

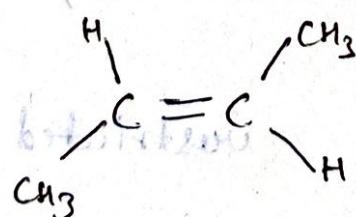
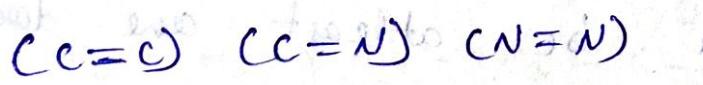
## Geometrical isomerism

Unit - II

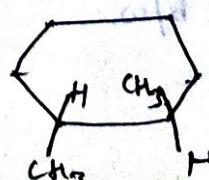
- \* The isomerism which arises due to restricted or frozen rotation about a bond in a molecule is ~~is~~ ~~as~~ geometrical isomerism.
- \* The rotation either about a double bond or about a single bond or in a cyclic compound can be seen.

- \* Geometrical isomerism is exhibited by variety of compounds like —

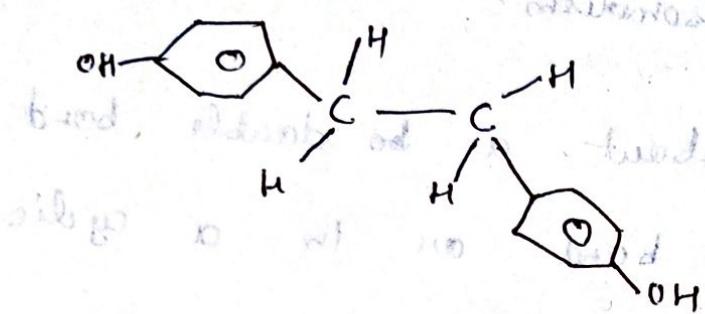
- Compound containing a double bond



- Compound containing cyclic structure, homocyclic or heterocyclic.



-II compound having restricted rotation about a single bond due to steric hindrance in biphenyl compound.



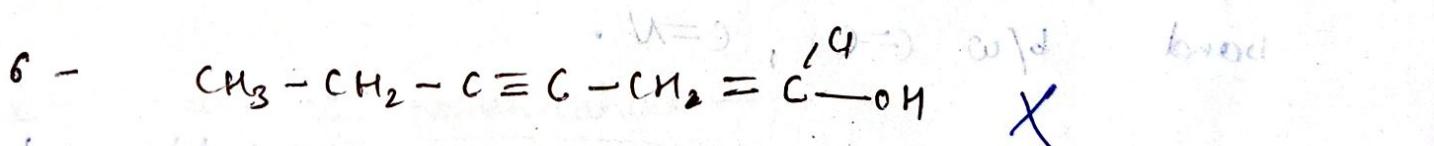
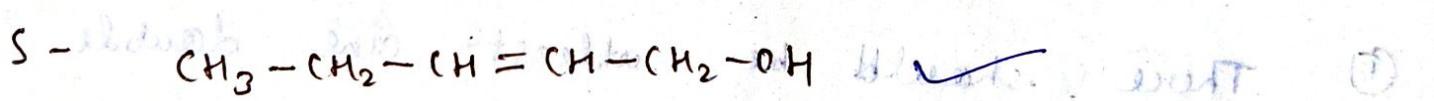
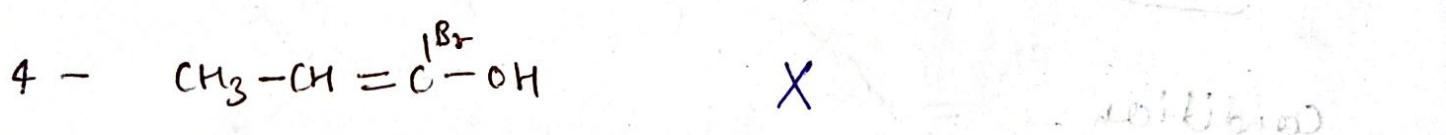
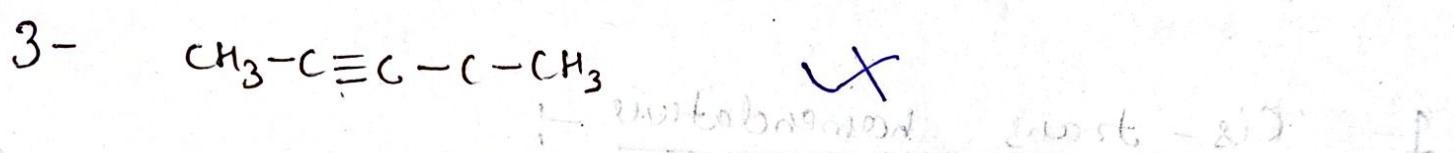
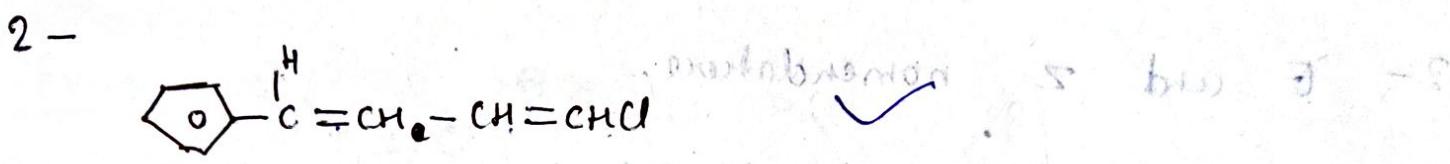
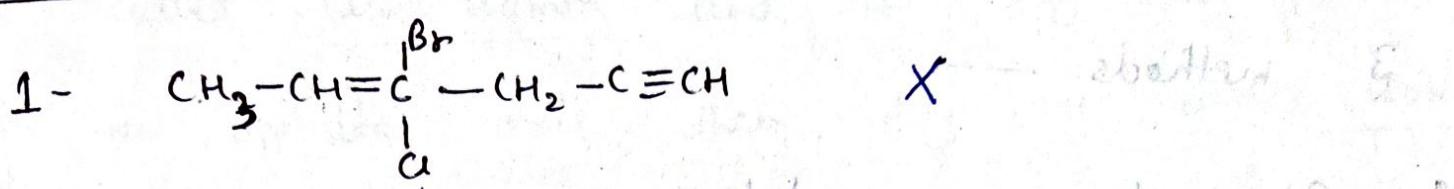
### Condition for geometrical isomerism

A compound will show geometrical isomerism if it fulfills following 3 conditions -

- 1- There should be (be) at least one double bond b/w carbon and carbon, carbon and nitrogen.
- 2- There should be / restricted rotation in double bond.
- 3- There should be at least one similar group b/w both double bonded carbon.

Q-3 Identify those compound which show geometrical isomerism.

A-3



## Nomenclature of geometrical isomerism

Geometrical isomers can be nomenclature by

3 methods →

1- Cis - trans nomenclature.

