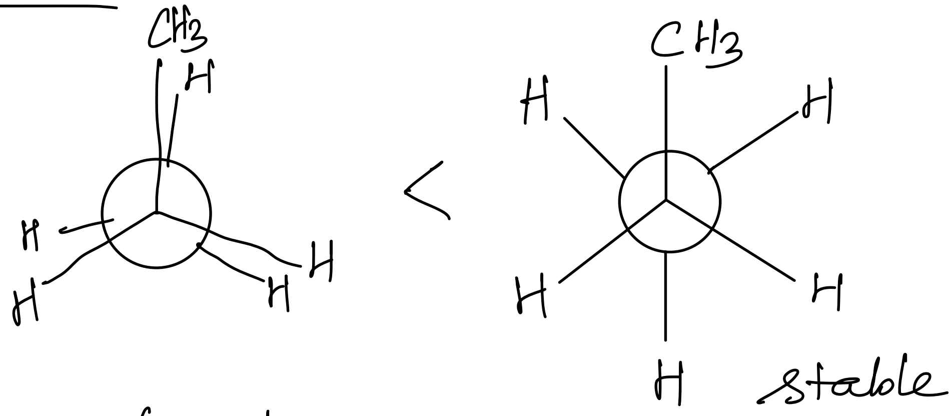


Eclipsed (Newmann)


H
0°
Ecl.
60°
60°
Stag.
60°
120°
Ecli
60°
180°
Stag.
60°
240°
Eclip
60°
300°
Stag.
60°
360°
Eclip



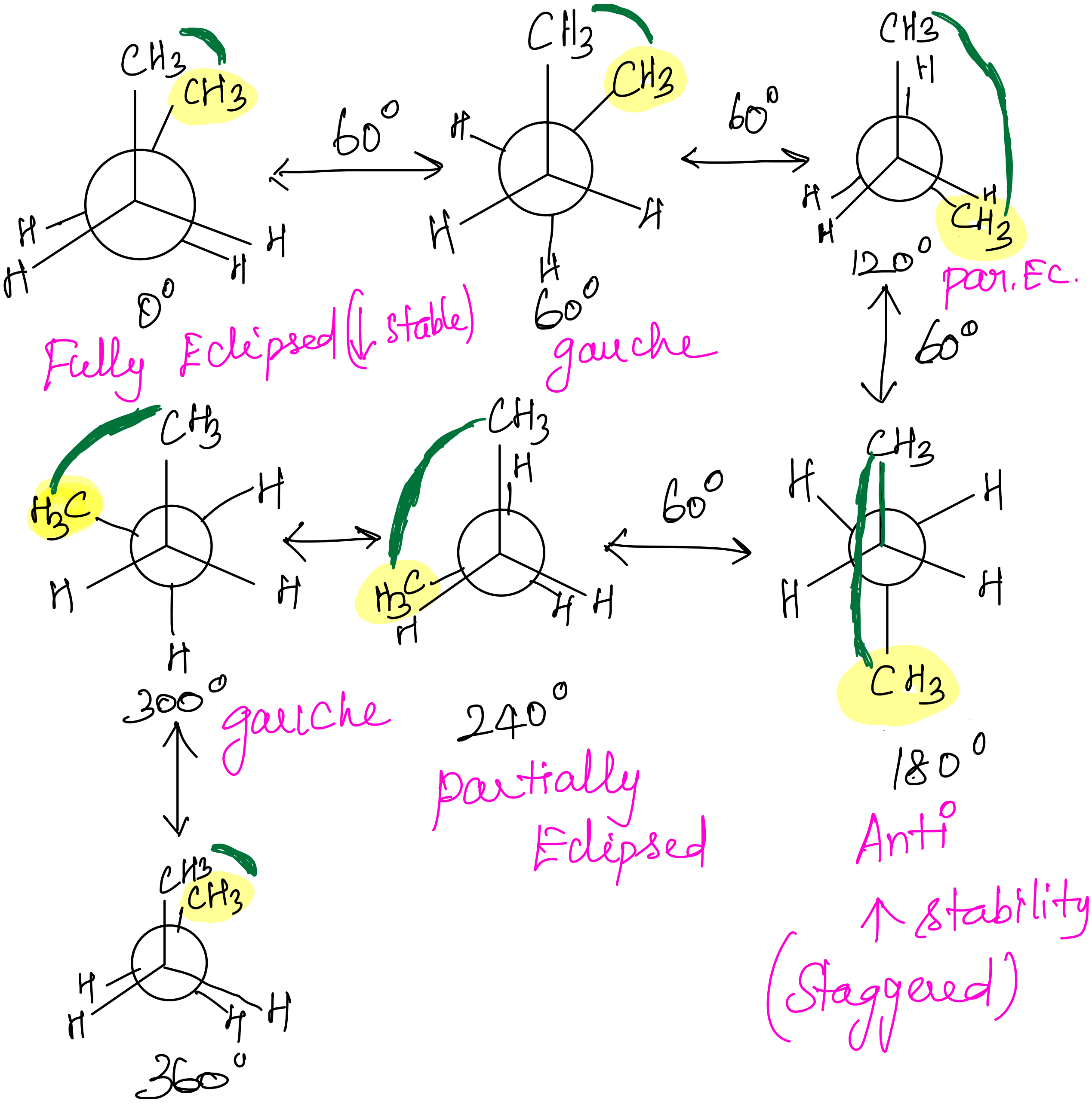
Propane :



