

General Organic Chemistry

Definition: Organic chemistry is the study of carbon containing compounds.

Organic is originally derived from living "Organism" i.e the study of compounds extracted from living organism. These compounds needed vital force to create them.

Significance: Organic chemistry has got enormous application in day to day life. Paints, plastics, food, explosives, drugs, petrochemicals, proteins, nucleic acids, and sugars etc which form the basis of all earthly life processes are applications of organic chemistry.

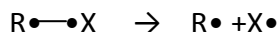
Before proceeding to the reactions and mechanism in the organic chemistry let us see some important terminology in the organic chemistry:

(A) Concept of bond breaking and bond formation:

A Covalent bond (formed by sharing of a pair of electron) between two atoms can be broken in two ways:

- (a) Homolytic fission/Homolysis
- (b) Heterolytic fission/Heterolysis

(a) Homolytic fission: Breaking of a bond in such a way that two electrons that are involved in the bond are distributed one by one to the two species.



The species formed ($R\bullet$ & $X\bullet$) are called *free radical*. These are highly reactive species.

(Note: Homolysis can be induced by irradiation in the UV region.)

(b) Heterolytic fission: Cleavage of a bond generating a cation and an anion. In this process the two electrons that make up the bond are assigned to the single atom.



When a positive charge is carried on carbon, the entity is known as *carbocation*, and When a negative charge is carried on carbon, the entity is called *carbanion*.

(B) Concept of electrophile and nucleophile:

Electrophile: An electrophile (literally electron-loving species) is a reagent and itself electron deficient, that participates in a chemical reaction by accepting an electron pair in order to bond to a nucleophile.

Species which can act as an electrophile:

- (i) All positive charge system can act as electrophile such as : NO_2^+ , NO^+ , X^+ , Ph-N_2^+ , $-\text{C}^+-$, H^+ , H_3O^+ , NH_4^+ , PH_4^+ etc.
- (ii) Neutral molecule are electrophile ex. Halides of group III BF_3 , BCl_3 , BBr_3
- (iii) Halides of atoms in which central atom has vacant d-orbital ex. SiCl_4
- (iv) Interhalogen compound ex. ICl , BrCl
- (v) Halogen act as electrophile ex. Br_2
- (vi) Carbonyl system also acts as electrophile. Ex. Reaction of formaldehyde with Grignard reagent
- (vii) Acidic oxide acts as electrophile. Ex. CO_2 , SO_2
- (viii) Nitrene $:\ddot{\text{N}}\text{H}_2$, Singlet carbene $:\text{C}\text{H}_2$ (since it has incomplete octet)

Nucleophile: These are nucleus loving species and itself electron rich.

Species which can act as a nucleophile:

- (i) All negative charge acts as a nucleophile. Ex. H^- , OH^- , NH_2^- , X^- , CN^- , HSO_3^- .
Indirect nucleophile. Ex. AlH_4^- , BF_4^- , BH_4^-
- (ii) Neutral molecule with central atom having at least one lone pair of electron. Ex. H_2O , NH_3 , aniline.
- (iii) π -electron system can acts as nucleophile. Ex. Alkene, alkyne etc.
- (iv) Metals can also act as a nucleophile. Ex. Na

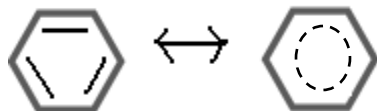
(C) Concept of Aromaticity:

Cyclic compound can be classified mainly into 3 broad categories: (i) Aromatic (ii) Non aromatic (iii) Anti aromatic

Criteria of aromaticity :

- (a) Cyclic, Planer
- (b) Must have $(4n+2)\pi$ electrons where $n \geq 0$ (This is also called Huckel's rule)
- (c) π electrons must be delocalized

Example: Benzene



Criteria of antiaromaticity :

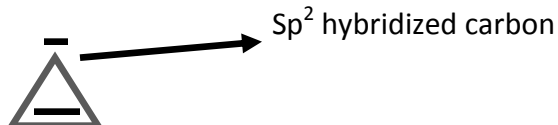
- (a) Cyclic, Planer
- (b) Must have $(4n)\pi$ electrons where $n > 0$
- (c) π electrons must be delocalized

Example:

Cyclobutadiene



Cyclopropenyl anion



(Note: Generally carbanions are Sp^3 hybridized but resonance stabilized carbanion are Sp^2 hybridized)

Criteria for non aromatic:

- (a) Cyclic compound
- (b) Not aromatic
- (c) Not anti aromatic

Example: Cyclopropene



2 π electron not delocalized

[Note: Quasiaromatic: When ions are aromatic then it is called quasiaromatic.

Example: Cyclopropenyl cation (smallest aromatic unit)]



Various important effects in Organic chemistry:

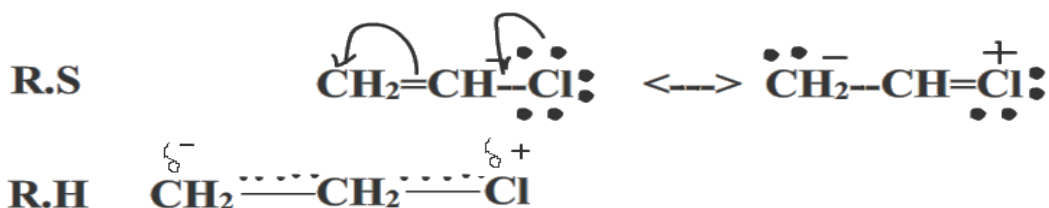
- (A) Resonance effect
- (B) Inductive effect
- (C) Mesomeric effect
- (D) Electromeric effect
- (E) Inductomeric effect
- (F) Hyperconjugation
- (G) Effect of Inertia
- (H) Ortho effect

(A) Resonance effect: Resonance is a hypothetical concept in which molecule is represented by more than one form called canonical form or resonating structure (R.S), and the property of the molecule is represented by combination of all canonical forms called resonance hybrid (R.H).

R.H => Having no real existence

R.S => Having real structure

Example : $\text{CH}_2^{\text{a}}=\text{CH}^{\text{b}}-\text{Cl}$

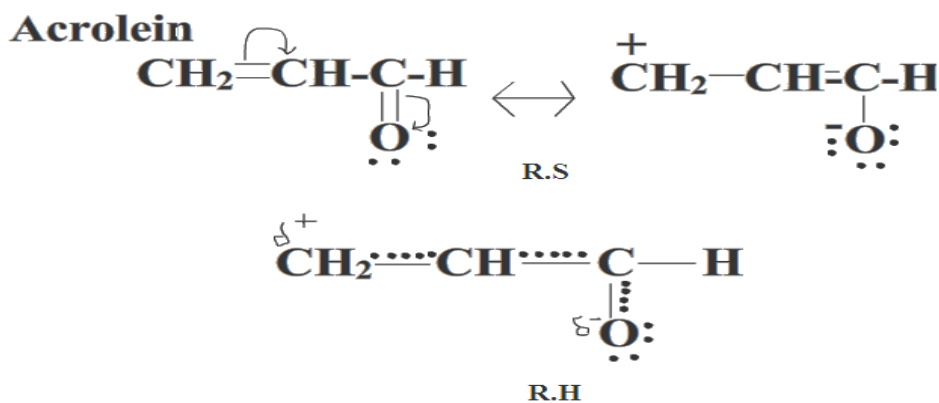


Explanation by experimental observation: a(bond length) > Pure C=C bond length, b(bond length) < Pure C-Cl bond length.

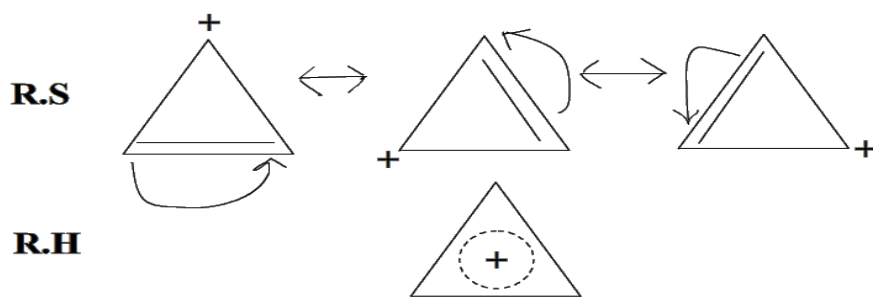
System showing resonance:

- (i) Double bond conjugated system
- (ii) π -bond in conjugation with +ve charged ion
- (iii) π -bond in conjugation with -ve charged ion
- (iv) π -bond in conjugation with neutral atom having at least one lone pair of electron
- (v) π -bond in conjugation with odd electron (free radical)