2- E and Z nomenclature.

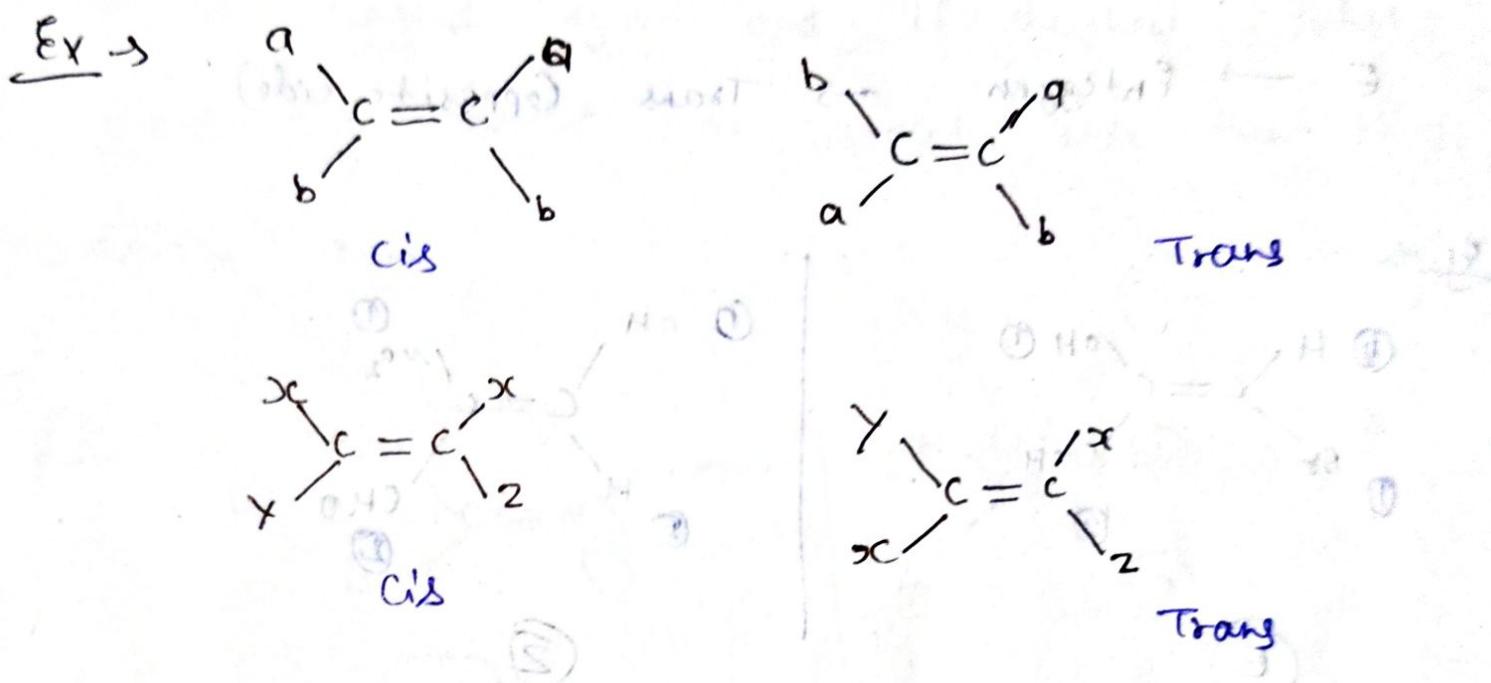
3- Syn and anti nomenclature.

1- Cis - trans nomenclature - I

Condition -

- ① There should be atleast one double bond b/w  $\text{C}=\text{C}$ ,  $\text{C}=\text{N}$ .
- ② There should be restricted rotation in double bond.
- ③ There should be atleast one similar group b/w both double bonded carbon.

If the similar atom or group is present on the same axis on both carbon then it is called cis isomer and if they are present on opposite axis then they are trans isomer.



## 2- E and Z nomenclature -

Condition -

- ① There should be atleast one double bond b/w carbon and C, and N or N and N.
- ② Four atoms or group which are held with both carbon should be different.

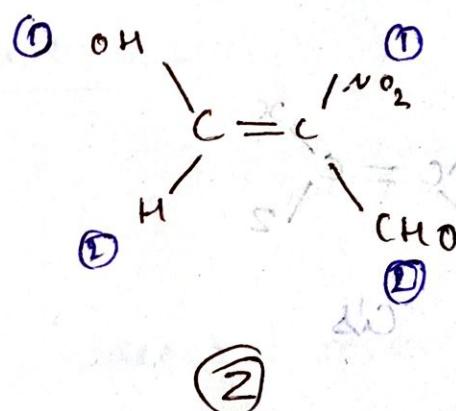
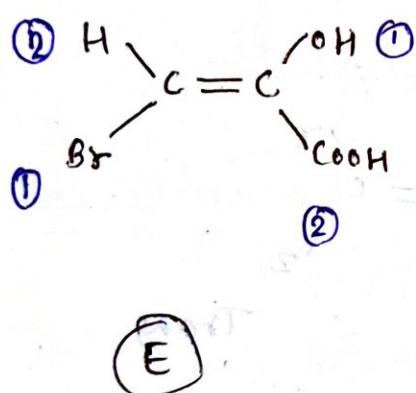
(iii) There should be restriction in rotation.

E and Z is derived from two German words —

Z → zusammen → Cis (same side)

E → Entgegen → Trans (opposite side)

e.g. →



### 3- Syn - Anti nomenclature -

\* This kind of isomerism is shown by those compound which have atleast one  $C=N$  or  $N=N$ .

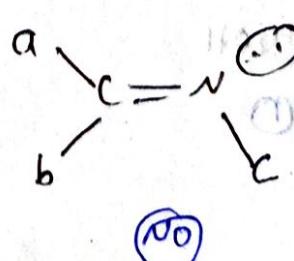
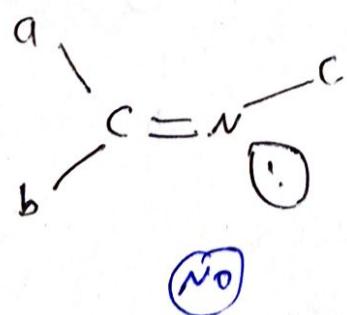
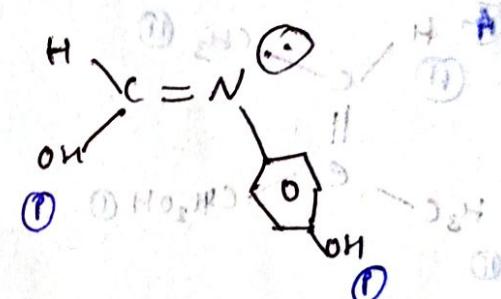
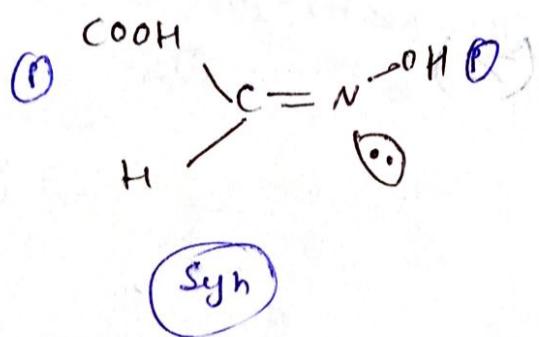
\* It is of two types —

