



Knowledge... Everywhere

Chemistry

General Organic Chemistry

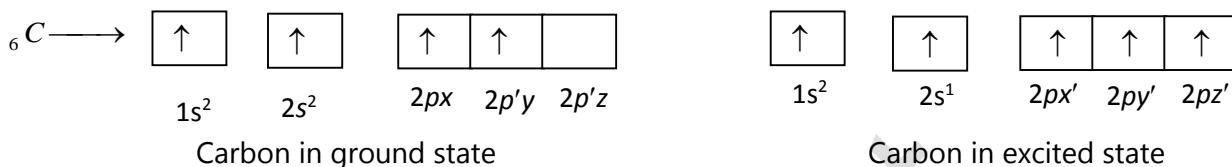
Table of Content

1. Bonding in organic compounds.
2. Hybridization in organic compounds.
3. Dipole moment of organic compounds.
4. Steric effect.
5. Intermolecular forces.
6. Mechanism of organic reactions.
7. Electronic displacement in covalent bonds.
8. Cleavage (fission or breaking) of covalent bonds.
9. Reaction intermediates.
10. Attacking reagents.
11. Types of organic reactions.
12. Isomerism.
13. Constitutional or structural isomerism.
14. Geometrical or cis-trans isomerism.
15. Optical isomerism.
16. Conformational isomerism.

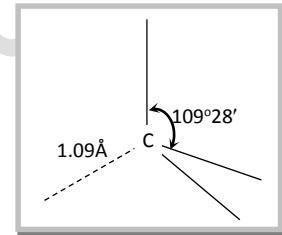


The chemical properties of an element depend on the electronic configuration of the outer shell. Carbon has four electrons in its outer shell.

According to the ground state electronic configuration of carbon, carbon is divalent. Tetravalency of carbon can be explained by promoting one $2s$ - electron to a $2p_z$ orbital. Some energy must be supplied to the system in order to effect this promotion. This promotion requires energy about 96 kcal/mol, but this energy is more than regained by the concurrent formation of chemical bonds.



The four valencies of carbon atom are similar and they are symmetrically arranged around the carbon atom. According to Le Bel and Van't Hoff the four valencies of carbon do not lie in one plane. They are directed towards the corners of a regular tetrahedron with carbon atom at the center and the angle between any two valencies is $109^\circ 28'$.



1. Bonding in organic compounds.

The organic compounds are carbon compounds consisting of one or more carbon atoms. Carbon must form only covalent bonds, i.e., it should share its valency electrons with other atoms.

According to the modern concept, a covalent bond is formed between two atoms if there is an overlapping of an atomic orbital of one atom with an atomic orbital of another atom. The overlapping is possible by two ways,

(1) **End to end overlapping:** This type of overlapping is possible between $s - s$, $s - p_x$ and $p_x - p_x$ atomic orbitals. The molecular bond formed is termed as sigma (σ) bond.

(2) **Sidewise or parallel or lateral overlapping:** Such overlapping is possible between $p - p$ atomic orbitals. The molecular bond formed is termed as $p\pi(\pi)$ bond.



σ -Bond	π -Bond
Formed by End to End overlap of AO's.	Formed by lateral overlap of p -orbitals.
Has cylindrical charge symmetry about bond axis.	Has maximum charge density in the cross-sectional plane of the orbitals.
Has free rotation	No free rotation, i.e., frozen rotation
Low energy	Higher energy
Only one σ bond can exist between two atoms,	One or two π bonds can exist between two atoms.
Sigma bonds are directional. Thus the geometry of the molecule depends on the σ bonds.	π Bonds are not directional. Geometry of the molecule not depends on π bond.
Area of overlapping is higher hence bond is stronger.	Area of overlapping is small hence bond is weaker.
σ Bond can have independent existence.	π Bond always exist along with a σ bond and π bond is formed after the formation of σ bond.

2. Hybridization in Organic Compounds

(1) The process of mixing atomic orbitals to form a set of new equivalent orbitals is termed as **hybridization**. There are three types of hybridization encountered in carbon atom. These are,

- (i) **sp^3 Hybridization** (involved in saturated organic compounds containing only single covalent bonds),
- (ii) **sp^2 Hybridization** (involved in organic compounds having carbon linked by double bonds) and
- (iii) **sp Hybridization** (involved in organic compounds having carbon linked by a triple bonds).