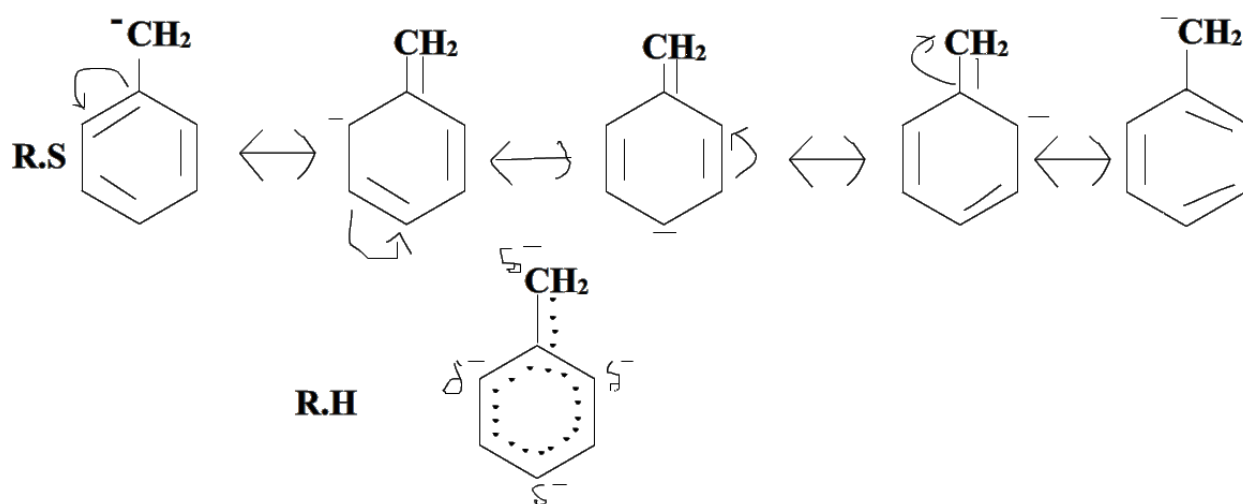
(i) Double bond conjugated system



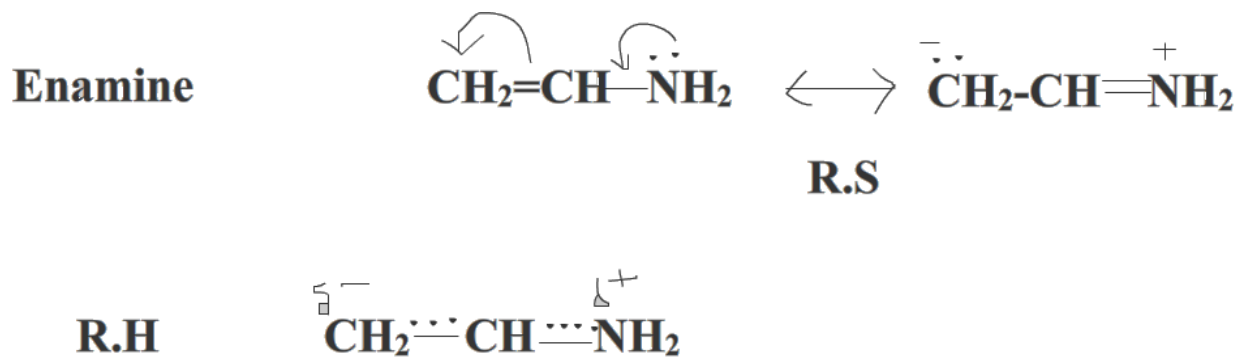
(ii) π -bond in conjugation with +ve charged ion



(iii) π -bond in conjugation with -ve charged ion

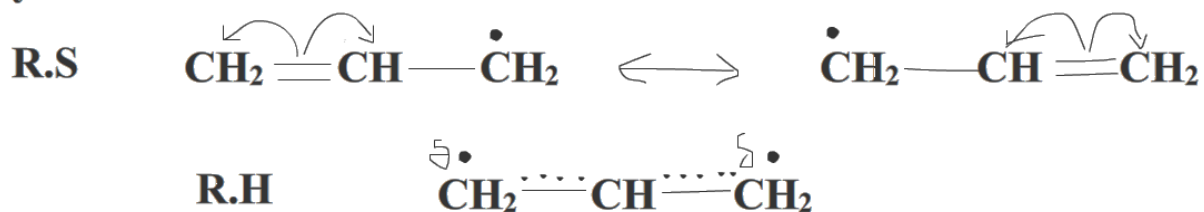


(iv) π -bond in conjugation with neutral atom having at least one lone pair of electron



(v) π -bond in conjugation with odd electron (free radical)

Allyl radical



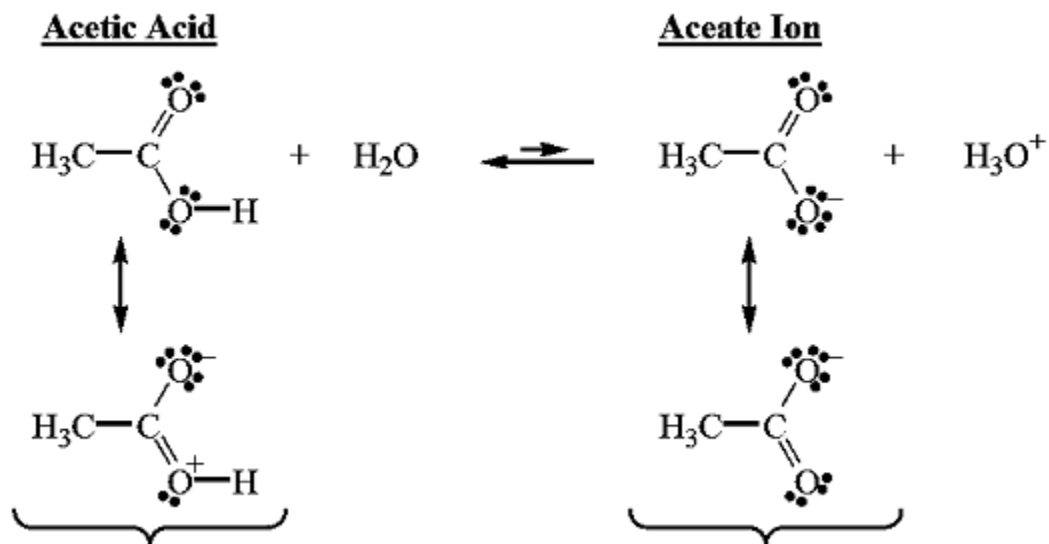
Note: Resonance involving free radical is called radical resonance.

Effect of Resonance:

- (1) Stability
- (2) Acidity
- (3) Basicity
- (4) Electrophilicity and Nucleophilicity

(1) Stability of compound

Resonance stabilizes acetate anion:

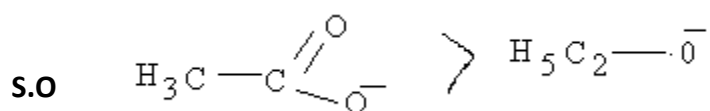


Charge delocalization in case of acetate ion leads to more stability. While in case of acetic acid, charge separation occurs, this decreases the stability of the compound.

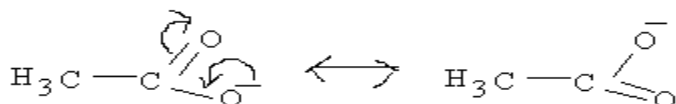
Rules to predict the stability of resonating structure/resonance hybrid:

- (A)** Resonance structure/hybrid, where charge delocalization takes place would be more stable as compare to resonance structure/hybrid where charge separation takes place.

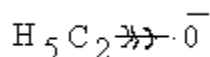
Example: stability order (S.O) between acetate anion and anion of ethyl alcohol



Acetate anion: Charge delocalization during resonance.

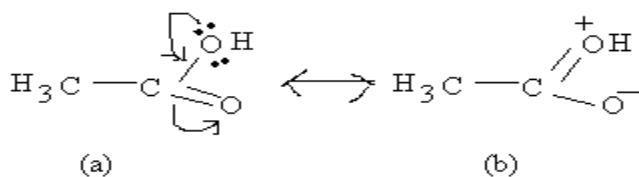


Anion of ethanol: Charge accumulation takes place due to +I effect of C_2H_5



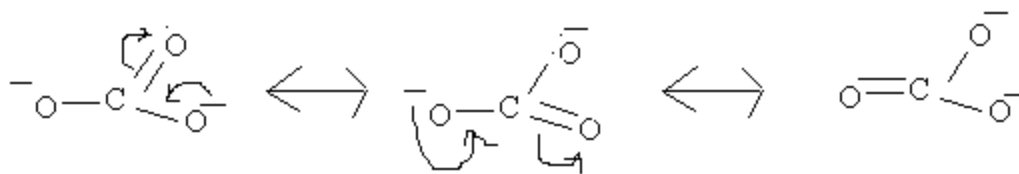
Note: Acetic acid is more acidic than ethyl alcohol because of the stability of acetate ion.

- (B)** Among resonating structures, uncharged structures are more stable than charged structure. Example:



Stability order : (a) > (b)

- (C)** Resonance hybrid having identical resonating structure is very stable and identical R.S has equal contribution. Example: CO_3^{2-} has three identical resonating structures. Application of this rule:: Calculation of bond order of C-O in CO_3^{2-}



In case of all identical R.S

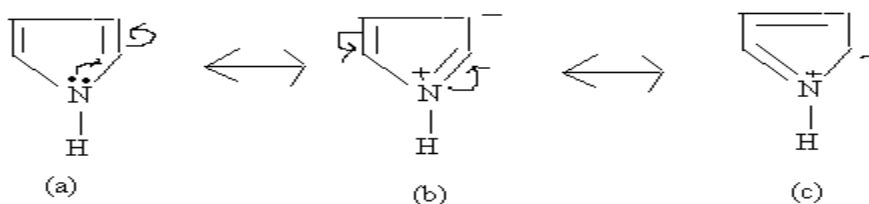
$$\text{Bond order} = \frac{\text{Total number of bonds between two atoms}}{\text{Total number of identical resonating structures}}$$

$$\text{Bond order of } \text{CO}_3^{2-} = \frac{4}{3} = 1.333$$

$$\text{Similarly bond order of } \text{PO}_4^{3-} = \frac{5}{4} = 1.25$$

(D) If charge separation takes place over a large distance, stability is reduced.