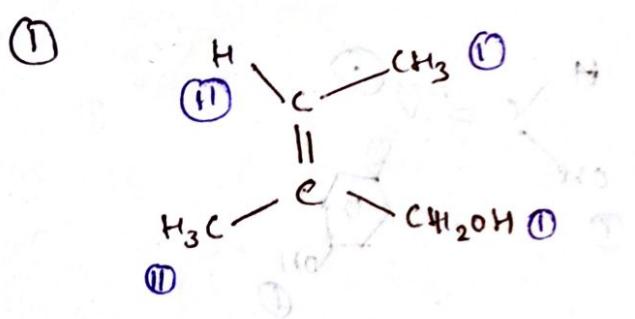
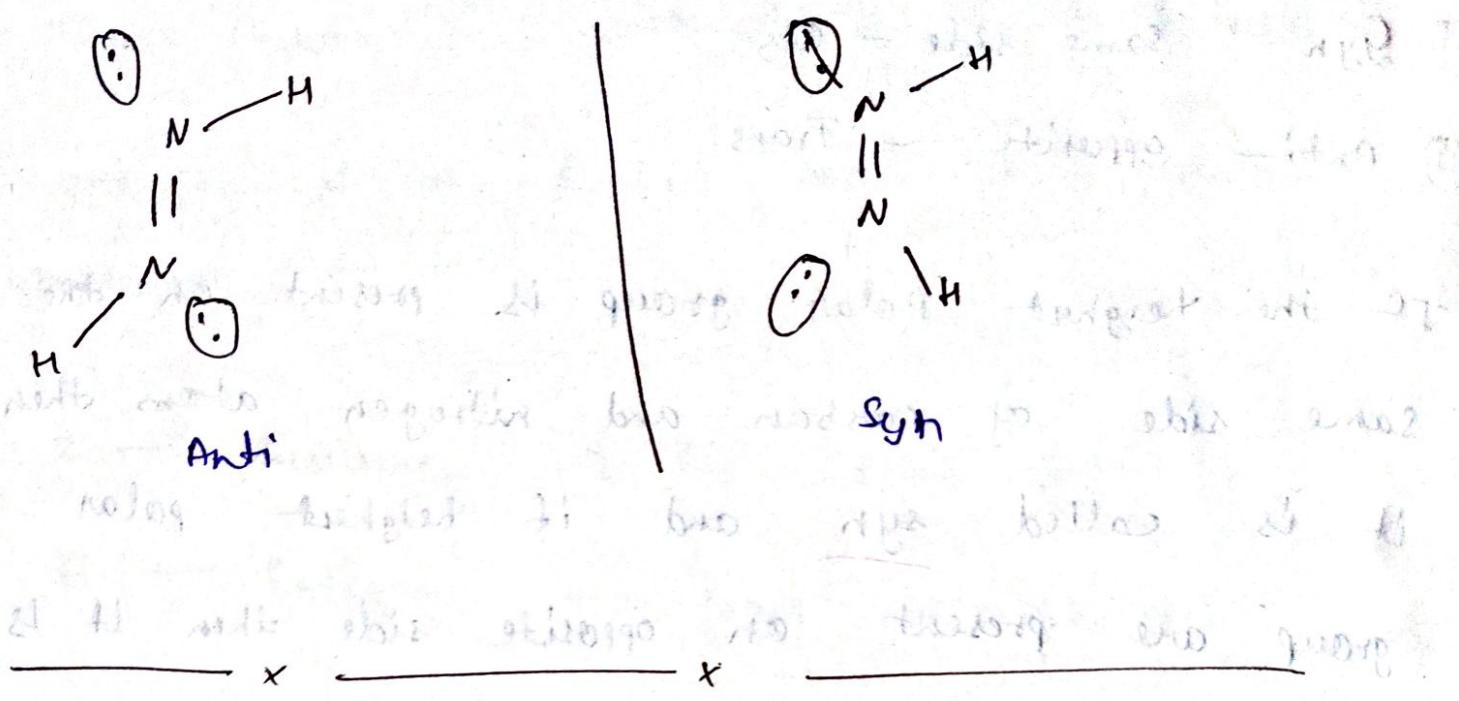
① Gyn - same side - Cl's

② Anti - opposite - Trans.

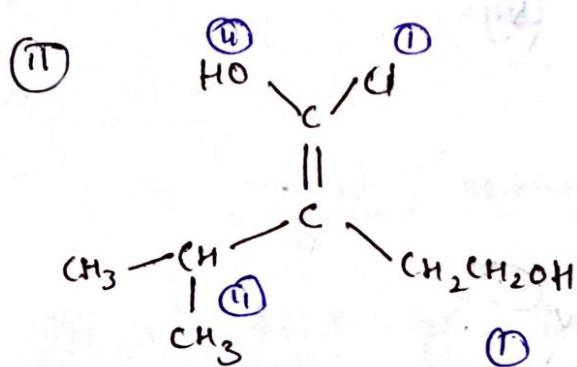
If the highest polar group is present on the same side of carbon and nitrogen atom then it is called syn and if highest polar group are present on opposite side then it is called anti.

Ex - 1

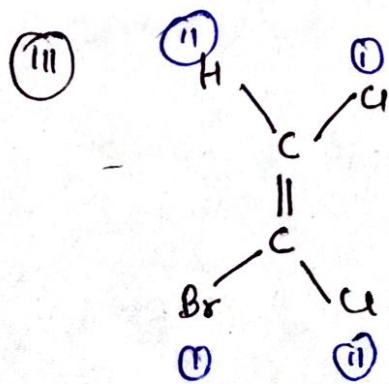




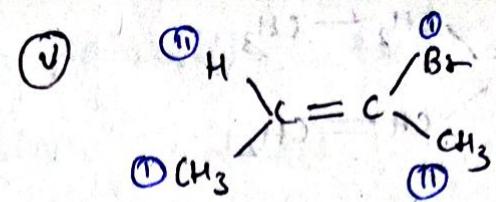
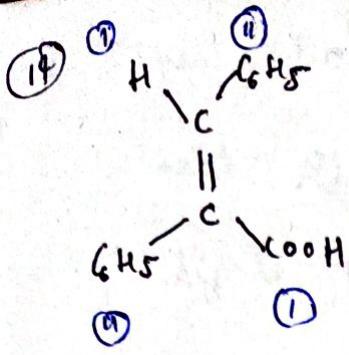
(Z)



