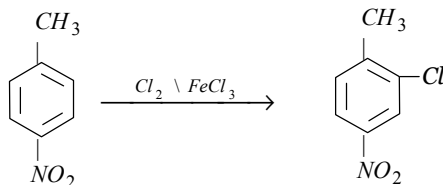


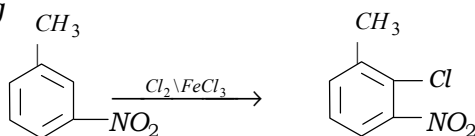
## ORGANIC CHEMISTRY

### Directive influence (Complex cases)

- When both *o*-, *p*- and *m*-directing groups support each other.

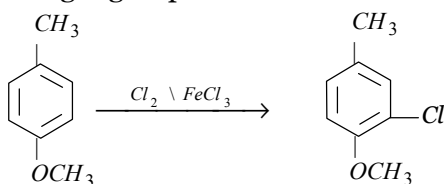


- If *o*, *p* and *m*-directing groups oppose each other than the 3rd electrophile will attach according to *ortho-para* directing group, eg



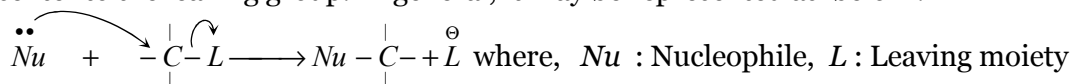
(Since  $-CH_3$  is *ortho-para* directing hence  $-Cl$  is *ortho* to  $-CH_3$  group.)

- If both are *ortho* and *para* directing groups than one of them is treated as stronger and other weak. Nature of product is decided by stronger group.



(since  $-OCH_3$  is stronger than hence  $-Cl$  is *ortho* to  $OCH_3$ )

(iii) **Nucleophilic substitution reactions** : Organic reactions in which a group or an atom is substituted by a nucleophile along with transfer of an electron pair from nucleophile to reaction center and from reaction center to the leaving group. In general, it may be represented as below :



The changes take place in this reaction : Making of a new covalent bond and breaking of old covalent bond. Therefore, these reactions on the basis of kinetics have been classified in two categories :

(a) Bimolecular nucleophilic substitution reaction ( $SN^2$ )

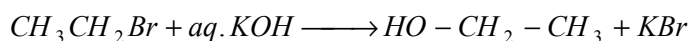
(b) Unimolecular nucleophilic substitution reaction ( $SN^1$ )

(a) **Bimolecular nucleophilic substitution reaction** ( $SN^2$ ) : Kinetic studies show that the rate of reaction depends upon the concentration of both reactant and the nucleophile, hence bimolecular, *i.e.*

$$\frac{-dx}{dt} \propto [\text{Reactant}] [\text{Nucleophile}]$$

The mechanism involves transition state. Since the nucleophile attacks from the side remote (opposite side in the same plane) to the leaving group, therefore, the reaction proceeds with inversion of configuration, *i.e.* if reactant is dextrorotatory, the product is laevorotatory and vice versa. This is the stereochemistry of the reaction.

*Examples* : Hydrolysis of primary alkyl halide



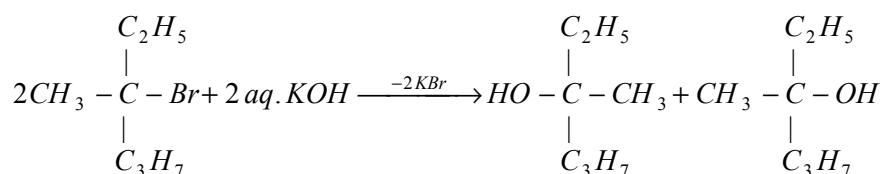
Hydrolysis of secondary alkyl halide .

## ORGANIC CHEMISTRY

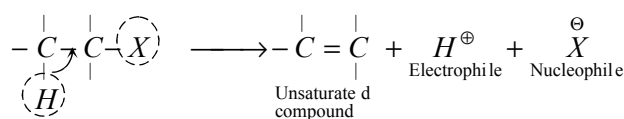
(b) **Unimolecular substitution reaction ( $SN^1$ )** : The rate of reaction is independent of concentration of nucleophile, hence unimolecular, *i.e.*  $-\frac{dx}{dt} \propto [\text{Reactant}] [\text{Nu}]^0$

The mechanism involves carbonium ions, *i.e.* first old bond breaks up and it is followed by formation of new covalent bond. Since carbonium ions are flat planar species, therefore, the nucleophile has equal probability to attack from front side as well as remote to the leaving group; as a result of this, the reaction proceeds with racemisation, *i.e.* reactant may be dextrorotatory or laevorotatory but the product is always a racemic mixture, *e.g.*

*Hydrolysis of tertiary alkyl halide :*



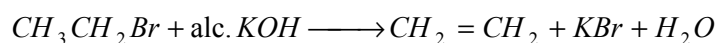
(3) **Elimination Reactions** : Organic reactions in which two groups or atoms are removed simultaneously, one in the form of a nucleophile and other in the form of an electrophile resulting in the formation of unsaturated compound, are known as elimination reactions, *e.g.*