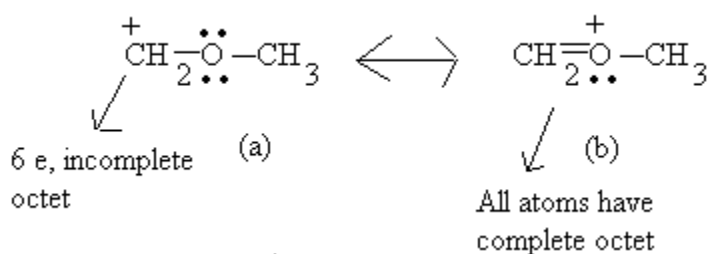
Example: Pyrrole



Stability order : (a)>(c)>(b)

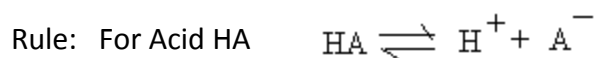
(E) Resonating structure having complete octet is more stable w.r.to R.S having incomplete octet and this octet factor predominates over other factor.

Example:



Stability order: (b) > (a)

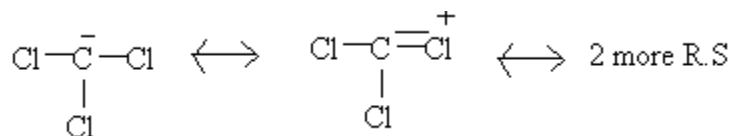
(2) Effect of resonance on acidity



More the stability of A^- , more is the acidity of HA

Example: CHCl_3 is more acidic than CHF_3

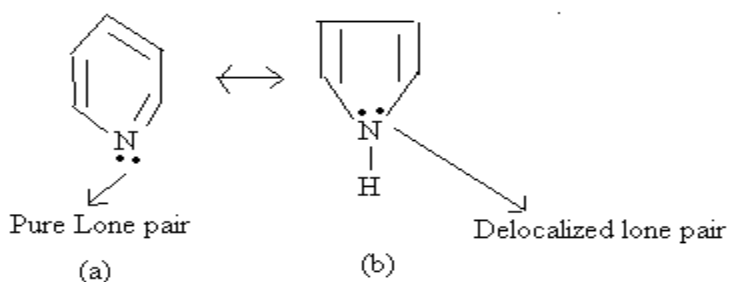
Explanation: Conjugate base of CHCl_3 i.e CCl_3^- is more stable than conjugate base of CHF_3 i.e. CF_3^- because of resonance in CCl_3^- .



No resonance in CF_3^- because of absence of vacant d-orbital in F.

(3) Effect of resonance on basicity

Rule: Basicity is directly proportional to lone lone pair availability. In presence of resonance involving lone pair, lone pair is delocalized so basicity decreases. Example:



Basicity order : (a)>(b)

(4) Effect on Electrophilicity/Nucleophilicity

Electrophilicity => Eletro (Electron)+ philicity (Loving) => Electron loving tendency.

For +vely charged system or system loving electron, in presence of resonance electrophilicity is reduced because system stabilizes by delocalization of +ve charge. Example: PhN_2^+ is a weak electrophile because of delocalization of +ve charge in the phenyl ring.

Similarly resonance affects nucleophilicity (nucleus loving tendency).

Concept of Resonance Energy:

The difference is the energy of the most stable resonating structure and the energy of resonance hybrid is called resonance energy.

Suppose resonating structure of compound A is shown as $A \longleftrightarrow B$

and A is more stable than B. Resonance energy is figuratively shown in the following figure.

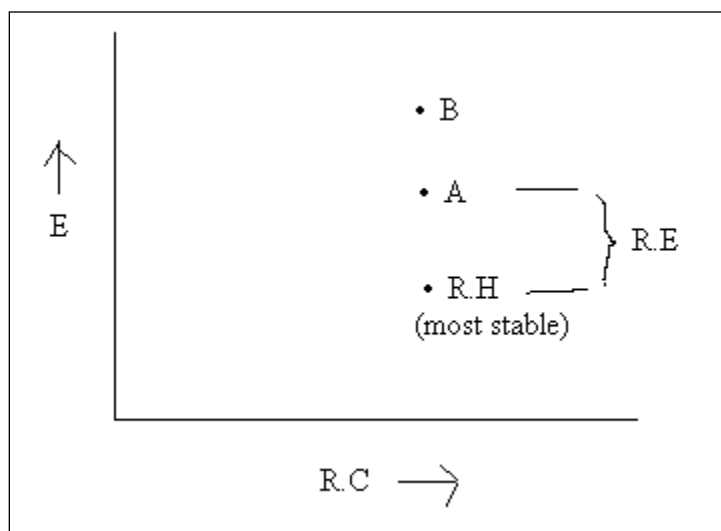
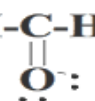
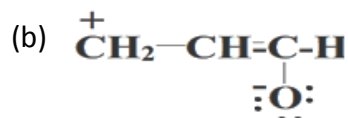


Figure 1. Plot of energy Vs Reaction co-ordinates

Problem 1. Acrolein having two canonical structures (a) $\text{CH}_2=\text{CH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$



Energy associated with one of them is 75 KJ/mol and with another is 100KJ/mol. Resonance hybrid has energy 60 KJ/mol. Find Resonance energy of acrolein.

Ans. As (a) is more stable than (b) because of charge separation in (b). Therefore

$$\text{R.E} = 75 - 60 = 15 \text{ KJ/mol}$$

(B) Inductive effect

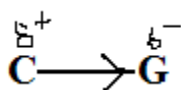
An inductive effect is an electronic effect due to the polarisation of σ bonds within a molecule or ion. It is typically due to electronegativity difference between the atoms at either end of the bond. Inductive effect can be further classified into two categories: (a) Positive inductive effect (+I effect) (b) Negative inductive effect (-I effect)

In a compound $-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{G}$

G can be more electronegative or less electronegative than C.

Negative Inductive effect (-I effect)

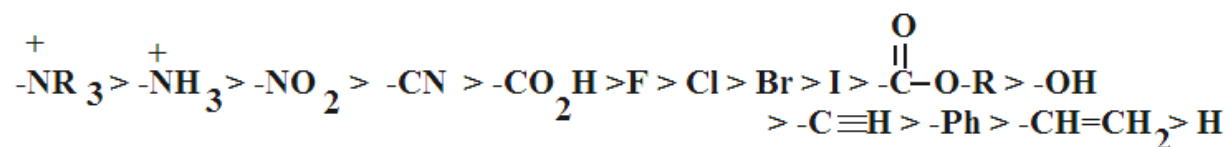
If electronegativity of $\text{G} > \text{C}$, sigma electron of C-G bond will be more attracted towards G. Hence G acts like an electron attracting group and it is said to exert -I effect.



-I effect decreases as we go away from G and after third carbon the effect is almost negligible.

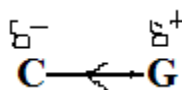
Example: Phenol is more acidic than water because of more electron-withdrawing capability of phenyl group (in phenol) compare to H (in water).

Groups having -I effect and their order



Positive Inductive effect (+I effect)

If electronegativity of G < C, sigma electron of C-G bond will be more attracted towards C. Hence G acts like an electron releasing group and it is said to exert +I effect.

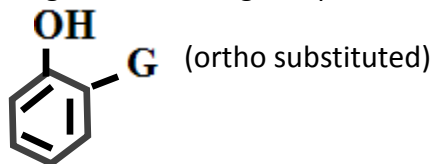


Groups having +I effect and their order



[Note: (a) Inductive effect is a permanent effect and has great impact on acidity and basicity of the compound. Therefore it is advisable to memorize the above mentioned order of +I and -I effect. (b) Resonance effect is more powerful than inductive effect (except the case of halogens) although both are permanent effect.]

Problem 1. Arrange the following compounds a,b,c in the increasing order of their acidity.



- (a) Ortho substituted
- (b) Meta substituted
- (c) Para substituted

Where G = Cl or Br

Ans: For -Cl/-Br -I effect predominates over +R effect

Considering -I effect, acidity order ortho > meta > para (because distance of OH to G is maximum in case of para and minimum in ortho).

Considering +R effect , ortho/para (+R effective), meta (+R not effective), therefore ortho=para<meta.

For halogens – L > +R. Hence acidity order will be (a)>(b)>(c)

(C) Mesomeric effect

It is also known as resonance effect but the difference between the two is, Mesomeric effect is not applicable for single bond system. For mesomeric effect (M effect), pi electron cloud is must whereas resonance can be applicable for sigma-bonded system ex. $\overset{+}{\text{CH}_2}-\ddot{\text{O}}-\text{CH}_3$ shows resonance but not mesomeric effect.

The group which shows +R effect (electron releasing) is equivalent to +M effect and the group shows –R effect (electron attracting) is equivalent to –M effect.

[Note: Resonance effect or Mesomeric effect are permanent effect and they effect the physical as well as chemical property of the compound.]

(D) Electromeric effect

It is a temporary effect and takes place between two atoms joined by a multiple bond, i.e., a double or triple bond. It occurs at the requirements of the attacking reagent, and involves instantaneous transfer of a shared pair of electrons of the multiple bonds to one of the linked atoms. It is denoted as E effect.

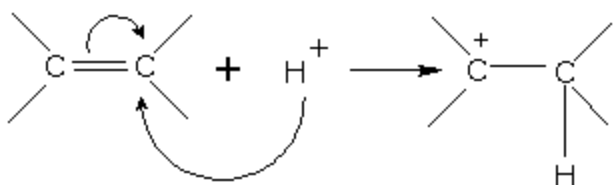
It is temporary in nature because the molecule acquires its original electronic condition upon removal of the attacking reagent.