(Z)

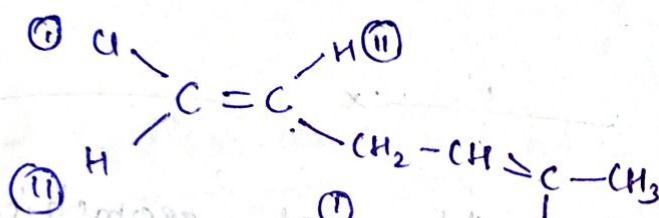
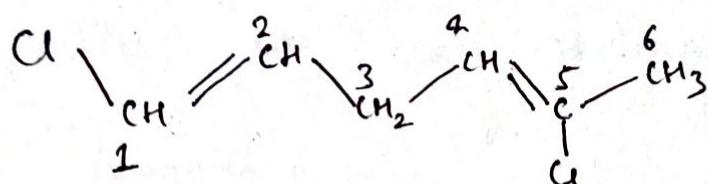


(E)

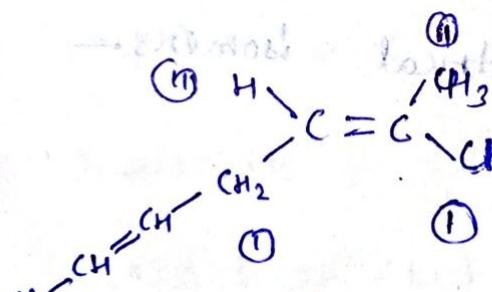


(E)

(E)



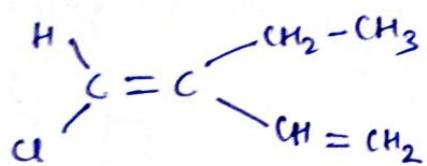
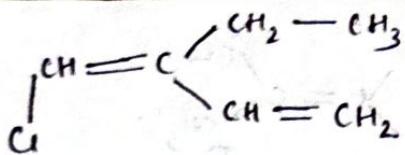
1E



4Z

(1E, 4Z)

(vii)



### Determination of configuration of geometrical isomers

There are a number of methods to determine the configuration of geometrical isomers.

- 1- Physical method.
- 2- Cyclisation method.
- 3- Conversion method.

#### 1- Physical method -

The melting point and intensity of absorption of cis isomer are lower than trans isomer.

- \* The boiling point, solubility, heat of combustion, heat of hydrogenation, density, refractive index, dipole moment and dissociation constant of cis isomer are greater than trans isomer.
- \* By the comparison of above these physical properties we can determine the configuration of isomers.

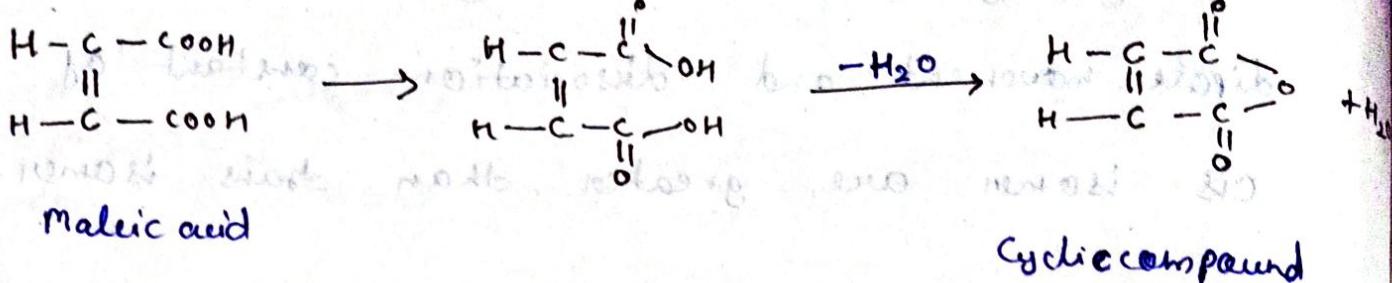
## 2- Cyclisation method -

Intermolecular rxn

are more likely to occur if the closer together are the reacting groups in the molecules ; cis isomer undergoes the cyclisation reaction but the trans isomer does not go for cyclisation.

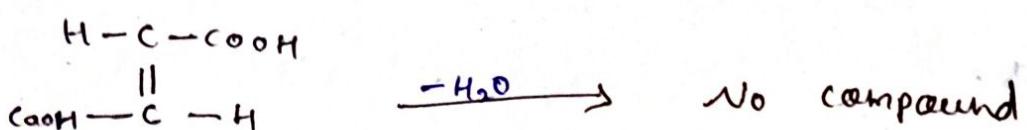
Ex -> Maleic acid after dehydration gives a cyclic compound maleic anhydride but fumaric acid do not gives dehydration rxn so maleic acid is

cis isomer and fumaric acid is trans isomer



(cis)