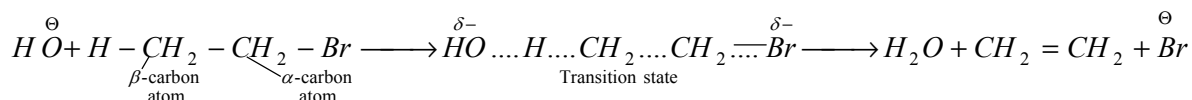
If the two groups or atoms are removed from same carbon atom, it is known as  $\alpha$ -elimination reaction. If these are removed from alternate carbon atoms, it is known as  $\gamma$ -elimination and it results a cyclic product. If these are removed from adjacent carbon atoms, it is known as  $\beta$ -elimination reaction. On the basis of kinetic studies, the  $\beta$ -elimination reactions have been classified in two categories :

(i) **Bimolecular elimination reaction ( $E_2$ )** : The rate of reaction depends upon the concentration of both species hence bimolecular. The mechanism involves transition state, *e.g.*

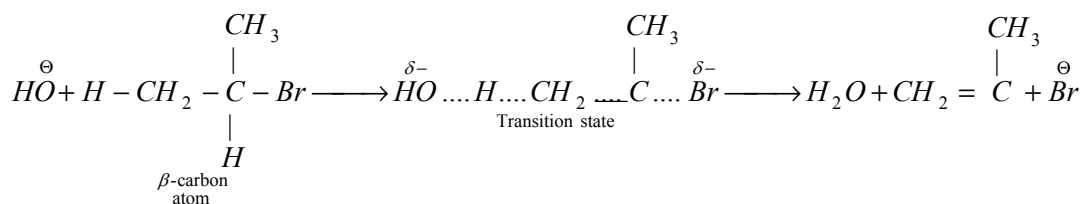
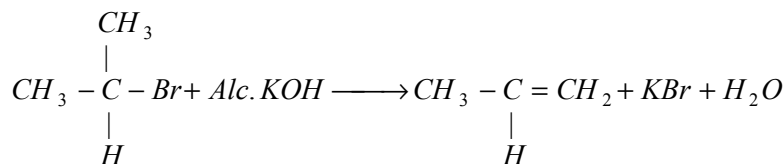
(a) **Dehydrohalogenation of primary alkyl halide :**



The mechanism is as follows :



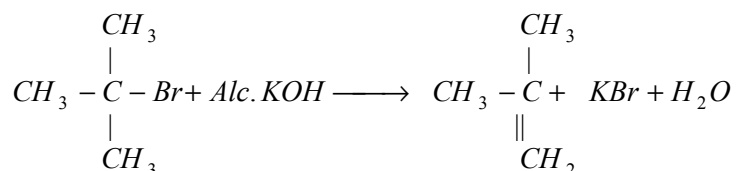
(b) **Dehydrohalogenation of secondary alkyl halide :**



## ORGANIC CHEMISTRY

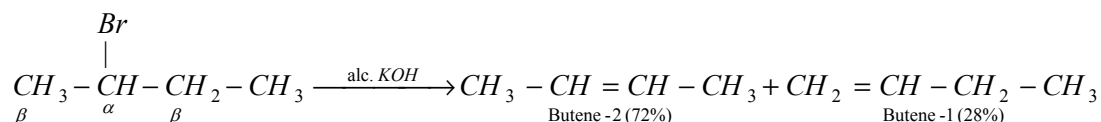
(ii) **Unimolecular elimination ( $E_1$ )** : Kinetic studies reveal that the rate of reaction depends upon the concentration of substrate only. The mechanism involves carbonium ion, *e.g.*

(a) **Dehydrohalogenation of tertiary alkyl halide :**



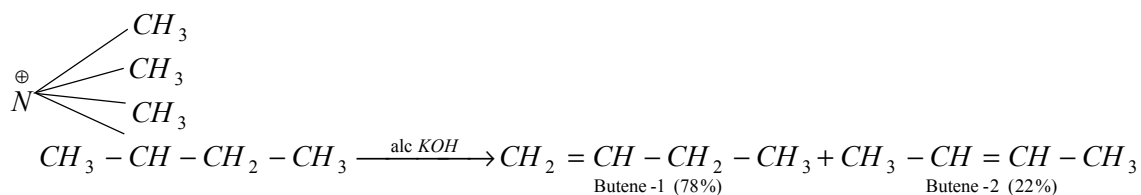
(b) **Dehydration of alcohols :**  $\text{RCH}_2\text{CH}_2 - \text{OH} + \text{H}^\oplus \longrightarrow \text{RCH} = \text{CH}_2 + \text{H}_2\text{O}$

• **Satzyeff rule :** It states that in the elimination reaction of neutral organic compounds, the hydrogen is eliminated from the  $\beta$ -carbon atom that carries least number of hydrogen atoms. *e.g.*

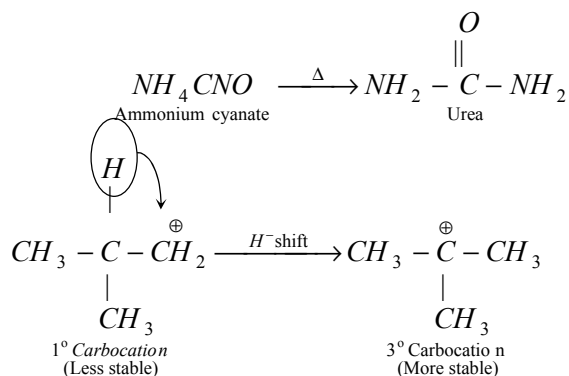


The course of reaction has been explained on the basis of the alkene formed. Butene-2 is more stable due to six hyperconjugating structures than butene-1.