For example, consider the carbonyl group, >C=O, present in aldehydes and ketones. When a negatively charged reagent say $:\ddot{\text{X}}^-$ approaches the molecule seeking positive site, it causes instantaneous shift of electron pair of carbonyl group to oxygen (more electronegative than carbon).

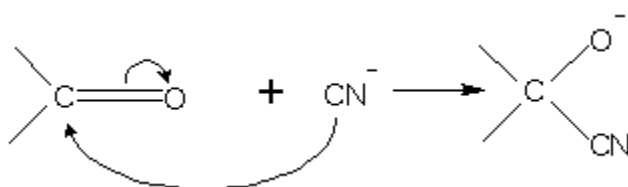


+E effect and –E effect

When the transfer of electrons takes place towards the attacking reagent, it is called + E (positive electromeric) effect. For example,



When the transfer of electrons takes place away from the attacking reagent, it is called, -E (negative electromeric) effect. For example,



[Note: Electromeric effect affects the chemical reactivity of molecules but has no effect on physical property]

(E) Inductomeric effect

It is a temporary effect and takes place in sigma-bonded system. In presence of attacking reagent, transfer of sigma electron cloud takes place more readily.

Example: $R-O \leftarrow H + B^-$ in presence of base (B), sigma electron transfer takes place faster.

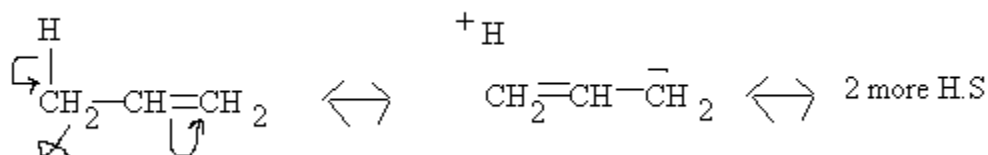
[Note: Like electromeric effect, inductomeric effect affects on chemical property but not on physical property.]

Difference between Electromeric effect and Inductomeric effect:

Electromeric effect takes place in π -bonded system, whereas Inductomeric effect takes place in sigma-bonded system.

(F) Hyperconjugation

It is a phenomenon in which system having $C=C/C^+/C^-$ etc. and w.r.to all α -carbon should have at least one hydrogen between. α -C and α -H is cleaved and delocalization of electron takes place. It is also called *no bond resonance*. Example: Propene $CH_3-CH=CH_2$



H.S => Hyperconjugative structure

Explanation with experimental observation: $\text{CH}_3\text{---}^{\text{a}}\text{CH}=\text{CH}_2^{\text{b}}$

(i) Bond length of b > pure C=C bond length

(ii) Bond length of a < pure C-C bond length

It means b must have some sigma bond character and a having pi bond character.

Note: As in hyperconjugation cleavage of sigma-bond takes place so it is thermodynamically less favourable w.r.to pure resonance. Hence Resonance effect predominates over hyperconjugation.

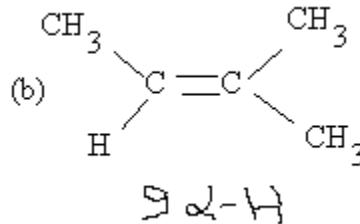
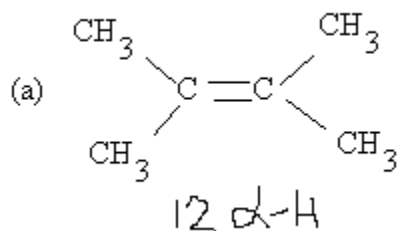
Effect of Hyperconjugation:

(i) Stability of carbocation and free radicals

The order of stability of carbocation is as follows: Tertiary > Secondary > Primary. This can be explained by hyperconjugation. Tertiary carbocation $\text{H}_3\text{C---C}^+(\text{CH}_3)_2$ has 9 α -H, Secondary carbocation $\text{H}_3\text{C---C}^+(\text{CH}_3)\text{H}$ has 6 α -H and primary carbocation $\text{H---C}^+(\text{CH}_3)\text{H}_2$ has only 3 α -H.

Similarly stability of free radicals can also be explained.

(ii) **Stability of alkene** : More alpha-H in alkene more stable. In other words more substituted alkene are more stable.



Stability order (a) > (b)

(iii) Heat of hydrogenation

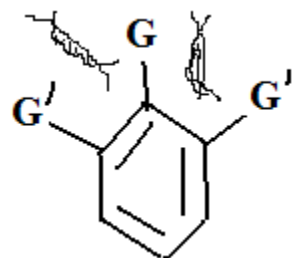
Rule: Stability of alkene is inversely proportional to heat of hydrogenation.

Hence Hyperconjugation => stability of alkene => Heat of hydrogenation

[Note: Hyperconjugation is a permanent effect. It is less powerful than resonance and more powerful than inductive effect.]

(G) Effect of Inertia/SIR (Steric effect of repulsion)

For resonance to occur, all the groups should be in the same plane i.e. molecule should be coplanar. For the system, if center bulky group is surrounded by two other bulky groups, center group experiences steric crowding and to minimize this, it goes out of plane. Therefore center group can't participate in resonance. Hence resonance is inhibited by steric effect. This is called SIR (steric effect of repulsion).

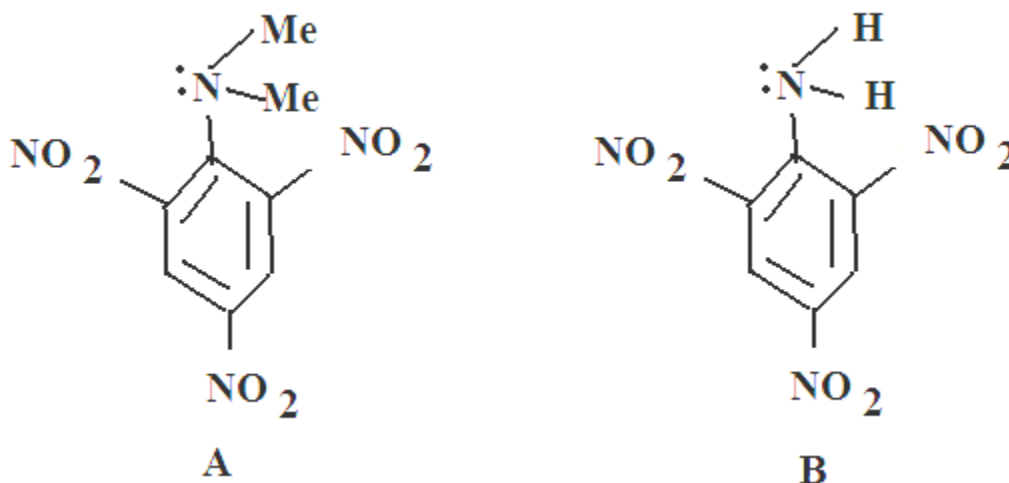


System showing SIR

If $G \Rightarrow -\text{SO}_3\text{H}, -\text{NMe}_2, -\text{NO}_2, -\text{I}, -\text{Br}, -\text{CMe}_3$ and $G \perp G', \parallel$ SIR is must.

If $G = -\text{OH}, -\text{NH}_2, -\text{CH}_3, -\text{F}, -\text{Cl}$ No SIR takes place.

Problem: A is 40000 times stronger base than B. Explain.



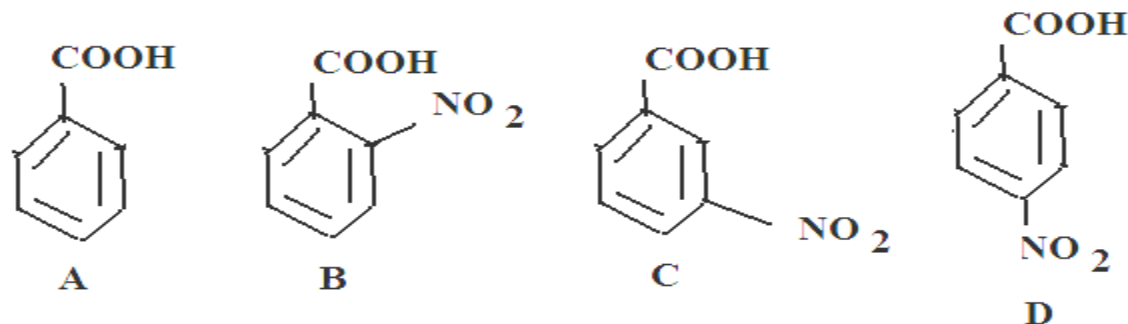
Explanation: SIR takes place in A, so lone pair NMe_2 goes out of plane and it does not participate in resonance. In case of B, lone pair is delocalized in the ring. Hence basicity i.e. lone pair availability in case of $A \gg \gg B$.

(H) Ortho effect

An ortho-substituted acid (take benzoic acid as an example) is more acidic than the meta or para-substituted form. Why?

Explanation: In presence of ortho derivative extent of resonance (due to some non-coplaner because of SIR) is reduced, so participation of -OH group with $\overset{\text{O}}{\parallel}{\text{C}}-\text{O}$ is more so acidity increases.

Example:



B is more acidic than A, C or D.

Acidity and Basicity

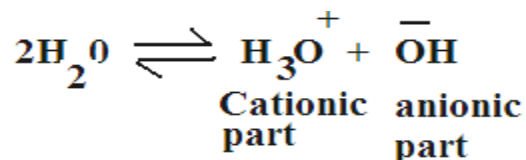
There are basically four theories to describe acids and bases:

- (i) Solvent system theory
- (ii) Bronsted and Lowry theory
- (iii) Lewis theory
- (iv) HSAB (Hard soft acid base) theory

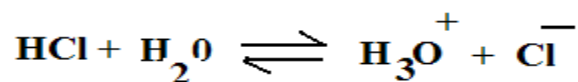
(i) Solvent system theory: A compound which gives the cationic part of the solvent is called acid and the compound which gives anionic part of the solvent is called base either with self ionization or reaction with solvent.