$\theta = 0^\circ / 120^\circ / 240^\circ$
360°

$\theta = 60^\circ / 180^\circ / 300^\circ$

Butane :



Fully Eclipsed (↓ stable)

gauche

par. Ec.

gauche

partially Eclipsed

Anti

↑ stability

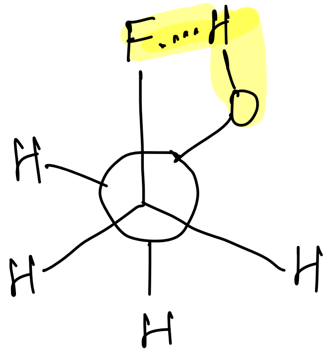
(Staggered)

Fully Eclipsed

Intramolecular H-bonding:

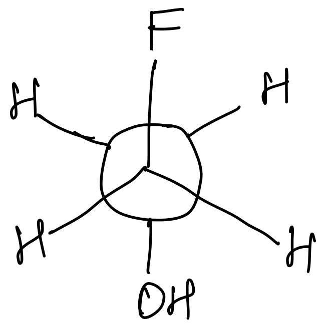
Incase of $G-CH_2-CH_2-OH$ the gauche form is more stable due to hydrogen bonding.

$-G \Rightarrow -OH, NH_2, -F, -NR_2, -NO_2, -COOH, -CHO$



Gauche

>



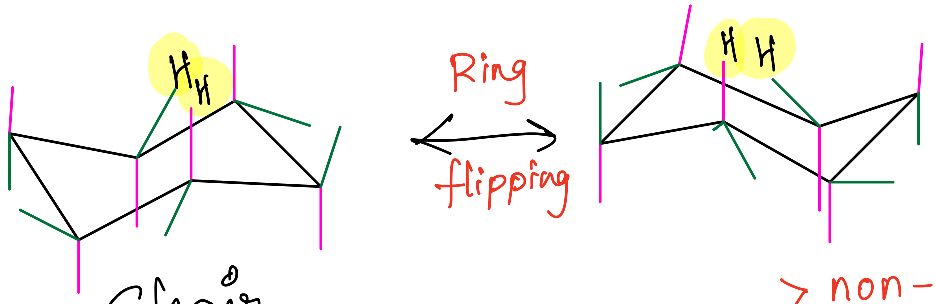
Anti

gauche > Anti > part. Eclip > Fully Eclispsed

Conformations of Cyclohexane:

Cyclohexane is stable than cyclopropane, cyclobutane and cyclopentane

- Chair (most stable)
- Boat
- Twist boat
- Half chair



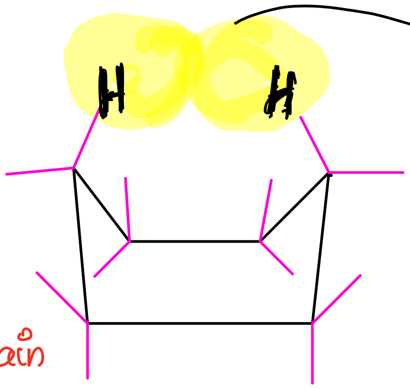
Chair

- non-planar
- Bond angle 111°
- Dihedral angle 56°
- More stable
- Min. Energy

—— ⇒ Equatorial

—— ⇒ Axial

Boat:



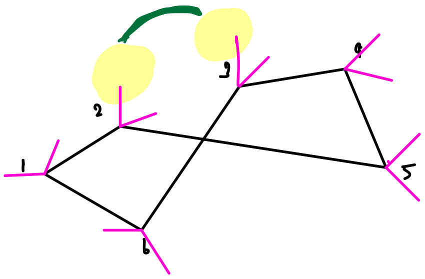
→ Flagpole interactions

⇓

Steric intrn between 1,4 Hydrogens cause instability.

- Torsional strain and Vandawaals strain.
- least stable

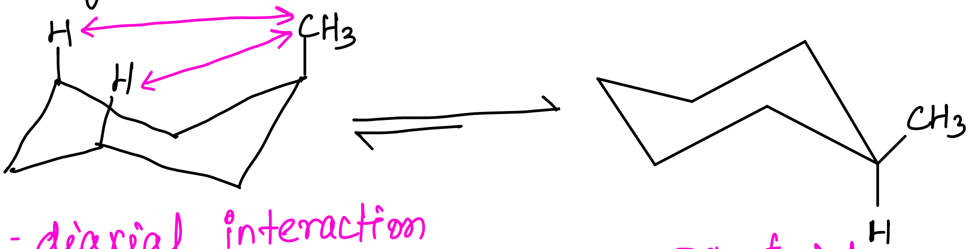
Twist boat:



- Vanderwaals strain, torsional strain.