Type of Hybridization	Number of orbitals used	Number of unused p-orbitals	Bond	Bond angle	Geometry	% s-character
sp^3	1s and 3p	Nil	Four - σ	109.5°	Tetrahedral	25 or 1/4
sp^2	1s and 2p	One	Three - σ One - π	120°	Trigonal	33.33 or 1/3
sp	1s and 1p	Two	Two - σ Two - π	180°	Linear	50 or 1/2



Preparation Classes



Counseling Sessions



Online Test



Free Trial Classes



www.testprepkart.com



info@testprepkart.com

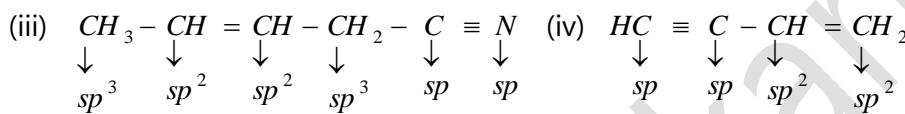
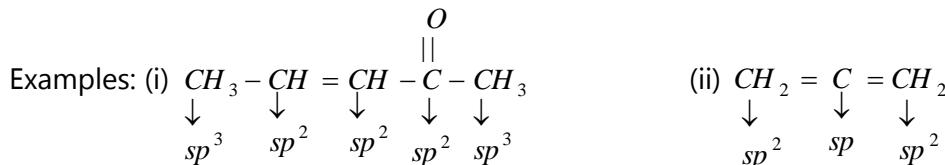


+91 - 8800 1234 92

(2) **Determination of hybridization at different carbon atoms:** It can be done by two methods,

(i) **First method:** In this method hybridization can be known by the number of π - bonds present on that particular atom.

Number of π - bond/s	0	1	2
Type of hybridization	sp^3	sp^2	sp



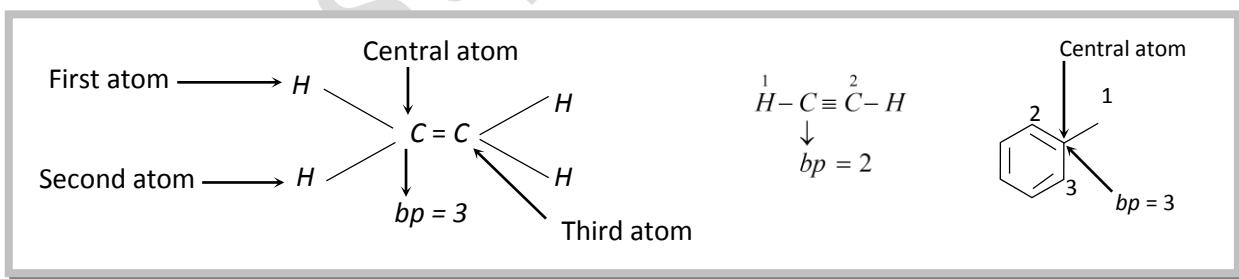
Note: In diamond carbon is sp^3 hybridized and in graphite carbon is sp^2 hybridized.

This method cannot be used for those atoms of the molecule which have positive charge, negative charge or odd electron.

(ii) **Second method:** (Electron pair method)

$ep = bp + lp$; where ep = electron pair present in hybrid orbitals, bp = bond pair present in hybrid orbitals

Number of bp = Number of atoms attached to the central atom of the species



Number of lp 's can be determined as follows,

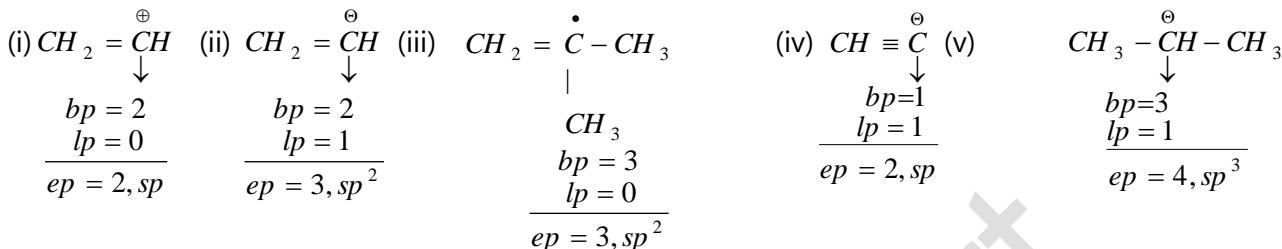
- (a) If carbon has π - bond/s or positive charge or odd electron, then lp on carbon will be zero.
- (b) If carbon has negative charge, then lp will be equal to one.

Number of electron pairs (ep) tells us the type of hybridization as follows,



ep	2	3	4	5	6
Type of hybridization	sp	sp^2	sp^3	sp^3d	sp^3d^2

Example:



(3) Applications of hybridization

(i) **Size of the hybrid orbitals:** Since s -orbitals are closer to nucleus than p -orbitals, it is reasonable to expect that greater the s character of an orbital the smaller it is. Thus the decreasing order of the size of the three hybrid orbitals is opposite to that of the decreasing order of s orbital character in the three hybrid orbitals.

$$sp^3 > sp^2 > sp$$

(ii) Electronegativity of different orbitals

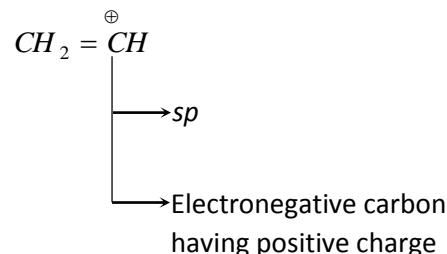
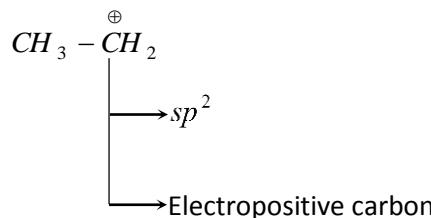
(a) Electronegativity of s -orbital is maximum.