(a) Considering H_2O as solvent

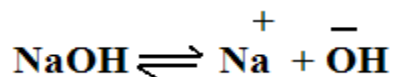
Compounds which ionize to give H^+ are acid and which ionize to give OH^- are called Bases. This is also known as **Arrhenius theory of acid-base**.



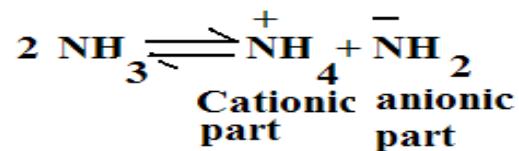
Compounds acts as acid in H_2O



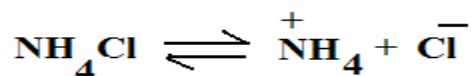
Compounds acts as base in H_2O



(b) Considering NH_3 as solvent

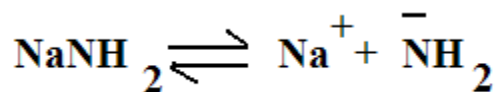


Compounds acts as acid in liquid NH_3



NH_4Cl gives cationic part of the solvent, so it is acid in liquid NH_3

Compounds acts as base in liquid NH_3



NaNH_2 gives anionic part NH_2^- , hence it is base.

(ii) Bronsted and Lowry theory

Acids are proton donor and Bases are proton acceptor



The conjugate base is the ion or molecule remaining after the acid has lost a proton, and the conjugate acid is the species created when the base accepts the proton. The reaction can proceed in either forward or backward direction; in each case the acid donates a proton to the base.

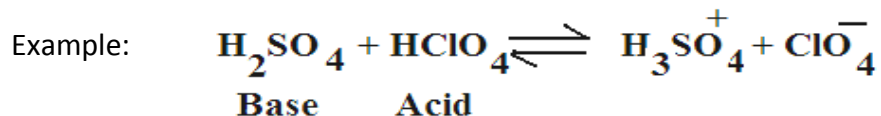
In the reaction between acetic acid $\text{CH}_3\text{CO}_2\text{H}$, and water, H_2O , water acts as a base and acetic acid as acid.



[Note: Substance which can act like acid and base both is called amphoteric. Example: Water. Water can act as acid in liquid ammonia solution and like base in acetic acid]

Problem: Can H_2SO_4 act as base? If yes, give an example.

Ans. Yes, H_2SO_4 can act as a base when react with stronger acid.



Acidity of Hydracids:

(a) Arrange the following compound in the decreasing order of their acidity

HF, HCl, HBr, HI

Ans: F, Cl, Br, I belong to same group with electronegativity $F > Cl > Br > I$. Therefore HF should be maximum acidic but acidity of HF is minimum. Why?

Rule: In the same group size factor is predominant than electronegativity (-I effect) and in the same period electronegativity factor predominates over size factor.

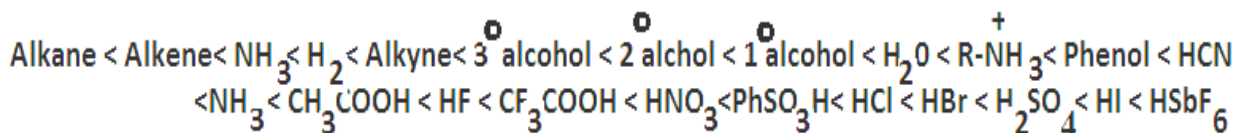
Size of $I > Br > Cl > F$, therefore Acidity order $HI > HBr > HCl > HF$

(b) Arrange the following compound in the increasing order of their acidity

CH_4 , NH_3 , H_2O , HF

Ans: In the same period electronegativity factor (-I effect) predominates. Hence acidity order $CH_4 < NH_3 < H_2O < HF$

Generalized acidity order:



[Note: Students are advised to memorize the above order of acidity order.]

Leveling effect: The strength of hydracids would be equal in presence of solvent having high basic character. For example: In presence of ammonia HI, HBr, HCl and HF all will have same acidity because all are 100% ionized and NH_3 levels the strength of acid. Similarly H_2O levels strong inorganic acids.

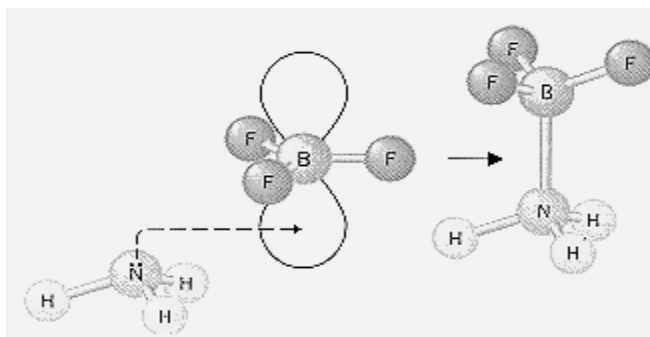
(iii) Lewis theory

Acids are acceptor of electron in either lone pair or π -electron and bases are donor of π -electron.

Hence Electrophiles are lewis acid and nucleophiles are lewis base.

Example: BF_3 as lewis acid

BF_3 is a trigonal-planar molecule because electrons can be found in only three places in the valence shell of the boron atom. As a result, the boron atom is sp^2 hybridized, which leaves an



empty $2p_z$ orbital on the boron atom. BF_3 can therefore act as an electron-pair acceptor, or Lewis acid. It can use the empty $2p_z$ orbital to pick up a pair of nonbonding electrons from a Lewis base to form a covalent bond. BF_3 therefore reacts with Lewis bases such as NH_3 to form acid-base complexes in which all of the atoms have a filled shell of valence electrons, as shown in the figure 2.

[Note: Basicity Vs Nucleophilicity: If attacking sight is same then basicity order=nucleophilicity order.]

Problem: Arrange the following compound in the increasing order of their basicity and nucleophilicity.

(a) Pyrrole (b) Pyridine

Ans: Basicity order (b)>(a)

Nucleophilicity order (a)>(b).

Explanation: Basicity order (b)>(a), because of delocalization lone pair in pyrrole. Nucleophilicity order (a)>(b), because in pyrrole electron density in ring is more, hence pyrrole is better nucleophile than pyridine.

(iv) HSAB theory (Hard soft acid-base theory)

Lewis acid can be categorized into 2 parts: (a) Hard acid (b) Soft acid

Characteristic of Hard acid/Base: Small size, high charge density, low polarizability, high electronegativity. Examples of hard acids are: H^+ , Li^+ , Na^+ , Ca^{2+} , Al^{3+} , BF_3 etc... Examples of hard bases are: OH^- , F^- , Cl^- , NH_3 , CH_3COO^- , CO_3^{2-} etc.

Characteristic of Soft acid/Base: Large size, low +ve charge density, high polarizability, low electronegativity. Examples of soft acids are: Cu^+ , Ag^+ , Au^+ , Pb_2^+ , Bi_3 etc... Examples of soft bases are: H^- , R_3P , SCN^- , I^- etc..

The gist of this theory is that *soft acids react faster and form stronger bonds with soft bases*, whereas *hard acids react faster and form stronger bonds with hard bases*.

Application of the theory:

Problem: AgI_2^- is stable but AgF_2^- is unstable. Explain.

Ans: Ag^+ -> Soft acid, I^- -> Soft base. It means soft-soft combination. But F^- -> hard base, therefore soft-hard combination. Hence AgI_2^- is stable but AgF_2^- not.

Isomerism

Isomerism: There are some compounds which have the same molecular formula but different physical and chemical properties. They are called as isomers and this phenomenon is called isomerism.

Types of isomerism: Two types: (A) Structural isomerism and (B) Stereoisomerism.

(A) Structural Isomerism: Compounds having the same molecular formula but different structures are structural isomers.

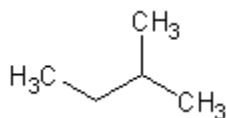
The various types of structural isomerism are:

- **Chain isomerism:** Similar molecular formula but different carbon skeletons.

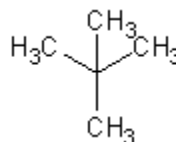
Ex. Pentane(C_5H_{12}) has three isomers



Pentane



2-Methylbutane
(Isopentane)

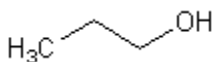


2,2-Dimethylpropane
(Neopentane)

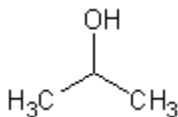
Problem: Find the no. of chain isomers in Butane (C_4H_{10}) and Hexane (C_6H_{14}).

- **Position Isomerism:** Same structure of carbon chains but differ only in the positions of functional group or the multiple bonds.

e.g.