• **Hofmann rule :** It states that in the elimination reaction of charged organic compounds like tetraalkyl ammonium salt and trialkyl sulphonium salt, the hydrogen is eliminated from  $\beta$ -carbon atom that carries maximum number of hydrogen atom (s), *e.g.*

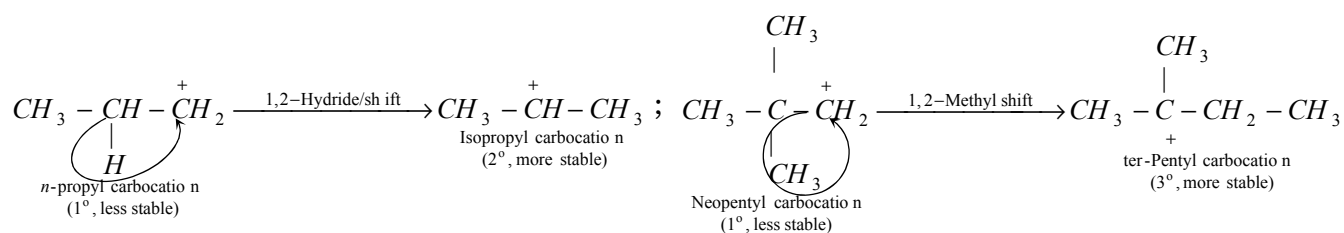


(4) **Molecular rearrangement reactions :** They involve the atomic rearrangement within the molecule or ion to give another species with different characteristics.



**Rearrangement of carbocations :** Carbocations are prone to rearrangements. During these rearrangements, less stable ( $1^\circ$  or  $2^\circ$ ) carbocations are converted into more stable ( $2^\circ$  or  $3^\circ$ ) carbocations either by 1, 2-hydride shift or by 1, 2-methyl shift. *For example,*

## ORGANIC CHEMISTRY



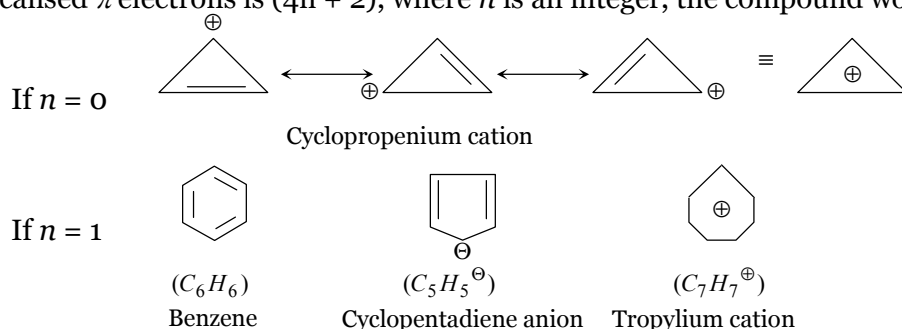
Carbanions and free radicals usually do not undergo rearrangements.

### Aromaticity and Anti – aromaticity

(1) **Aromaticity** : The term “Aromaticity” means ability of an organic compound containing conjugated, planar, cyclic ring to undergo substitution reaction rather than addition and to resist oxidation.

**Criteria for aromaticity** : An organic compound is aromatic if it fulfils following essential conditions.

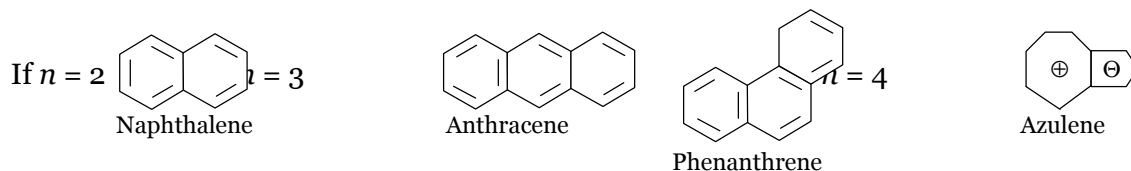
- (i) It should have conjugated, planar, cyclic ring,
- (ii) Although unsaturated, as evidenced from its molecular formula, it must undergo substitution reaction rather than addition reaction.
- (iii) It should resist oxidation.
- (iv) It should have  $sp^2$  hybridised carbon atom.
- (v) It should follow Huckel’s rule which states, “If in a conjugated, planar, cyclic polyene, the number of delocalised  $\pi$  electrons is  $(4n + 2)$ , where  $n$  is an integer, the compound would have aromatic stability”, e.g.