Chair > Twist boat (22 kJ/mol) > Boat (28 kJ/mol) > Half chair (38 kJ/mol)

Substituted Cyclohexane:

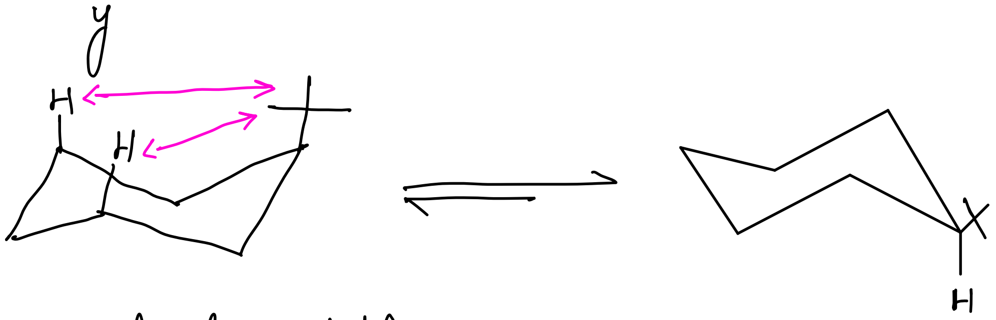


1,3-diaxial interaction
Less stable

equatorial
(more stable)

Axial and equitorial Conformers are diastereomers.

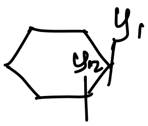
2)



axial less stable

Equitorial more stable

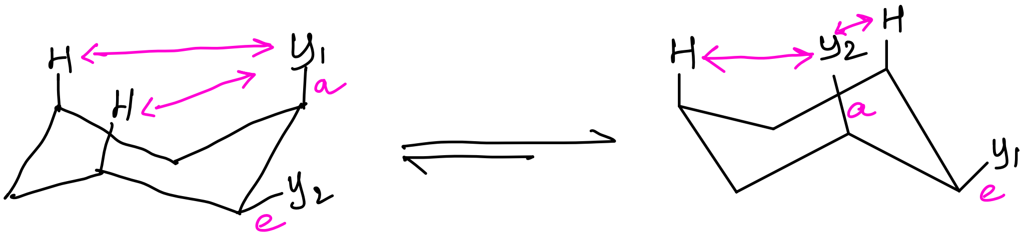
Disubstituted Cyclohexane:



ae

cis

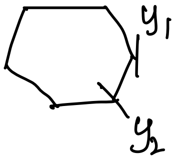
aa



a,e

1,3 diaxial interaction (unstable)

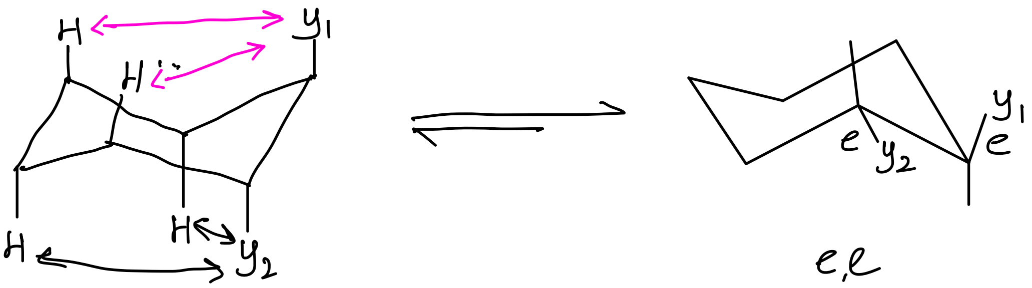
e,a



aa

Trans

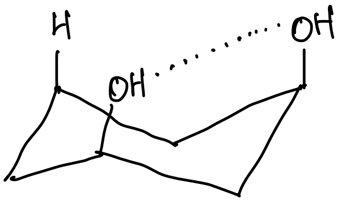
ee



a,a
Unstable.

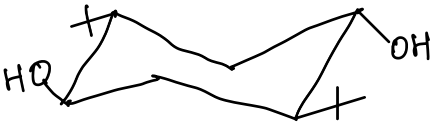
e,e
More stable

Exceptions:

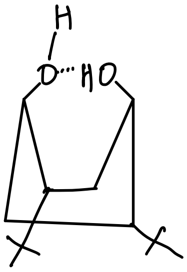


More stable (axial)
due to H-bonding.

2,5-tert-butyl cyclohexane 1,4-diol.