malic anhydride

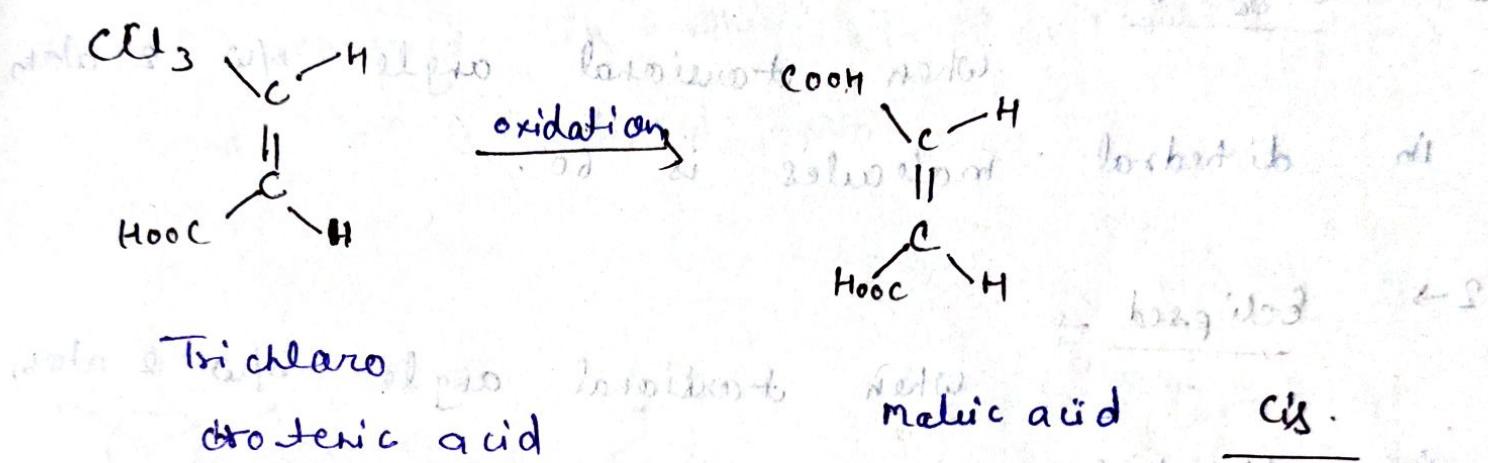
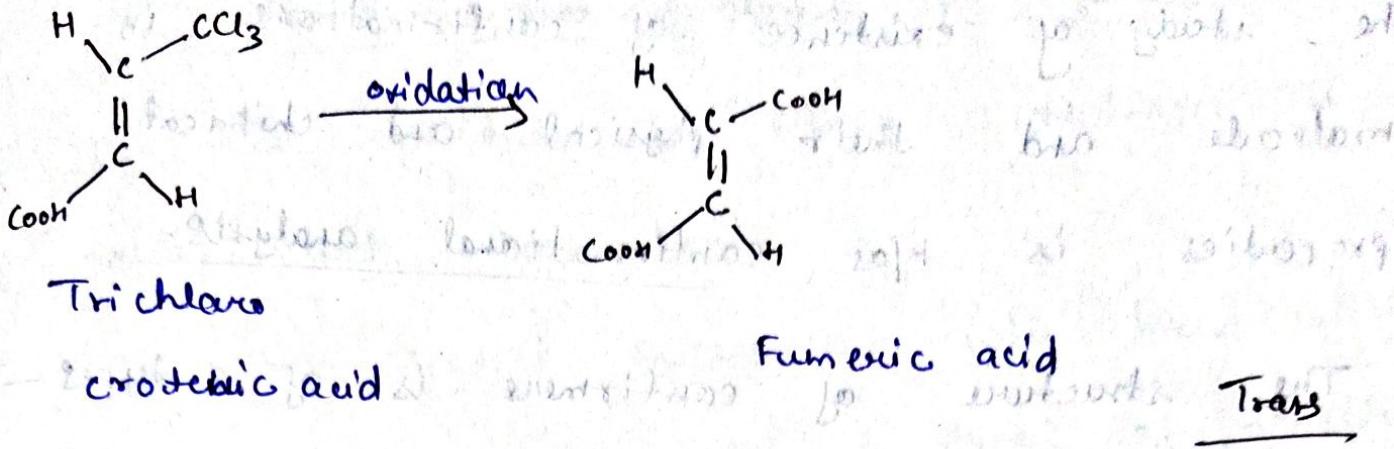


(trans)

3. Conversion method -

In this method the unknown compound is converted into the known compound after chemical reaction, and by this conversion method we can determine the configuration of compounds.

Ex → If tri chloro crotonic acid after oxidation gives fumaric acid then it is trans and if it gives malic acid then it is cis or trans.



### Confirmational analysis

- \* Different spatial arrangement of atoms in a molecule which are readily interconvertable by rotation of single bonds are called confirmation.
- \* Confirmation represents conformer which are readily interconvertable so they are not be separated.

(\*) The study of existence of conformations in molecule and their physical and chemical properties is known as conformational analysis.

\* The structure of conformers is of 2 types -

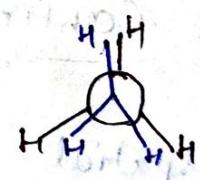
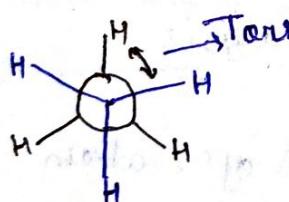
1 → Staggered -:

When torsional angle b/w 2 atoms in dихедрал molecules is  $60^\circ$ .

2 → Eclipsed -:

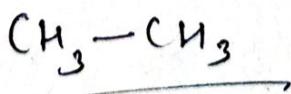
When torsional angle b/w 2 atoms in dихедрал molecules is  $0^\circ$ .