**Note** :  $\square$  In general, no. of delocalised  $\pi e^- = \text{No. of carbon atoms}$ , e.g.  $\text{C}_6\text{H}_6$

or No. of carbon atoms + No. of negative charge, e.g.  $\text{C}_5\text{H}_5^- = 5 + 1 = 6$

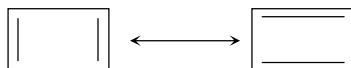
or No. of carbon atoms – No. of +ve charge, e.g.  $\text{C}_7\text{H}_7^+ = 7 - 1 = 6$



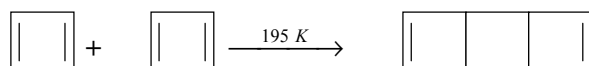
Besides above, the aromatic compounds generally undergo Friedel Craft reaction and forms sulphonic acid when treated with  $\text{H}_2\text{SO}_4$ .

## ORGANIC CHEMISTRY

(2) **Antiaromaticity** : The term antiaromaticity has been introduced by *Breslow* (1967) to describe the unstable nature of the monocyclic conjugated polyene in comparison to the corresponding *acyclic polyene*. For example, cyclobutadiene is a monocyclic conjugation diene and is a hybrid of the following structures :



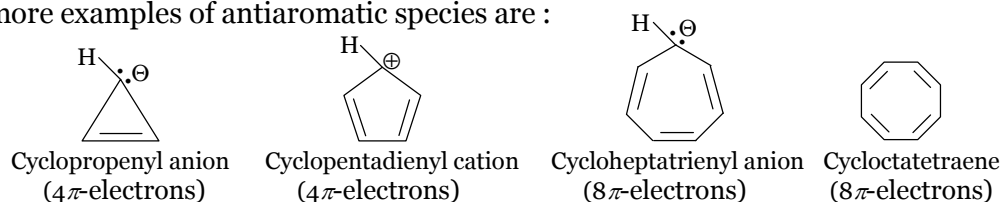
Due to resonance, the compound is expected to be more stable than the corresponding acyclic diene i.e., 1, 3-butadiene but in fact, cyclobutadiene is less stable, than 1, 3-butadiene. Cyclobutadiene is such an unstable molecule that even at 195 K, it undergoes Diels-Alder cycloaddition to form a dimer. This reactivity is probably due to antiaromaticity.



Cyclobutadiene and other similar cyclic polyenes which are relatively unstable than the corresponding acyclic polyenes inspite of their conjugated structures, are said to be antiaromatic compounds and the phenomenon is called antiaromaticity.

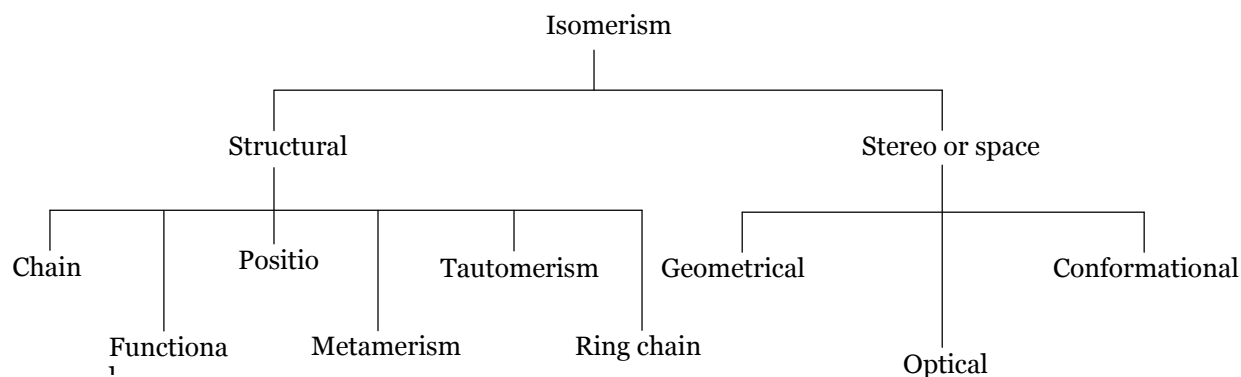
In terms of Huckel rule, *antiaromatic compounds* have cyclic, planar structures with  $4n$   $\pi$ -electrons. They are destabilised by resonance.