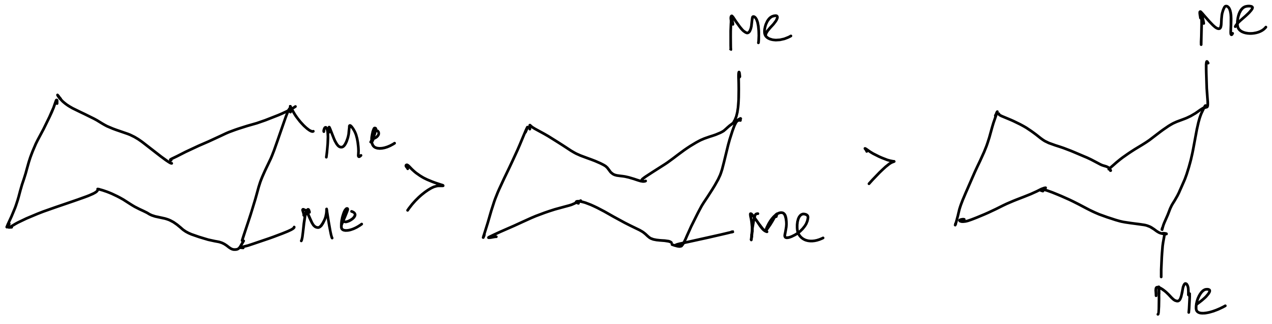


Less stable



More stable (boat)
Hydrogen bonding

Order of Stabilities:



Optical Isomerism:

Chiral:

An object that is non-Superimposable on its mirror image

⇒ property ⇒ Chirality

Achiral:

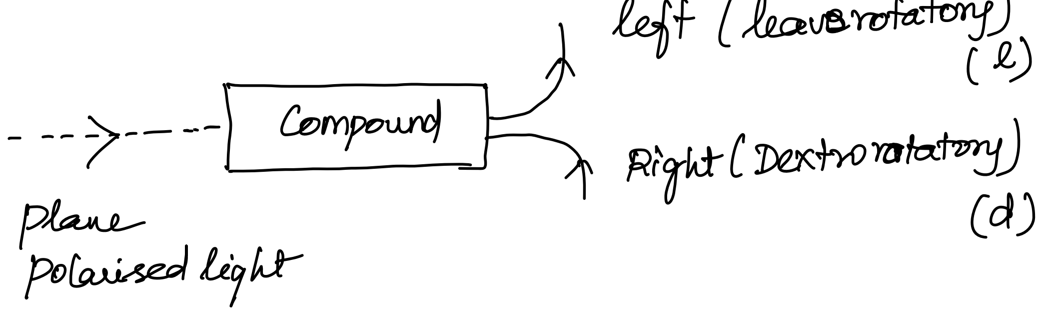
- > Lacks Chirality
- > Mirror images are Superimposable

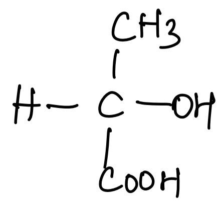
Asymmetric Carbon:

- > Carbon bonded to 4 diff groups
- > Stereogenic center / Assymmetric centre

Optical Activity:

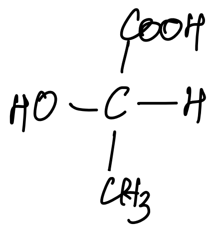
The Substance which can rotate plane polarised light ⇒ op. active





$$\begin{array}{ccc} & CH_3 & \\ & | & \\ H- & C & -OH \\ & | & \\ & COOH & \end{array}$$

d-lactic acid



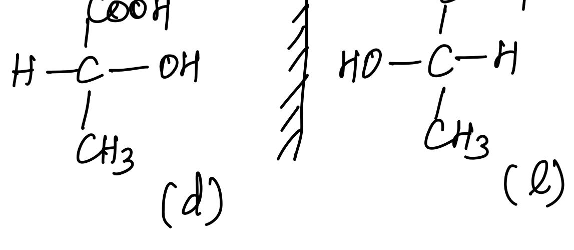
$$\begin{array}{ccc} & COOH & \\ & | & \\ HO- & C & -H \\ & | & \\ & CH_3 & \end{array}$$

l-lactic acid.

- Cpds shows op. activity exhibits op. isomerism
- pair of d, l isomers ⇒ optical isomers.

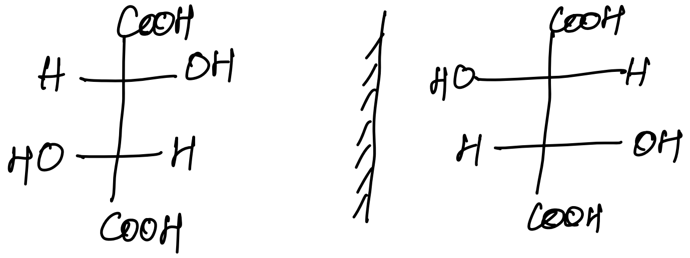
Enantiomers:

Non-Superimposable mirror images.



$$\begin{array}{ccc} & COOH & \\ & | & \\ H- & C & -OH \\ & | & \\ & CH_3 & \end{array} \qquad \begin{array}{ccc} & COOH & \\ & | & \\ HO- & C & -H \\ & | & \\ & CH_3 & \end{array}$$

(d) (l)



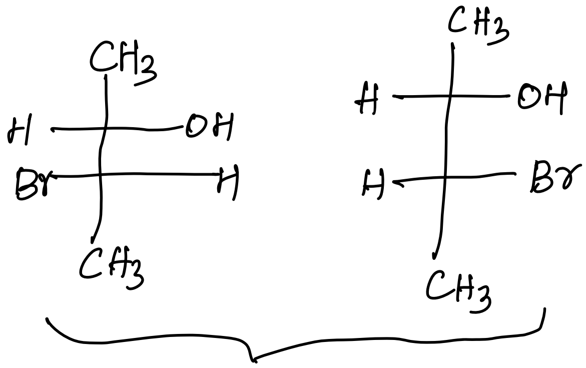
d-tartaric acid   l-tartaric acid

- Always op. active. Seperation done by resolution method.