Ex - 1



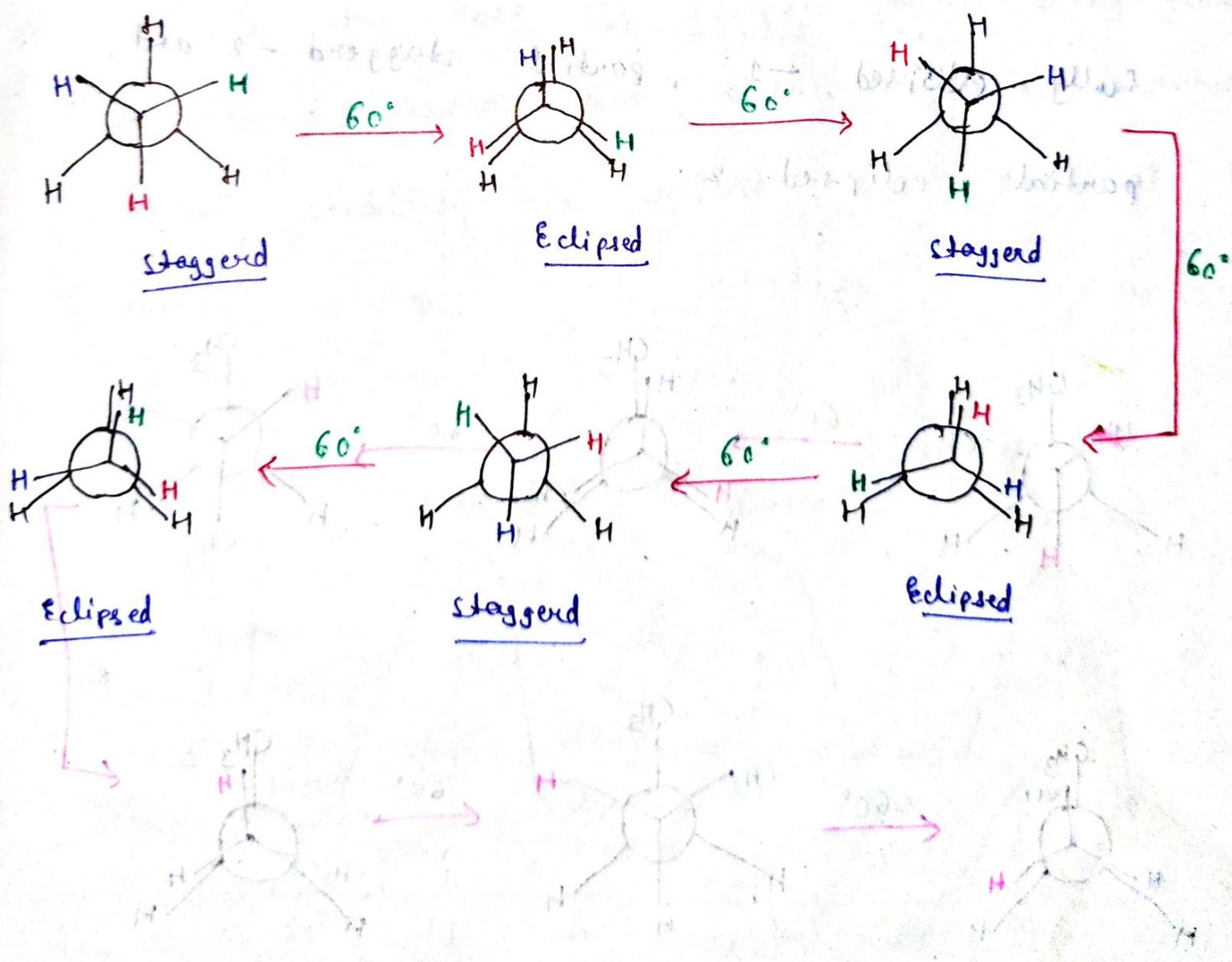
Staggered

Eclipsed



## Conformational analysis in ethane

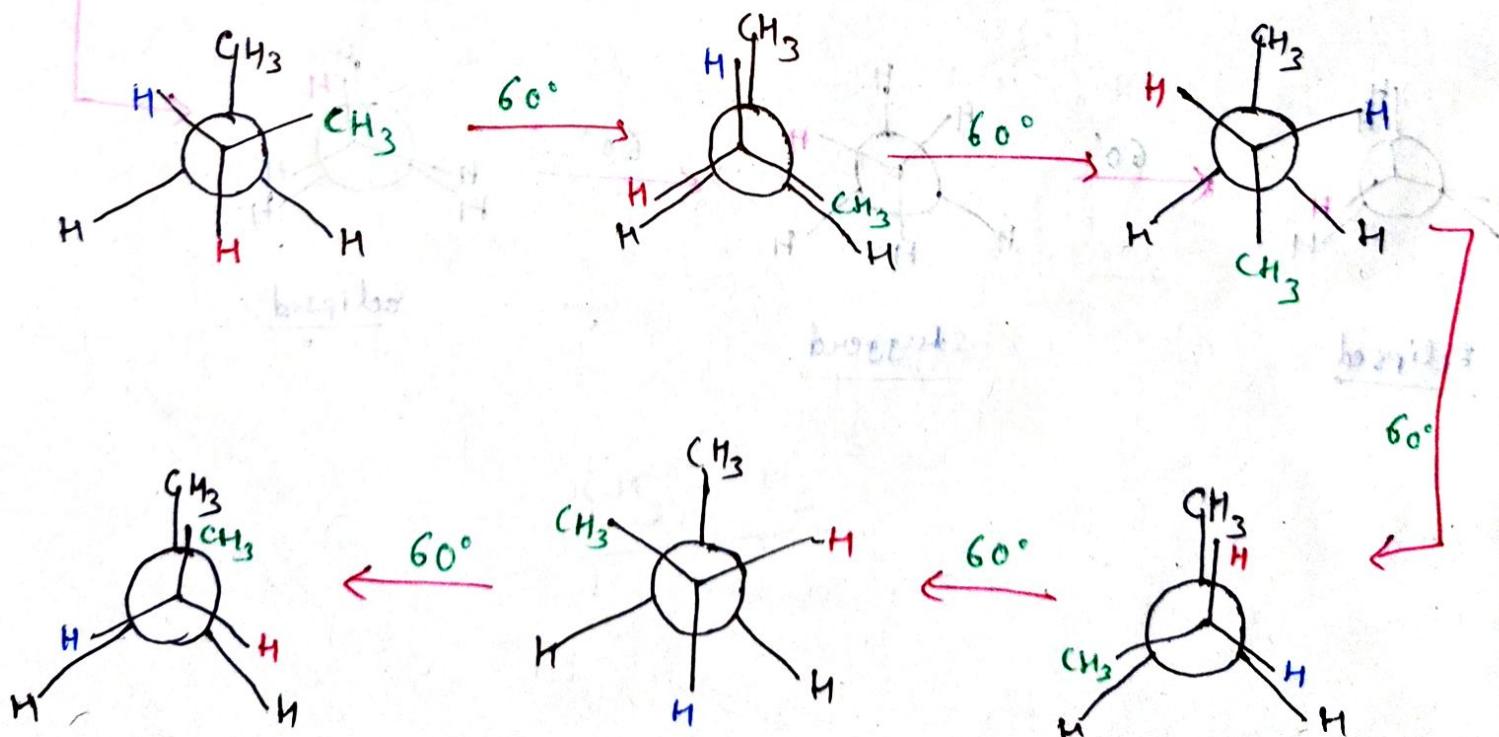
- \* In the structure of ethane 3 hydrogen is single bonded with both carbon.
- \* In the special arrangement when bond is rotated  $60^\circ$  then total 6 types of structure is obtained in which 3 is staggered form and 3 is eclipsed form.



## Conformational analysis in butane

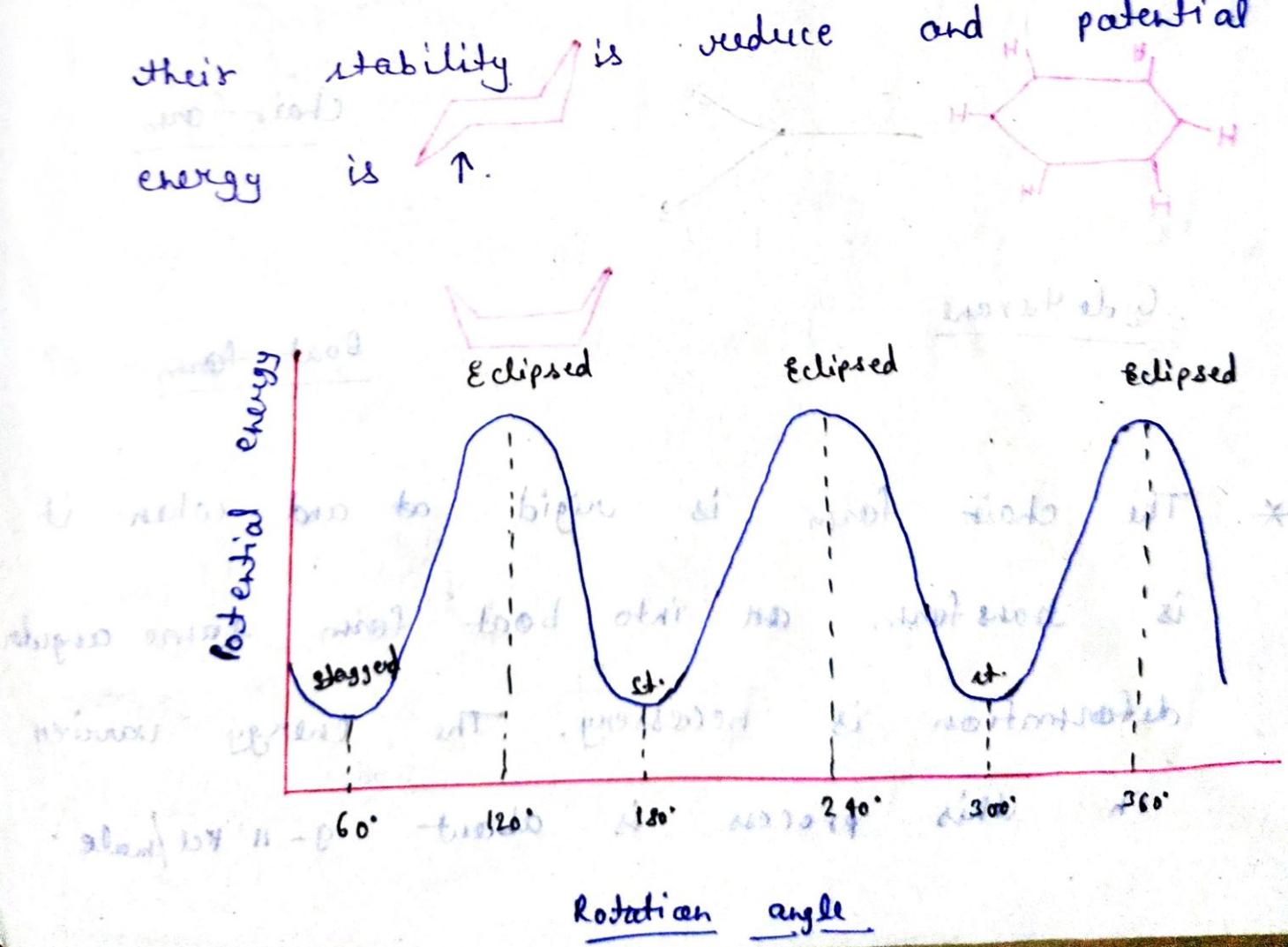
\* In the structure of n-butane 2 hydrogen and 1 methyl group is present on both carbon.