Some more examples of antiaromatic species are :



## Isomerism

Compounds having the same molecular formula but different physical and chemical properties (due to different arrangement of atoms within their molecules) are called isomers and the phenomenon is known as isomerism. The term was given by **Berzelius**. The different types of isomerism are :

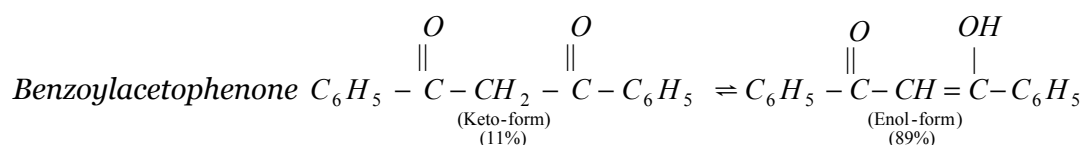
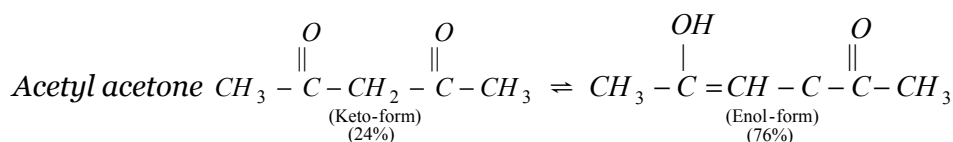
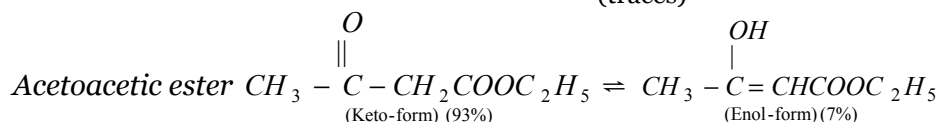
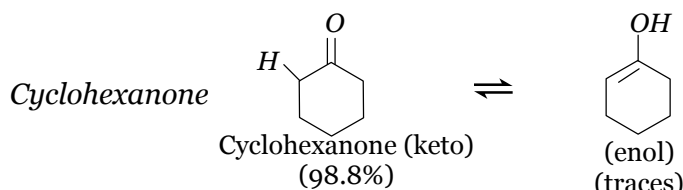
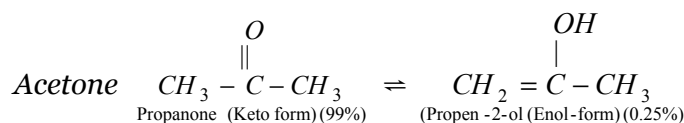


### (1) Structural isomerism

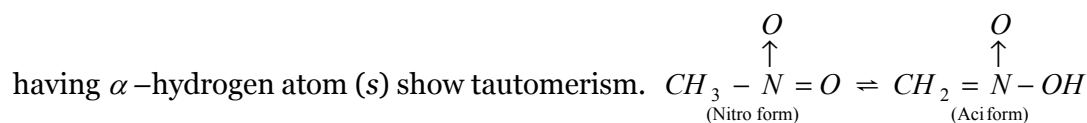
Compounds having the same molecular formula but which differ in the arrangements of atoms within the molecule are called *structural isomers* and the phenomenon is called *structural isomerism*. Various types of structural isomerism are:



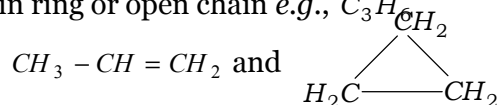
## ORGANIC CHEMISTRY



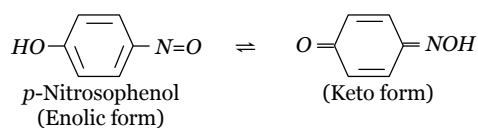
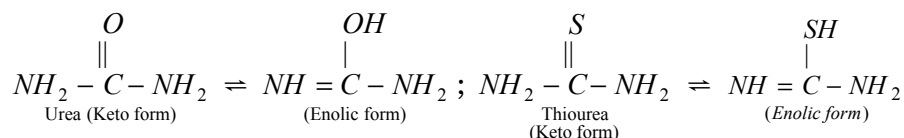
(b) **Nitro-aci tautomerism** : Compounds containing a free nitro group on 1° and 2° carbon and also



(vi) **Ring chain isomerism** : This type of isomerism arises due to difference in mode of linking of carbon atoms in ring or open chain e.g.,  $\text{C}_3\text{H}_6$



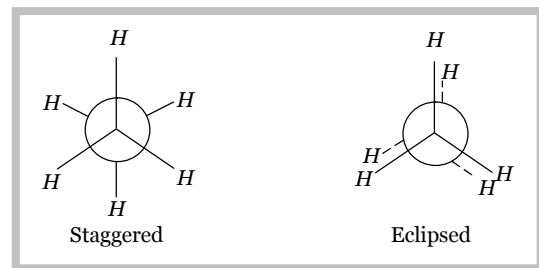
Certain amides such as urea, thiourea and nitrosophenol also show tautomerism.