Diastereomers:

They are non-superimposable, non-mirror images.

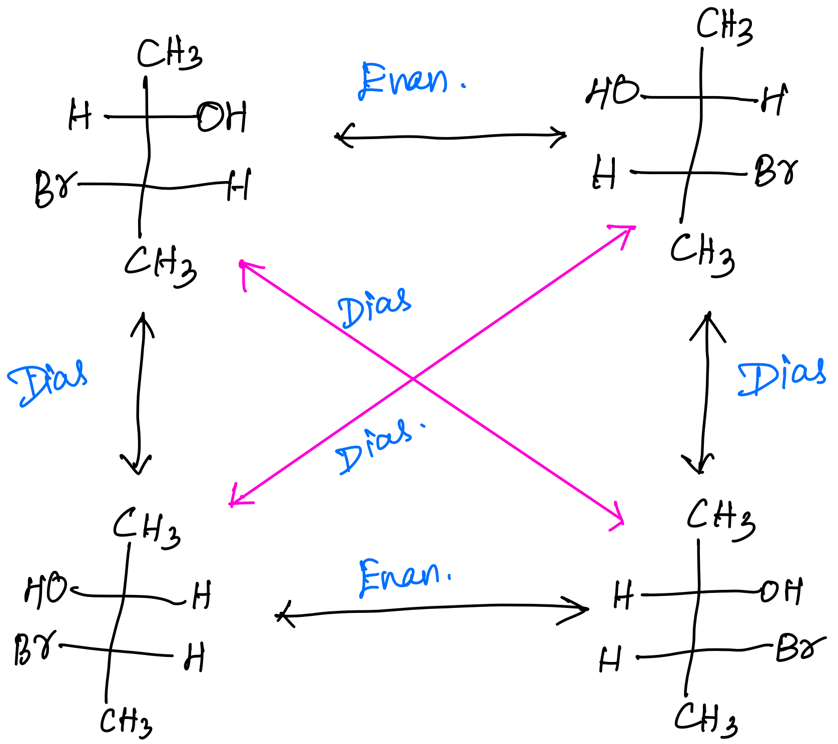
3-bromo 2-butanol.

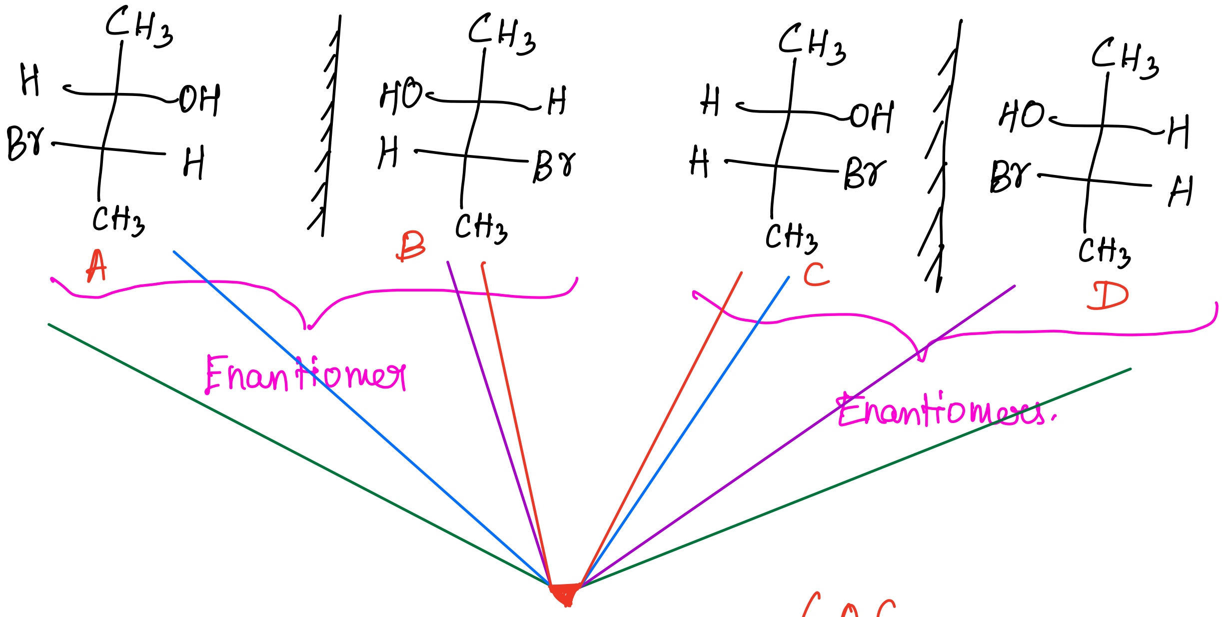


Diastereomers.