Propan-1-ol

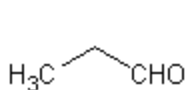


Propan-2-ol

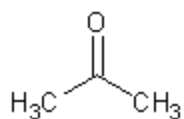
Problem: Find the position isomer of But-2-ene, 2-Pentanone, o-Xylene

- **Functional Isomerism:** Same molecular formula but different functional groups.

e.g. C_3H_6O represents an aldehyde and a ketone as shown below



Propanal

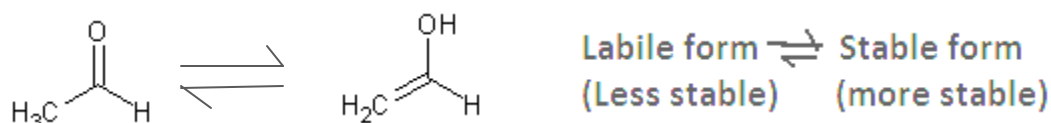


Propanone

Problem: Find the Functional isomers of Ethanol, Propanoic acid, 1,3-Butadiene, Nitroethane, Propanamine, Ethanenitrile and Benzyl alcohol.

- **Metamerism:** This is because of the different alkyl groups on either side of functional group. e.g. $\text{CH}_3\text{OC}_3\text{H}_7$ and $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$

- **Tautomerism:** It is a phenomenon in which isomers are in dynamic equilibrium. Example:

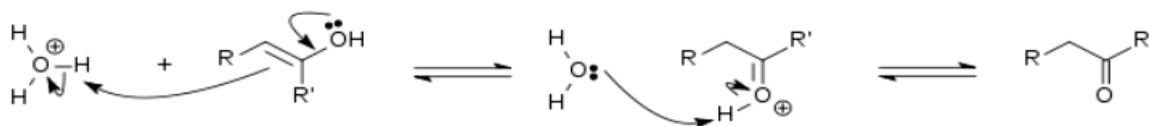


Overall reaction and reaction mechanism for keto-enol tautomerism are shown below:

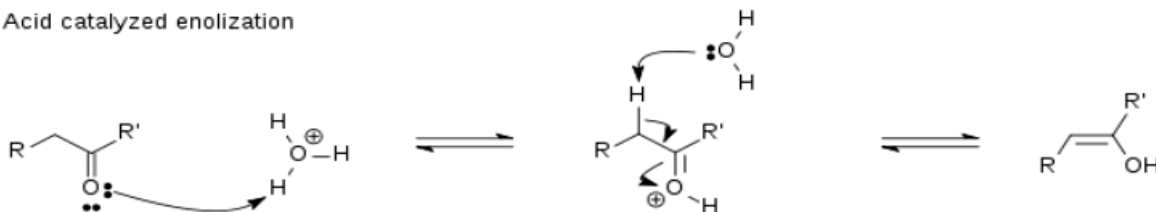
Overall reaction:



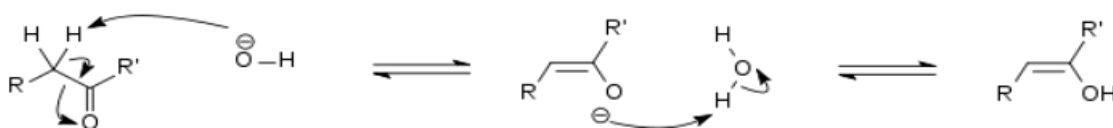
Reaction mechanism



Acid catalyzed enolization

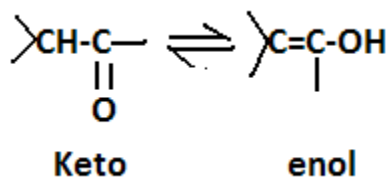


Base catalyzed enolization

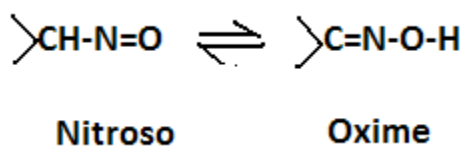


System showing tautomerism:

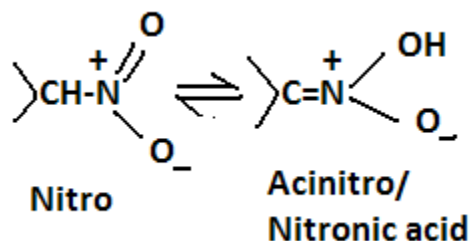
(i) Keto-enol system



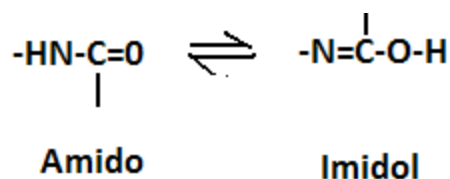
(ii) Nitroso-oxime system



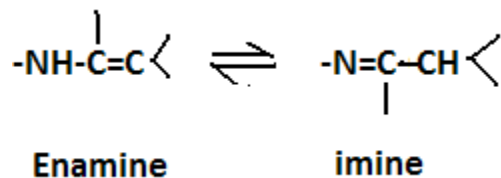
(iii) Nitro-Acinitro



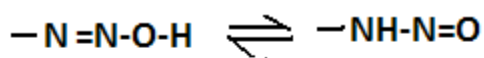
(iv) Amido-Imidol system



(v) Enamine-Imine system



(vi) Nitroso amine system

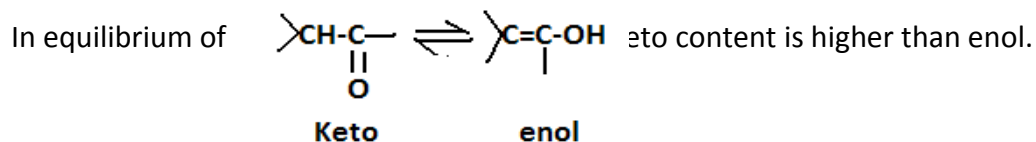


Nitroso amine system

In addition to above mentioned tautomerism, there are other systems also which show tautomerism. For example: azo system, triazen system, 3 C-system etc.

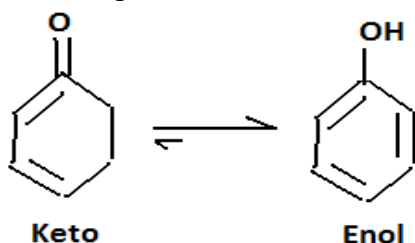
Rules to decide Keto-enol content:

- (i) In case of straight chain system keto form is more stable than enol form. Therefore keto form will have higher content in the equilibrium mixture. Example:



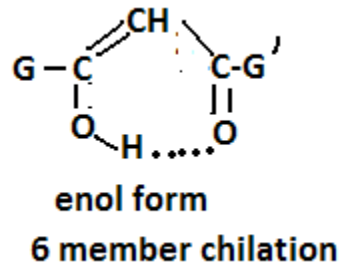
- (ii) If at equilibrium, enol form gains aromaticity then enol form would be more stable than keto form and will have higher content.

Example:



In this reaction equilibrium shifts almost 100% in the forward direction.

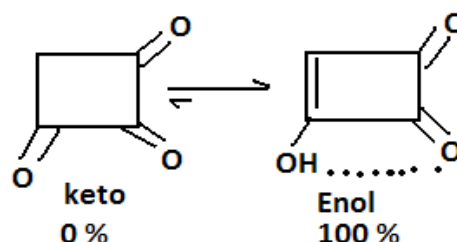
- (iii) System of type $\text{G-C(=O)-CH}_2\text{-C(=O)-G'}$ enol content is high. This is because of H-bonding in enol form having 6 member chilation.



Problem: Triketo form of cyclobutene has 100% enol content. Explain.

Ans. Keto-enol tautomerism of triketo form of cyclobutene is shown below:

During enolization aromaticity is gained and also presence of intra molecular H-bonding makes the enol form highly stable.



[Note: Tautomerism can be divided into two parts:

(a) Cationotropy (Migration of cation during tautomerism) (b) Anionotropy (Migration of anion during tautomerism)]

- **Ring chain Isomerism:** same molecular formula but possessing cyclic and open chain structures.
e.g. Propene and Cyclopropane

Problem: Find the ring chain isomers of But-1-ene and But-2-ene.

Problem: Find the structural isomers for C_3H_6O including the tautomers also.

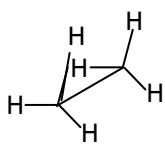
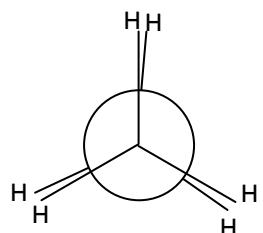
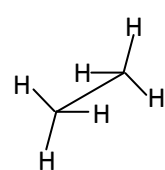
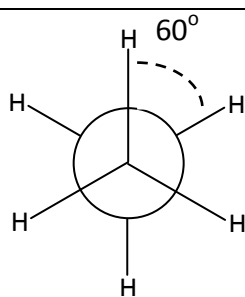
(B) Stereoisomerism:

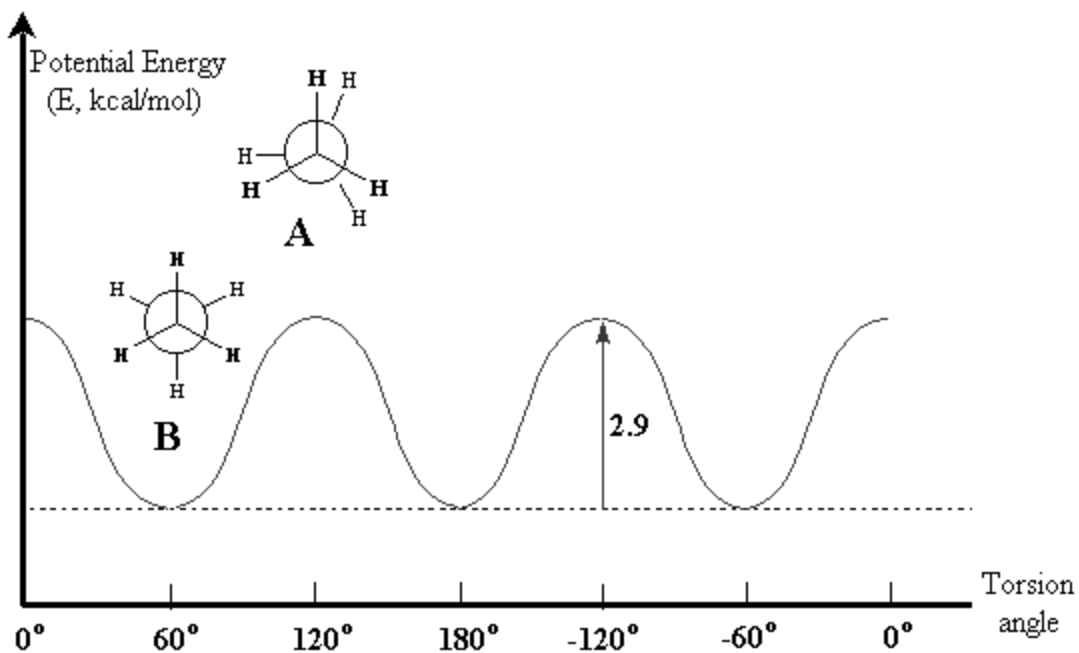
Isomers which have the same structures but differ in the relative arrangements of atoms or groups in space are called stereoisomers. These are of three types

(a) Conformational Isomerism (b) Geometrical Isomerism and (c) Optical Isomerism

(a) Conformational Isomerism: The isomers obtained because of the rotation about a single bond are conformational isomers.

Conformations of ethane: Keeping one methyl group fixed, when we rotate the ethane molecule about the C-C bond, there are infinite number of conformers possible. But there are two extreme conformations, staggered and eclipsed.

A. Eclipsed		B. Staggered	
			
Sawhorse projection	Newmann projection	Sawhorse projection	Newmann projection



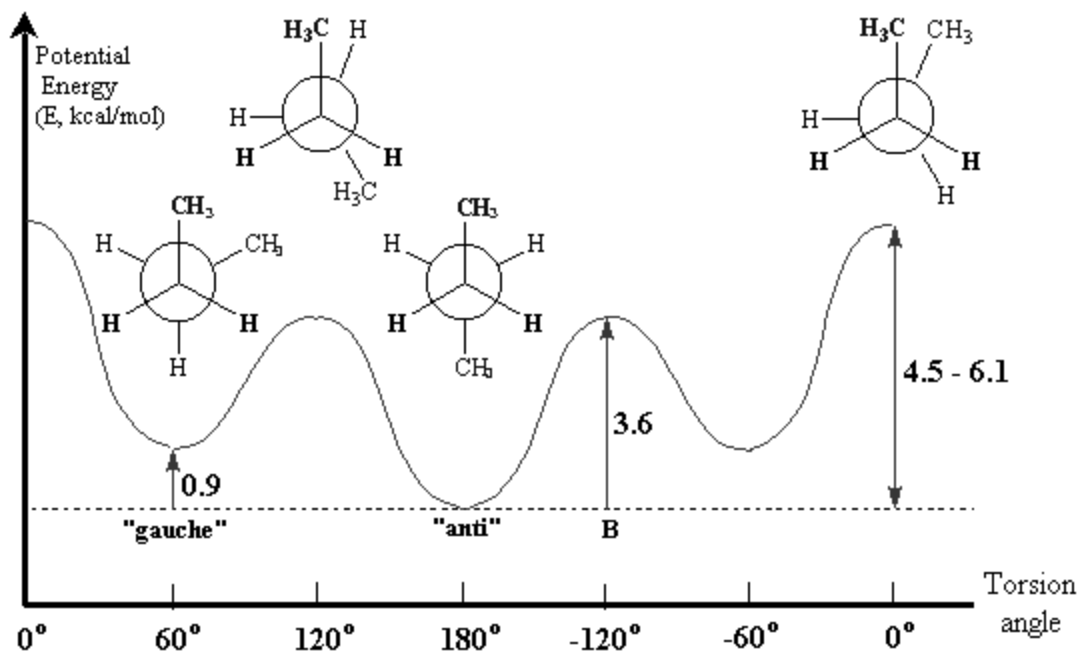
Potential energy of ethane as a function of the torsion angle.

Staggered is more stable than eclipsed.

[Note: In staggered conformation of ethane torsion/Dihedral angle (Angle between H-C-C plane and C-C-H plane = 60°). In Eclipsed conformation torsion angle = 0°]

Conformations of n-Butane:

Staggered or anti	Gauche or skew	Partially eclipsed	Fully eclipsed



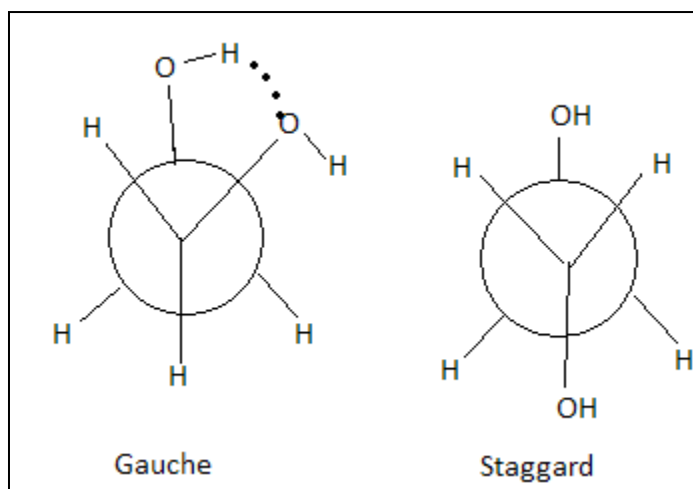
Potential energy of butane as a function of the torsion angle.

The decreasing order of the stability of these conformations is as follows:

Staggered (anti) > gauche > partially eclipsed > fully eclipsed

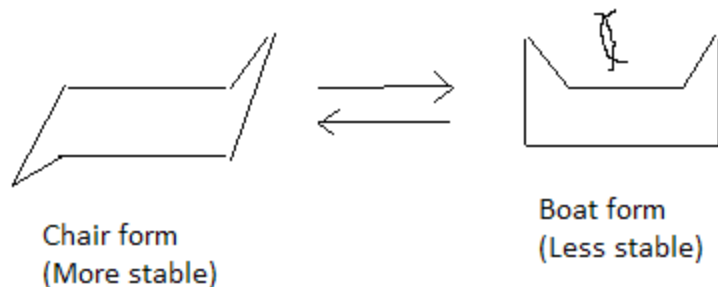
Problem: Can gauche be more stable than staggard? If yes explain with example.

Ans. Yes, Gauche can be more stable than staggard if there is H-bonding or strong electrostatic attraction in gauche form. Example: In case of ethylene glycol gauche form is more stable than staggard.



Conformers of Cyclohexane (boat-chair form):

The cyclohexane ring can take many shapes due to rotation around C-C bonds. The chair form and boat form are the extreme cases shown below

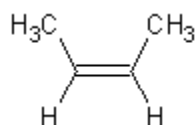


Each carbon atom of cyclohexane is bonded with 2 hydrogen atom. The bond to one of it lies in the plane of ring called Equatorial hydrogen and another C-H bond is parallel to the axis, this hydrogen is called axial hydrogen.

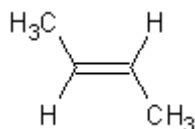
Chair form is more stable than boat form because of steric hindrance in boat form.

(b) Geometrical Isomerism: The compounds containing a double bond have two types of bonds, σ -bond and π -bond. π -bond forms because of the lateral overlap of p-orbitals. So rotation about double bond is difficult as it will break the π -bond (which requires high energy). So the groups attached to the Carbon get fixed. These types of stereoisomers which have the same structural formula but differ in the spatial arrangement of atoms around the double bond are called **geometrical isomers**. The isomer in which the two similar atoms/groups lie on the same side of the double bond is called the **cis-isomer** while that isomer in which the two similar atoms/groups lie on the opposite side of the double bond is called the **trans-isomer**.

e.g.



Cis-But-2-ene



trans-But-2-ene

Compounds of type $abC=Cab$, $abC=Cad$ and $abC=Cde$ exhibit geometrical isomerism.

Problem: The dipole moment of trans-isomer is less than cis-isomer. Why? (Figure out yourself)

Compounds containing C=N and N=N also shows geometrical isomerism because of the lone pairs on Nitrogen atom.

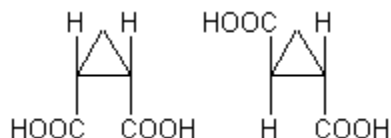
e.g.



Here syn and anti are used instead of cis and trans.

Geometrical Isomerism can also be shown where there is no double bond but rotation is hindered.

e.g.



Optical Isomerism:

There are some compounds which can rotate the plane of polarized light and so are called optically active compounds. Rotation can be either on the left side or on the right side.

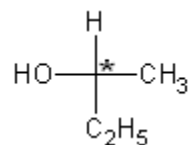
Isomer which rotates the plane of polarized light to the right is called dextrorotatory while the other which turns it to the left is called laevorotatory.

How to find the optical isomers of a molecule? For that Lets discuss chirality first.

Chiral objects (molecules). An object or molecule is said to be chiral if it is not superimposable on its mirror image. For examples, some letters of alphabet such as P, F, R, G, J, shoe, glove, your hand etc.

The molecules or objects which are superimposable on its mirror image are called achiral objects. e.g. letters of alphabets such as A, B, C, D, E etc.

Chiral carbon is the carbon atom which is attached to 4 different atoms or groups and so it is not superimposable on its mirror image.