## ORGANIC CHEMISTRY

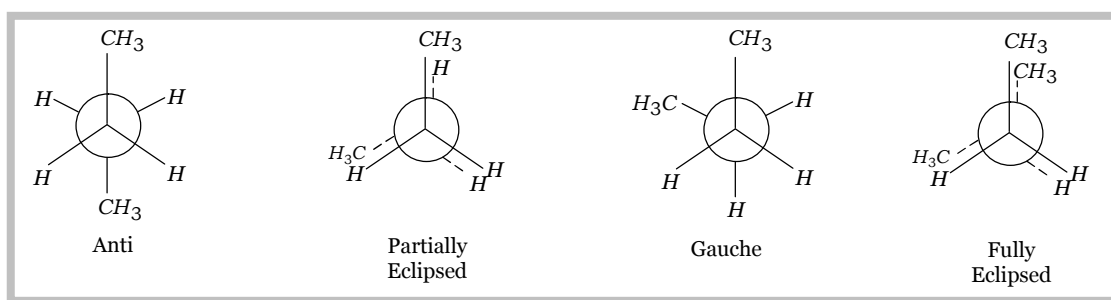
(2) **Stereo-isomerism** : Compounds with the same molecular formula but having difference in the spatial arrangement of atoms or groups are called stereo isomers and the phenomenon is called stereoisomerism. Various types of stereoisomerism are:

(i) **Conformational isomers**. These are different spatial arrangements of atoms or groups which can be converted into one another by rotation around the  $C - C$  single bond. The various conformations of a compound differ slightly in their energy content and cannot be separated. *For example* (a) Ethane has the following two extreme conformations out of infinite total conformations.



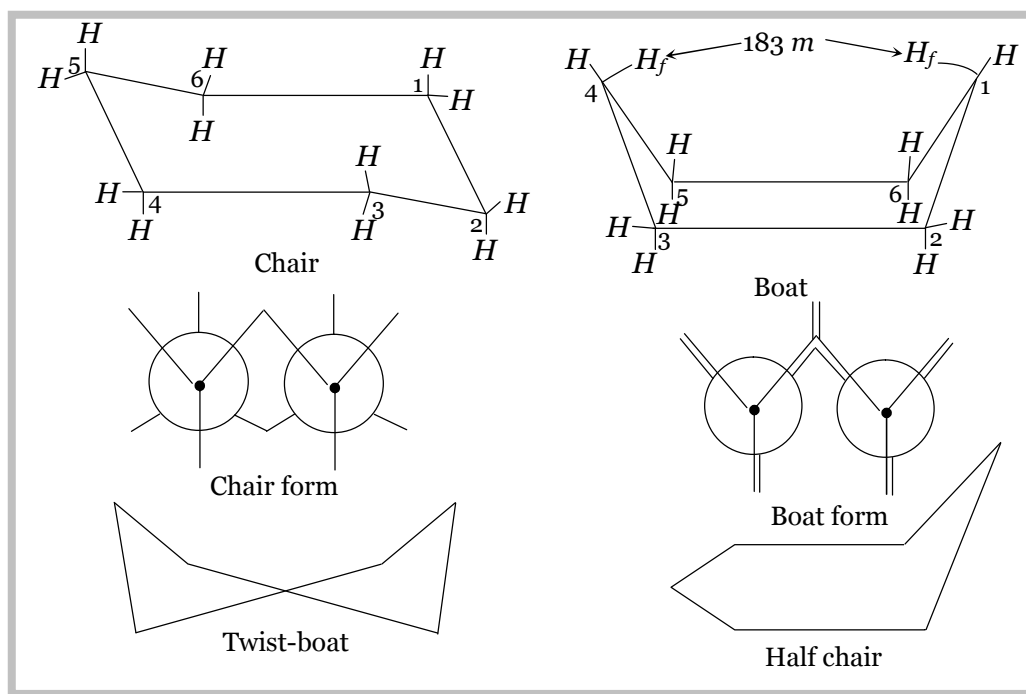
The staggered form is more stable than the eclipsed form by about  $12.55 \text{ kJ mol}^{-1}$  or  $3.0 \text{ kcal mol}^{-1}$ .

(b) Butane has four extreme conformations out of infinite number of total conformations.



The energies of various conformations of butane are anti ( $0.0 \text{ kJ mol}^{-1}$ ) skew or gauche ( $3.35 \text{ kJ mol}^{-1}$ ), partially eclipsed ( $12.13 \text{ kJ mol}^{-1}$ ), fully eclipsed ( $15.06 \text{ kJ mol}^{-1}$ ). The increasing order of stability of these conformations: Fully eclipsed < Partially eclipsed < Gauche < Anti

(c) Cyclohexane has many conformations such as *chair form*, *boat form*, *twist boat form* and *half chair form*. Among these the two extreme conformations are *boat* and *chair form*.





## ORGANIC CHEMISTRY

The chair conformation is more stable than the boat conformation because of the following two reasons:

- In chair conformation, all the H-atoms on  $C_1 - C_2, C_2 - C_3, C_3 - C_4, C_4 - C_5, C_5 - C_6$  and  $C_6 - C_1$  are in more stable staggered orientations and hence there is no *torsional strain*. On the other hand, in boat conformation, the adjacent hydrogens on  $C_2 - C_3$  and  $C_5 - C_6$  are in the less stable *eclipsed orientation*. These eclipsing interactions raise the energy of the boat form relative to the chair form.