\* During conformational analysis after rotation of  $60^\circ$  in each time there is total of 6 structures is formed in which full staggered is 1, fully eclipsed -1, partial staggered -2 and partial + eclipsed -2.



## Energetics in n-butane

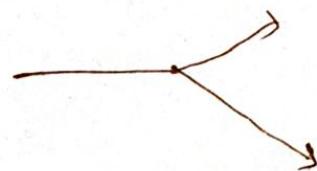
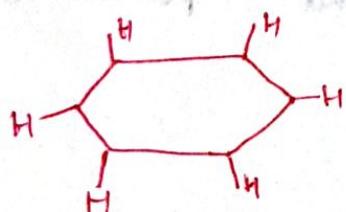
- \* In the conformational analysis there are 10 conformations which 3 form is staggered form and other 3 is eclipsed.
- \* In staggered form no steric hindrance occurs so they are stable and their energy is low.
- \* But in the case of eclipsed form bulky groups are comes closer and due to steric hindrance their stability is reduce and potential energy is ↑.



## (i) Conformational analysis in cyclohexane

\* Cyclohexane is a cyclic compound which shows conformational analysis by rotation or straining of bonds. Mohr and Sacke in 1890-91 gives the idea of conformational analysis in cyclohexane.

\* After angle strain cyclohexane shows 2 forms of structure —



Chair form



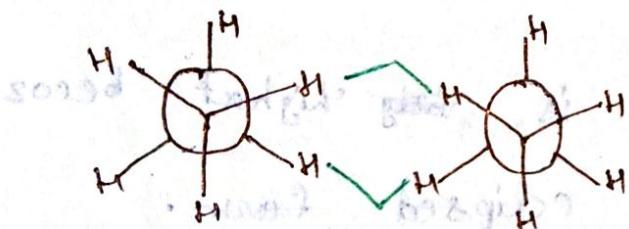
Boat form

\* The chair form is rigid and when it is transformed into boat form some angular deformation is necessary. The energy barrier in this process is about 9-11 kJ/mole.

- \* This value is large enough for each conformation to retain its identity.
- \* The chair and boat form are free from angle strain but because of difference in steric strain and bond a position state the 2 forms are differ in energy content.

Chair form →

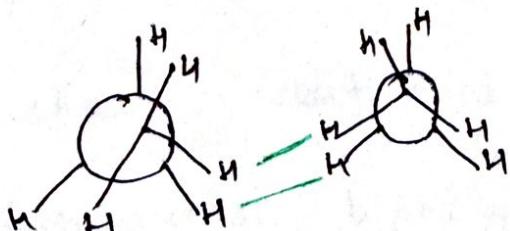
C1CC[C@H]1C[C@H]2C[C@H]1C[C@H]2C



Chair

Boat form →

C1CC[C@H]1C[C@H]2C[C@H]1C[C@H]2C



Boat

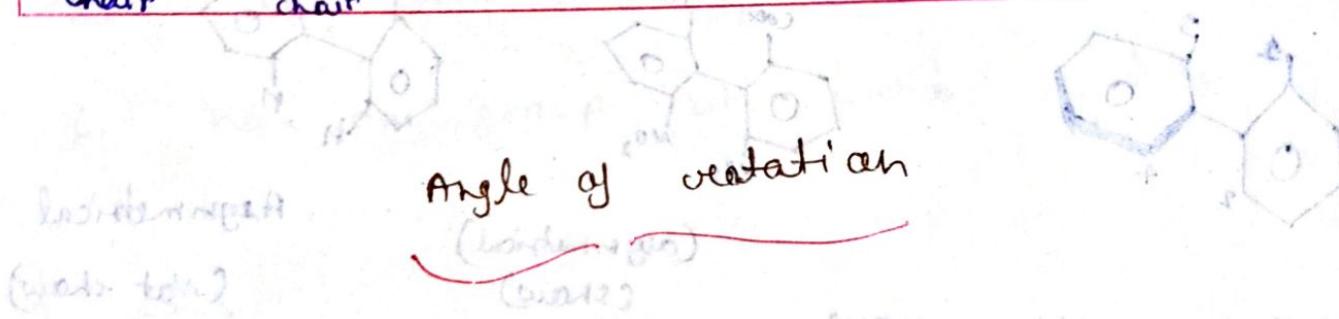
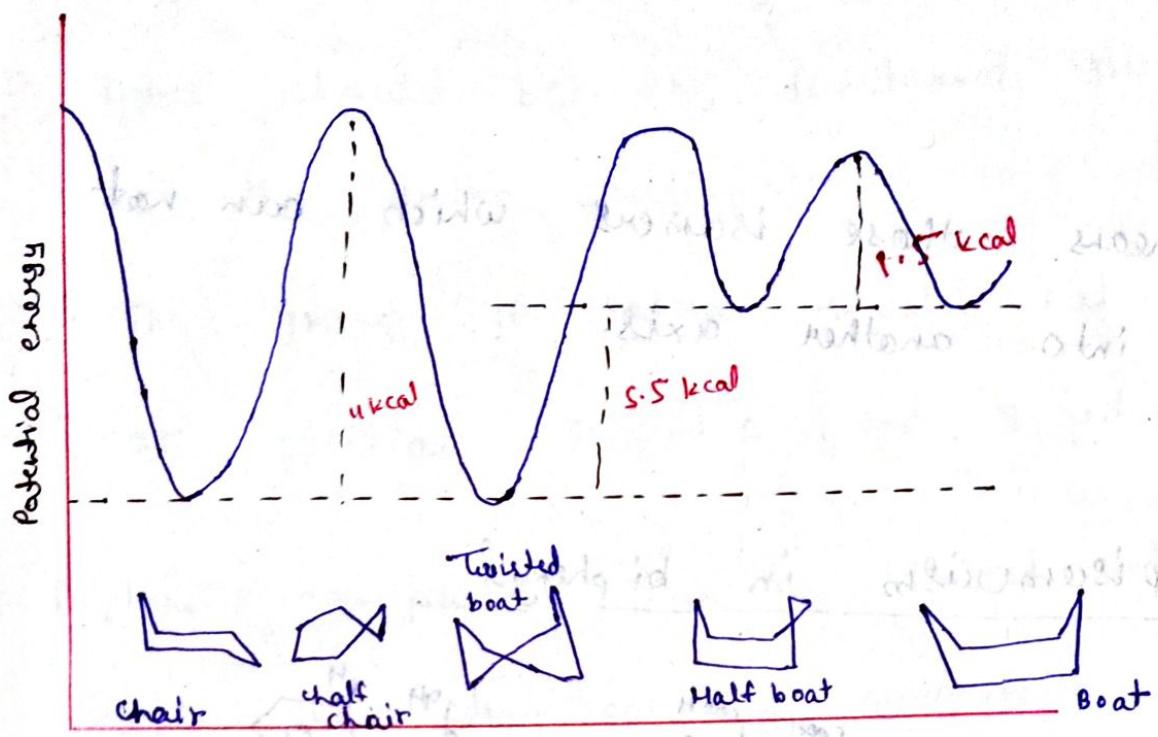
## Energetics in cyclohexane