- Can be seperated by physical methods like, frac. distillation, crystallisation.
- May or may not be optically active.

Eg:



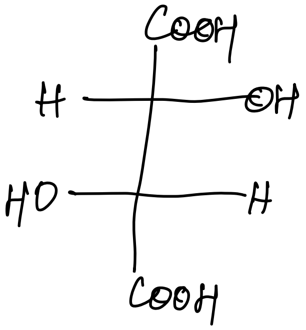


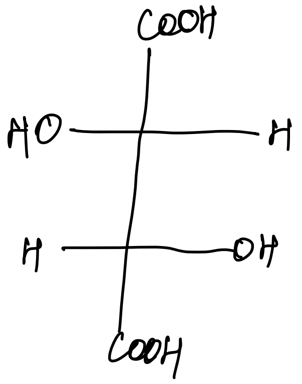
Diastereomers. (A, C
A, D
B, C
B, D)

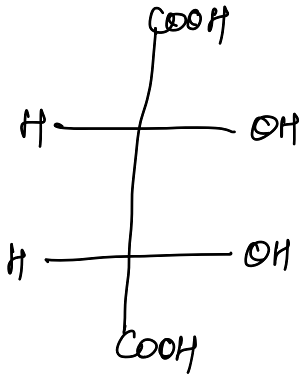
Meso compounds:

> Have plane of Symmetry. ⇒ Optically inactive

Eg:







Meso compound.
(op. inactive)
Internal compensation

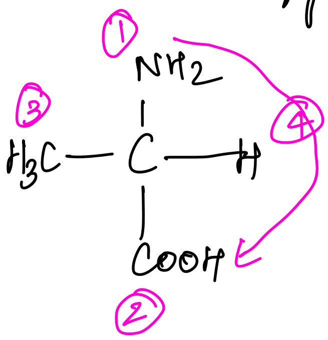
Racemic Mixture: (±)

Mixture of equal parts of d and l isomers ⇒ Optical inactive

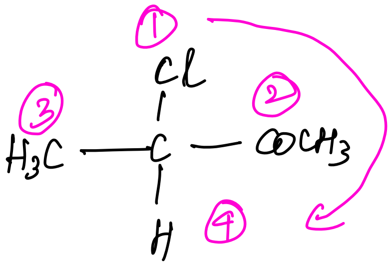
Rotn cancelled by each other ⇒ external Compensation

R, S Notation : CIP Rule :

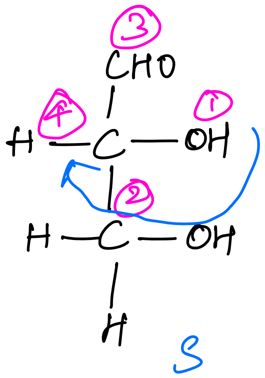
- Priority to Atomic number (first fails go with next one)
- A doubly or triply bonded atom equal to two or three such atoms.
- Clockwise – 'R' Anticlockwise – S
- Least priority grp is horizontal invert the config. R → S S → R



R Horizontal 'H'
So 'S'

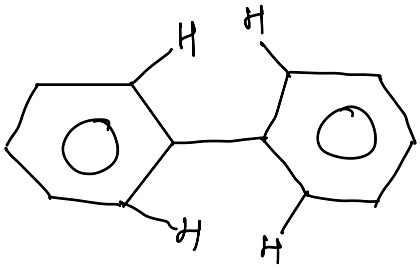


R



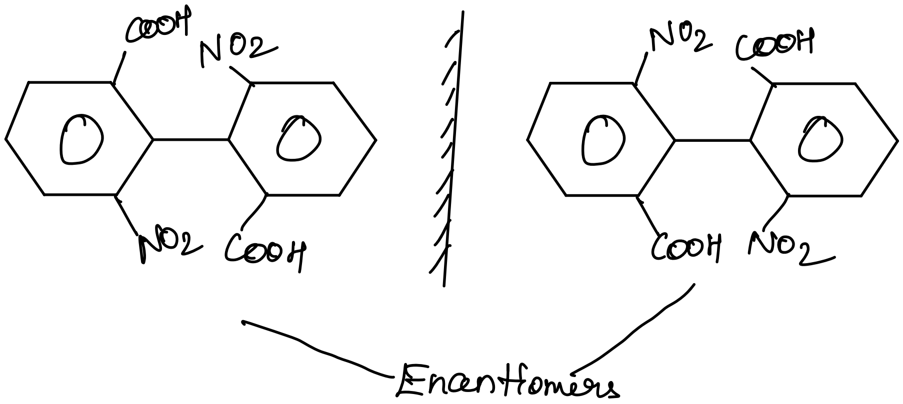
S

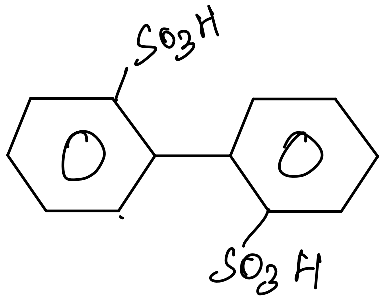
Biphenyls :