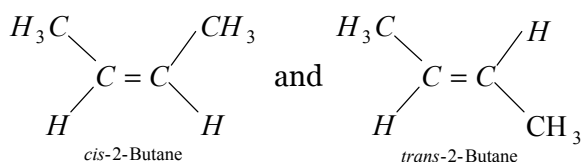
- The two hydrogen atoms (marked  $H_f$ ) are called flagpole hydrogens. In boat form these are quite close to each other ( $1.83 \text{ \AA}$ ) as compared to chair form ( $2.29 \text{ \AA}$ ). These hydrogens strongly repel each other as such this introduces *steric strain*.

- The two other conformations *i.e.*, twist boat and half chair conformations are unstable. The relative energies of various conformations are: chair form ( $0.0 \text{ kJ mol}^{-1}$ ); twist boat ( $23.0 \text{ kJ mol}^{-1}$ ); boat form ( $29.7 \text{ kJ mol}^{-1}$ ); half chair ( $44.0 \text{ kJ mol}^{-1}$ )

(ii) **Geometrical isomerism** : In alkenes, this type of isomers have different spatial arrangements of atoms or groups around the  $C = C$  bond. When two similar groups lie on same side of double bond, the arrangement is called **cis-isomer**. When two similar groups lie on the opposite side of the double bond, the arrangement is called **trans-isomer**.

The cis and trans forms differ from each other in respect of many physical properties. Trans isomers are more stable, have higher melting points, high densities, low solubilities, low dipole moments, low boiling points and low refractive indices than those of the corresponding cis-isomer.

*Cause of geometrical isomerism in alkenes* : The cause of geometrical isomerism is the restricted or hindered rotation about carbon-carbon double bond. For example

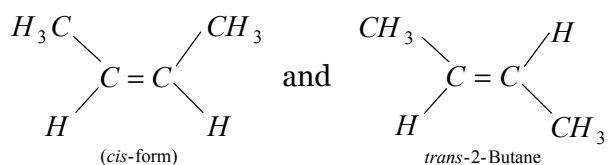


*Conditions necessary for geometrical isomerism in alkenes* :

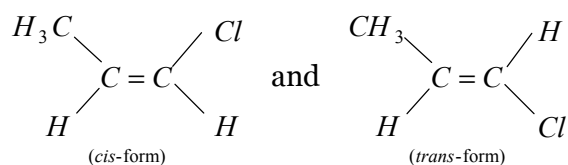
The molecule must contain a carbon-carbon double bond. Geometrical isomerism is exhibited only by such molecules in which each carbon atom of the double bond has different atoms or groups. Compounds of the type  $abC = Cab$ ,  $abC = Cde$  and  $abC = Cad$  show this type of isomerism.

Some examples of compounds showing geometrical isomers are shown below :

**Type  $abC = Cab$**



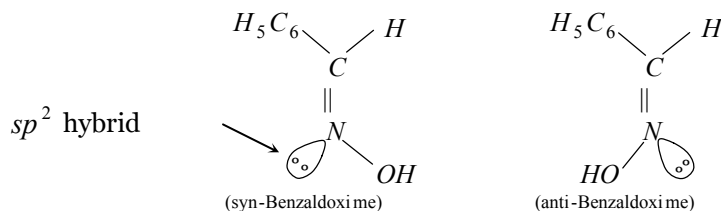
**Type  $abC = Cad$**



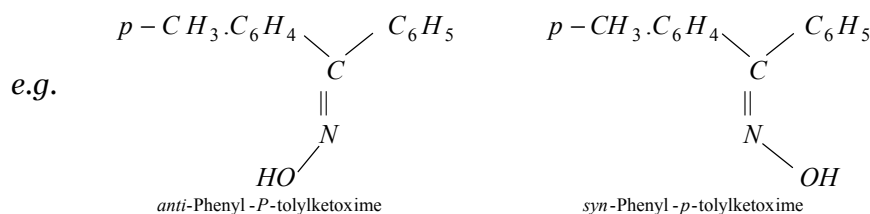
*Other Examples of Geometrical isomers*

## ORGANIC CHEMISTRY

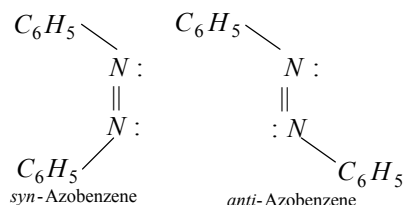
**Due to C = N bond.** In aldoximes and ketoximes, geometrical isomerism arises due to restricted rotation around C = N bond. In aldoximes, the isomer is named as **syn** if hydrogen and hydroxyl groups are on the same side of C = N bond. If these are on the opposite side then the isomer is named a **anti**.



In ketoximes, the prefixes syn and anti indicate which group of ketoxime is syn or anti to the hydroxyl group.



**Due to N = N bond.** The isomer is syn if the two groups are on the same side and anti if the two groups are on the opposite sides e.g.



### (iii) Optical isomerism and optical activity

Substances having the ability to rotate the plane polarised light either to the right or to the left are termed as optically active and the property is called optical activity.

(a) **Plane polarised light** is the light whose vibrations occur only in one plane.