\* when chair form structure of cyclohexane is converted into boat form then they change into total five structures.

- 1- Chair.
- 2- Half chair.
- 3- Twisted boat.
- 4- Half boat.
- 5- Boat.

\* The energy of chair form is ~~is~~ highest becoz this is similar to the eclipsed form.

\* The energy of boat form is very less is about to 1.5 kcal.



### Stereoisomerism in biphenyl compounds (Atropisomers)

\* These single bonded compounds in which 2 cyclic group or bulky group are present, they also show restricted rotation, that's why these compounds biphenyls also shows stereoisomerism.

\* Stereoisomerism in biphenyl ~~flavours~~ compounds is also known as atropisomerism.

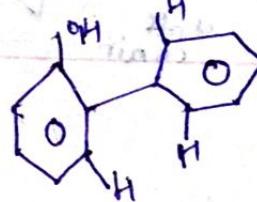
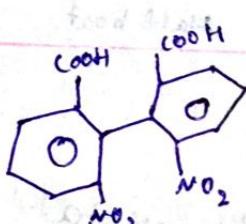
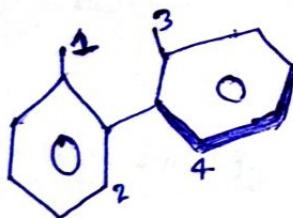
\* The term atrop isomerism consist of 3 words

A + Trop + isomerism

↓  
Non  
Term

\* It means those isomers which can not touch into another axis.

### Atrop isomerism in bi phenyl



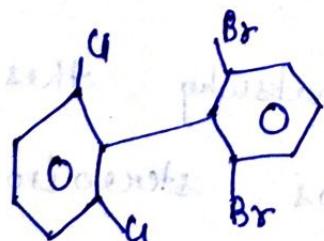
(asymmetrical)  
(skew)

Asymmetrical  
(Not skew)

① Ortho position group.

②  $1 \neq 2$

$3 \neq 4$



(Asymmetrical)

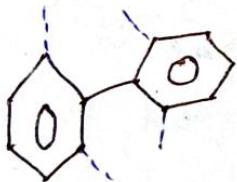
\* There are basically 2 condition for showing

atropisomerism —

- ① There should be any functional group or atom at the ortho position.
- ② The group on atom should not be similar at position 1 and 2, and 3 and 4.

\* Diphenyl compounds can be divided into 2 equal

half so they can be symmetrical ~~if~~ there is no any group at ortho position.

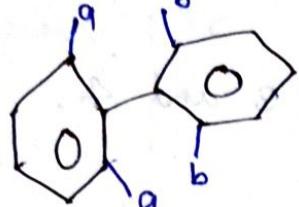


Symmetrical

(X)

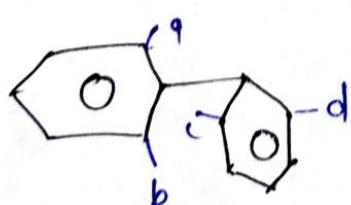


(\*) But when any functional group or atom is attached at ortho position but they are similar then again it will be symmetrical. and don't show atropisomerism.



Symmetrical  
(x)

\* But when different atom or group is attached with ortho position then it will be asymmetrical and shows atropisomerism.

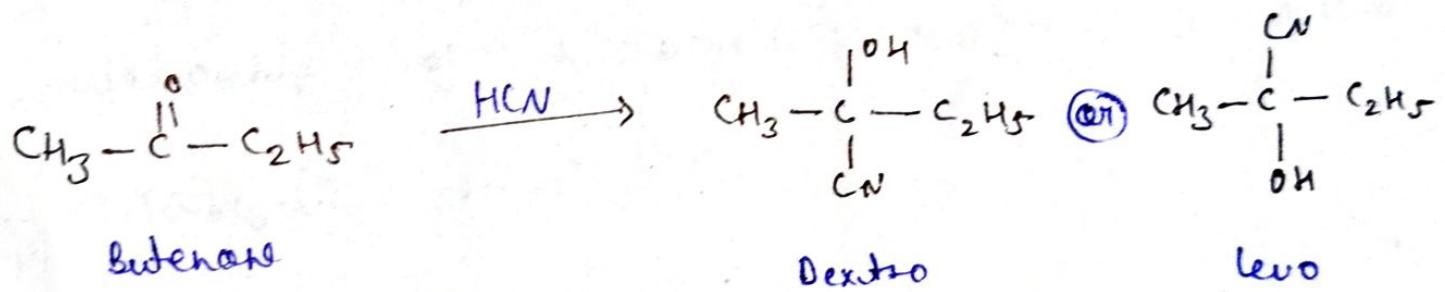


Asymmetrical



## Stereospecific and stereoselective rxn

- \* Those chemical rxn after which a stereo compound is form which is either may be dextro or levo then this is called stereo specific rxn.
- \* In this type of rxn both dextro and levo compound can be synthesized in different proportion.



## Stereo selective rxn -

Those chemical rxn after which only one dextro or levo compound is form and which is 100% selective, they are called stereoselective rxn.