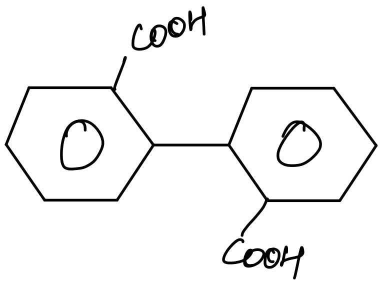


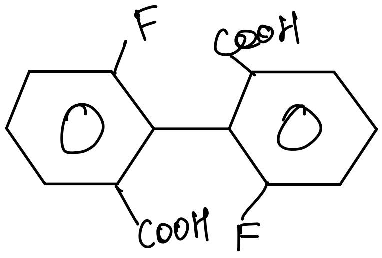
- Bulky grp are subs. in ortho position rings become perpendicular to each other
- Optically active

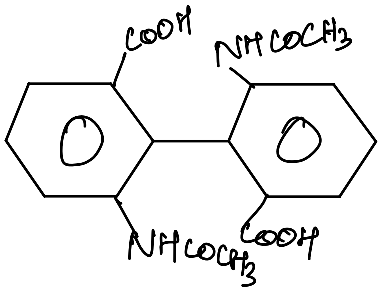
Opt. isomerism due to restricted rotation is called atropisomerism

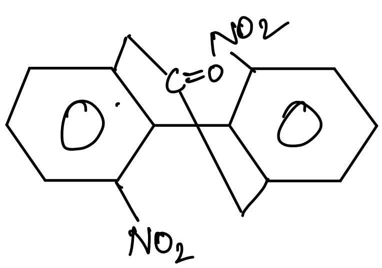


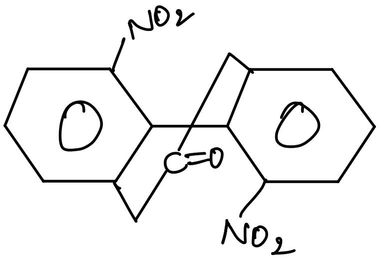




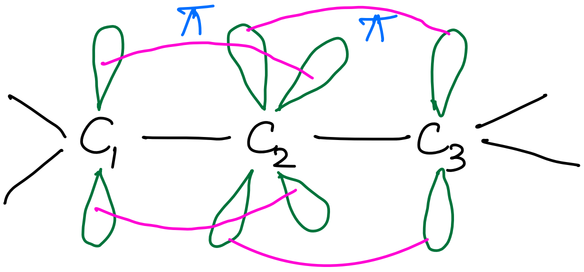


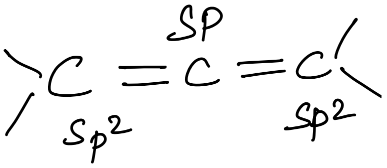






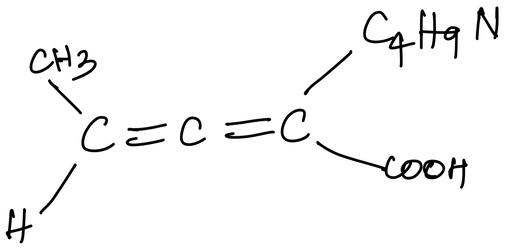
Stereochemistry of Allenes

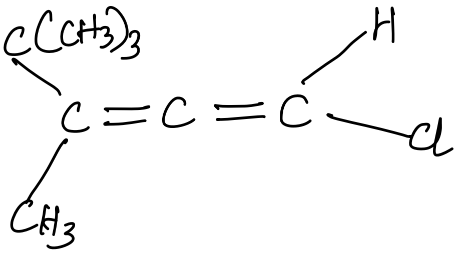


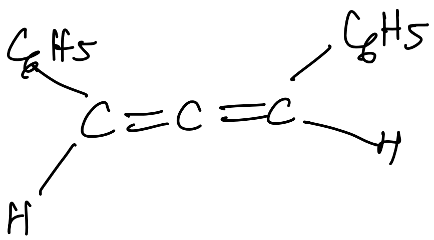


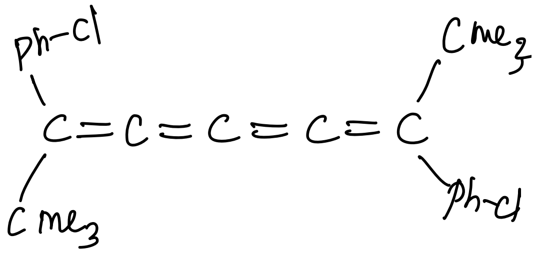
- One π-plane is perpendicular to another π-plane ⇒ No Centre of Symmetry / plane of symmetry.