Try-1: Find the alkane with least Carbon atoms which contains a chiral carbon.

Can we say that chirality of carbon atom is the best way to find if the compound is optically active or not?

Concept of specific rotation: The specific rotation of a chemical compound $[\alpha]$ is defined as the observed angle of optical rotation α when plane-polarized light is passed through a sample with a path length of 1 decimeter and a sample concentration of 1 gram per 1 millilitre. The specific rotation of a pure material is an intrinsic property of that material at a given wavelength and temperature. The formal unit for specific rotation values is $\text{deg cm}^2 \text{g}^{-1}$. A negative value means levorotatory rotation and a positive value means dextrorotatory rotation.

For pure liquids:
$$[\alpha]_{\lambda}^T = \frac{\alpha}{l \times d}$$

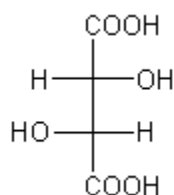
Where l is the path length in decimeters, and d is the density of the liquid in g/mL , for a sample at a temperature T (given in degrees Celsius) and wavelength λ (in nanometers).

For solutions, a different equation is used:
$$[\alpha]_{\lambda}^T = \frac{100\alpha}{l \times c}$$

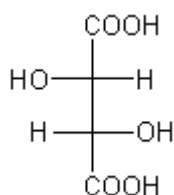
Where l is the path length in decimeters and c is the concentration in g/100mL , for a sample at a temperature T (given in degrees Celsius) and wavelength λ (in nanometers).

Enantiomers: Stereoisomers which are non-superimposable mirror images of each other are called enantiomers and the phenomenon is called enantiomerism. Enantiomers have the same physical and chemical properties but they are different towards their action on plane polarized

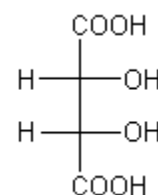
light. One enantiomer rotates the plane of polarized light to the right (dextrorotatory) while the other will turn it to the left (laevorotatory) and with same angle.



(I)



(II)



(III)

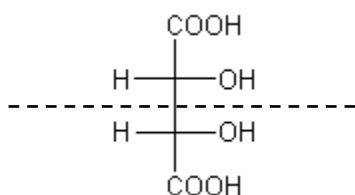
(I,II) are enantiomers.

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

From the figures (I), (II) and (III) we can say that (I,II) and (I,III) are diastereomers.

[Note: Diastereomers are optically active compounds.]

Compounds which contain chiral carbon atoms but do not show optical activity are called **meso compounds**. This is because of presence of plane of symmetry in the compound. See (III)



It has a plane of symmetry, so the mirror image is superimposable.

So chirality of carbon atom is not the criteria for optical activity. It is the chirality of molecule which decides its optical activity.

So what is the criterion for that? It is the lack of symmetry in the compounds.

The compounds which possess centre of symmetry, axis of symmetry, plane of symmetry are not optically active.

Let see the elements of symmetry here.

Plane of symmetry: You have already seen this in the meso compounds. It is the plane through the molecule which divides the molecule into two equal parts. One part is the mirror image of the other.

Axis of symmetry: It is a line through which if molecule is rotated, the molecule will repeat itself before complete rotation.

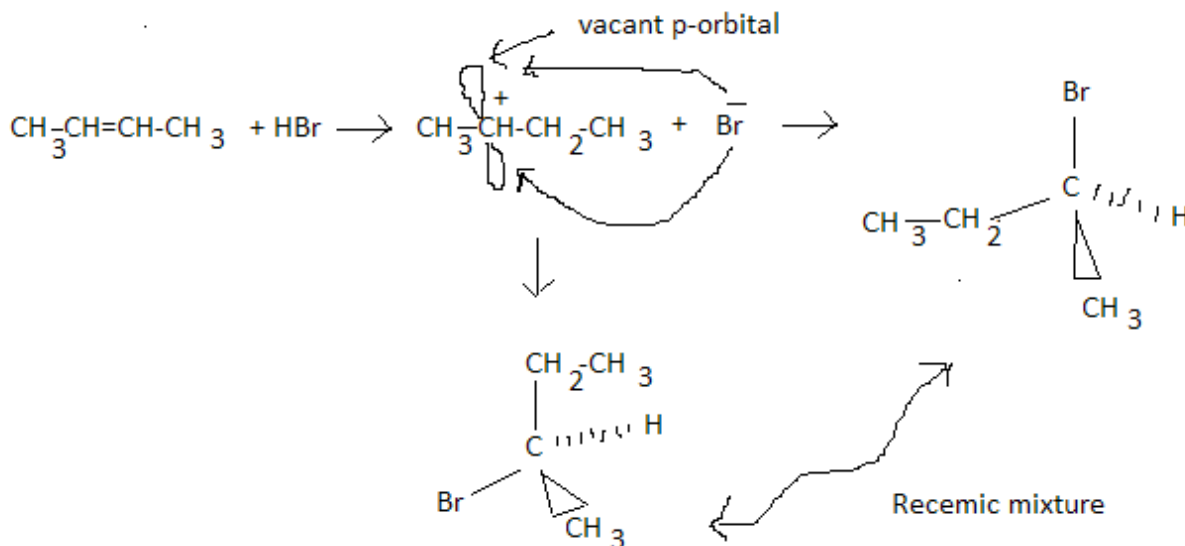
Centre of symmetry: It is a point in the molecule through which if any line is drawn, it will have similar groups on both sides of the point.

So the absence of these elements of symmetry is required for a compound to be optically active.

Concept of racemic mixture: A racemic mixture is one that has equal amounts of left- and right-handed enantiomers of a chiral molecule. A racemic mixture is optically inactive, meaning that it does not rotate plane-polarized light. This is because the two isomers rotate plane-polarized light in opposite directions, and they optically cancel out.

Problem: Addition of HBr to 2-butene gives product which does not rotate plane polarized light. Explain.

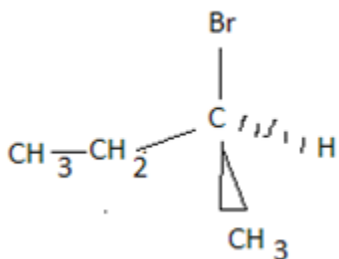
Ans. Reaction of HBr to 2-butene is shown below



Since the product formed is racemic mixture, which is optically inactive. Therefore, the product does not rotate plane polarized light.

R & S configuration:

Wedge Dash formula:

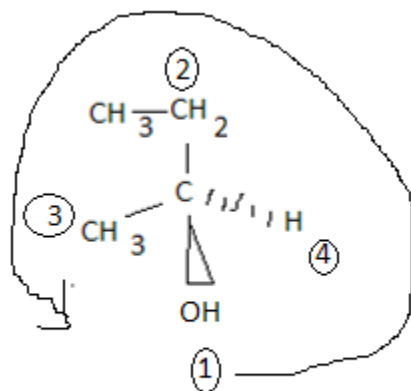


////// indicates away from the viewer and \blacktriangle indicates towards the viewer. R&S system for nomenclature of enantiomers in wedge and dash formula. It is also called Cahn-Ingold-prelong system.

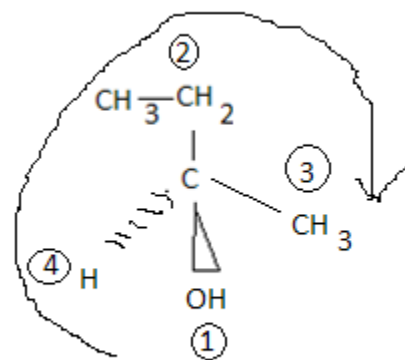
R stands for rectus, a latin word for right and S stands for sinister, a latin word for left.

Rules to decide R and S:

- (i) Groups around the stereocenter are arranged in their order of priority. Higher atomic number will be given high priority. We will see directly attached element with stereocenter and so-on.
- (ii) Lowest priority group should be away from the viewer.



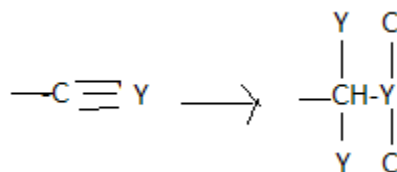
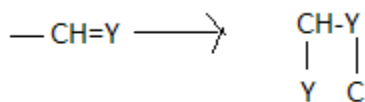
S-2-Butanol



R-2-Butanol

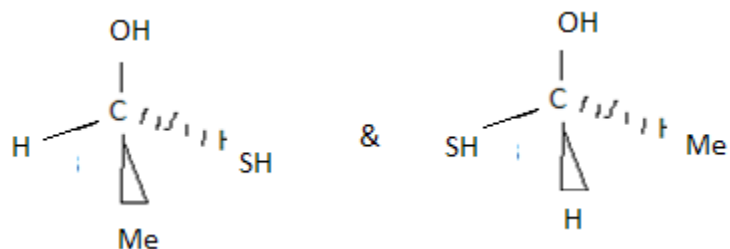
Note: When contradiction occurs then we select higher priority on them and then compare. Priority is given on the basis of atomic number. Higher atomic number should be ranked first.

- (iii) While giving priority double and triple-bond groups will be treated as shown below:



- (iv) If lowest priority group is not away from the viewer, bring it to that position by interchanging the position of groups. By interchanging one pair of group (or odd number of changing) about the chiral center we will its opposite configuration (i.e. its enantiomer) and by interchanging two pairs of group (or even number of changing) across the chiral center we will get identical compound.

Problem: Check whether the following compounds are pair of enantiomers or not?



Hint: Follow rule no. (4). Ans: No, they are identical compounds.