(b) **Angle of rotation** is the angle through which an optically active substance rotates the plane of polarised light. It is measured with the help of an instrument called **Polarimeter**.

**Specific Rotation :** It is the angle of rotation produced by a solution of length 10 cm (or one dm) and having unit concentration ( $1g/cm^3$ ) for the given wave length ( $\lambda$ ) of light at a given temperature ( $t$ ). It is given as:

$$\text{Specific rotation, } [\alpha]_{\lambda}^t = \frac{100 \times \text{observed angle of rotation } (\theta)}{\text{length in } dm \times g \text{ of solute in } 100 \text{ cm}^2 \text{ solution}} = \frac{100 \times \theta}{l \times c}$$

(c) **Optical isomerism :** The stereoisomers which differ in their behaviour towards plane polarised light are called optical isomers and the phenomenon is called optical isomerism. As these isomers differ from one another only in the way the atoms are oriented in space, therefore, optical isomerism is a kind of stereoisomers.

**Enantiomerism** is the simplest kind of optical isomerism which was discovered by French chemist *Louis Pasteur* in 1848. Isomers which are mirror images of each other are called **enantiomers** (Greek : *enantio* = opposite).

**Conditions for enantiomerism :** The necessary and sufficient condition for a molecule to exhibit enantiomerism is chirality of the molecule i.e., the molecule and its mirror image must be non-superimposable. It may or may not contain a chiral carbon atoms.

## ORGANIC CHEMISTRY

(d) **Maximum number of optical isomers** : In general, the maximum **number** of optical isomers for a compound with  $n$  number of different asymmetric carbon atoms will be  $2^n$  (Vant Hoff rule).

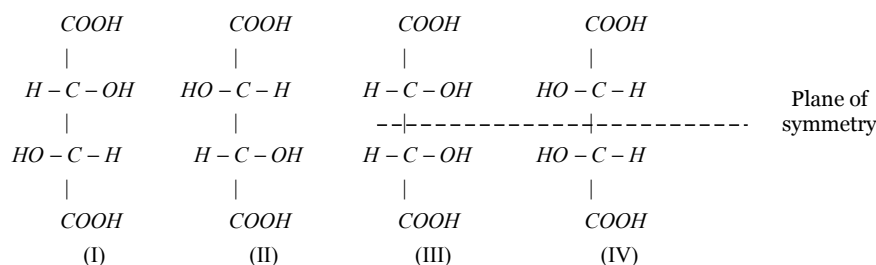
**Characteristics of enantiomers (*d*- and *l*-isomers)** : They have identical physical properties. They rotate the plane polarised light equally but in opposite directions. They have identical chemical properties, however, they differ in the rate of reactions with optically active reagents. They have different biological properties. *e.g.*

(+)- tartaric acid is consumed by mould penicillium glaucum but (–)-tartaric acid is not consumed.

(e) **Racemic mixture of racemic modification** : When two enantiomers of same substance are mixed in equal proportions an optically inactive solution is obtained. It is called racemic mixture (*dl* or  $\pm$  form). The absence of optical activity in *dl*-mixture is due to **external compensation**.

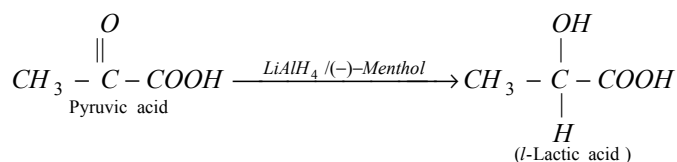
(f) **Diastereomers** : Stereoisomers which are not mirror images of each other are called diastereomers. These differ in physical properties and can be separated from each other by fractional distillation, fractional crystallization or chromatography etc.

(g) **Meso compound** : The compounds which do not show optical activity inspite of presence of chiral carbon atoms are called meso compounds. The absence of optical activity in meso compounds is due to an element of symmetry (plane, axis or point). In other words, the molecule of a meso compound is achiral.

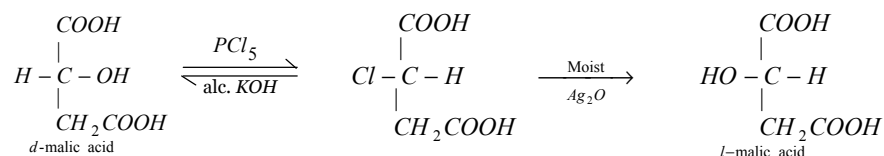


In the above example, the *structure I and II* are **enantiomers**. While *structure I and III* are **Diastereomers**. *Structure III and structure IV* are identical and represent **meso compounds**.

• **Asymmetric synthesis**. The synthesis of an optically active compound from an optically inactive molecule in the presence of a suitable chiral reagent is called asymmetric synthesis *e.g.*,



• **Walden inversion**. The conversion of *d*-form of an optically active compound into *l*-form of the same or of different compound or vice versa is known as walden inversion.



• **Resolution**. The separation of *d* and *l* isomers from the *dl* mixture is referred to as resolution. This can be done by (A) Mechanical separation (B) Biochemical separation and (C) Chemical method (best method).

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