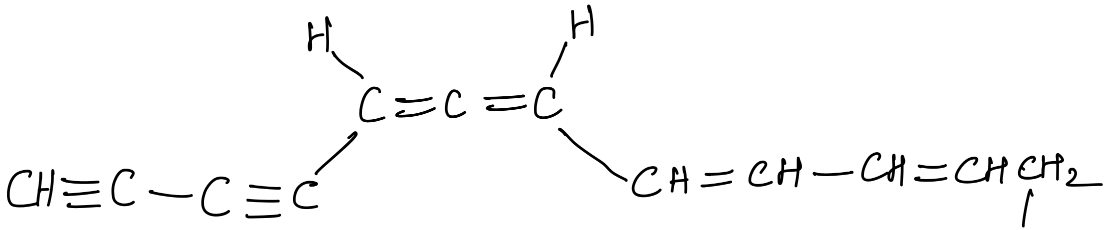
Ex!





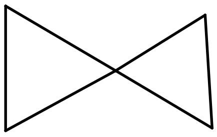




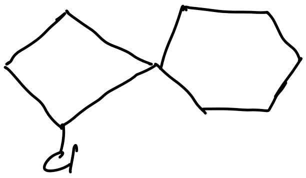


Mycomycin (antibiotic)

Spirans: ⇒ Optically active like allenes.



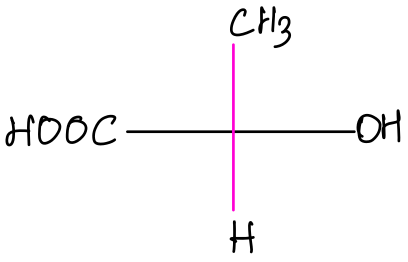
Spiro[2,2]-pentane



1-Chlorospiro[5,3]nonane

Projection formula:

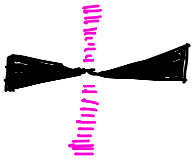
Fischer projection



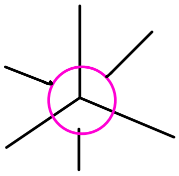
— behind the plane.

— above the plane.

≡



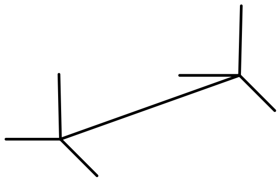
Newmann Projection:



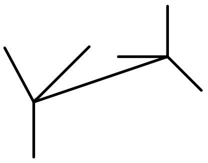
• — Above the plane.

○ — below the p

Sawhorse projection:

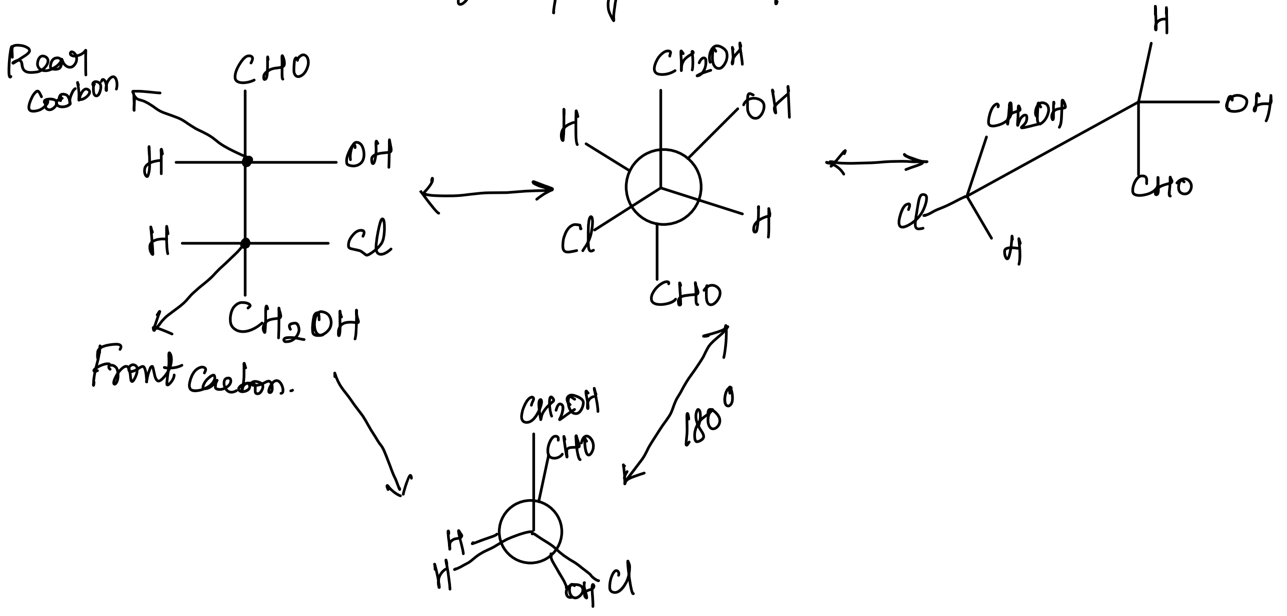


Eclipsed



Staggered.

Interconversion of projection formula:



Ex: 2