(b) Electronegativity of hybrid orbital \propto % s -character in hybrid orbitals

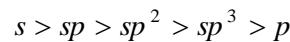
Orbital % s - character	sp	sp^2	sp^3
	50	33.33	25

s -character in decreasing order and electronegativity in decreasing order

Thus sp -hybrid carbon is always electropositive in character and sp^3 -hybrid carbon is electropositive in character. sp^2 -hybrid carbon can behave as electropositive (in carbocation) as well as electronegative (in carbanion) in character.



(c) Electronegativity of different hybrid and unhybrid orbitals in decreasing order is as follows



% s - character in decreasing order and electronegativity in decreasing order.

(iii) Bond length variation in hydrocarbons

$$\% \text{ s orbital character} \propto \frac{1}{C - C \text{ bond length}} \propto \frac{1}{C - H \text{ bond length}}$$

Bond type (C – H)	Bond length	Bond type (C – C)	Bond length
$sp^3 - s$ (alkanes)	1.112 Å	$sp^3 - sp^3$ (alkanes)	1.54 Å
$sp^2 - s$ (alkenes)	1.103 Å	$sp^2 - sp^2$ (alkenes)	1.34 Å
$sp - s$ (alkynes)	1.08 Å	$sp - sp$ (alkynes)	1.20 Å

Note: C–C bond length in benzene lies between single and double bond due to resonance. (1.40 Å).

(iv) Bond strength in hydrocarbons: The shorter the bond, the greater the compression between atomic nuclei and hence greater the strength of that bond is. Thus the bond formed by sp hybridized carbon is strongest (i.e., it has maximum bond energy) while that formed by sp^3 hybridized carbon is the weakest (i.e., it has minimum bond energy). This is evident by the bond energies of the various types of C–H and C–C bonds.

Bond type (C – H)	Bond energy (kcal/mole)	Bond type (C – C)	Bond energy (kcal/mole)
$sp^3 - s$ (in alkanes)	104	$sp^3 - sp^3$ (in alkanes)	80 – 90
$sp^2 - s$ (in alkenes)	106	$sp^2 - sp^2$ (in alkenes)	122 – 164
$sp - s$ (in alkynes)	121	$sp - sp$ (in alkynes)	123 – 199

(v) Acidity of hydrocarbons

- (a) Hydrogen present on electronegative carbon is acidic in character.
- (b) Acidity of hydrogen is directly proportional to the electronegativity of atom on which hydrogen is present.



Thus

$H-O-H$	NH_3	$CH \equiv CH$	
Electronegativity of atom in decreasing order			
Acidity of compounds in decreasing order			
(c) Acidity of hydrocarbon \propto % s-character			
$CH \equiv CH$	$CH_2 = CH_2$	$CH_3 - CH_3$	
% s-character 50	33.33	25	
pK_a	25	44	50
s- Character in decreasing order and acidity in decreasing order			

Note: Acidity $\propto K_a$ and Acidity $\propto \frac{1}{pK_a}$ ($pK_a = -\log K_a$)

Order of acidic nature of alkynes is, $HC \equiv CH > HC \equiv C - CH_3$

The relative acidic character follows the order;



Obviously, the basic character of their conjugate bases follows the reverse order, i.e.



3. Dipole moment of Organic Compounds.

(1) Due to differences in electronegativity polarity develops between two adjacent atoms in the molecule (i.e., in a bond). The degree of polarity of a bond is called dipole moment. Dipole moment is represented by μ and its unit is Debye (D).

$$\mu = e \times l$$

Where, e = magnitude of separated charge in e.s.u., l = internuclear distance between two atoms i.e., bond length in cm.

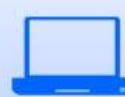
The dipole moment is denoted by arrow head pointing towards the positive to the negative end (\rightarrow).

(2) Dipole moment of the compound does not depend only on the polarity of the bond but also depends on the shape of the molecule. Dipole moment of symmetrical compound is always zero, ($\mu = 0$). Symmetrical compounds are those compounds which fulfil following two conditions,

(i) Central atom is bonded with the same atoms or groups. Examples: $H_2, BF_3, CS_2, CH_2 = CH_2, CH \equiv CH$
Symmetrical molecules

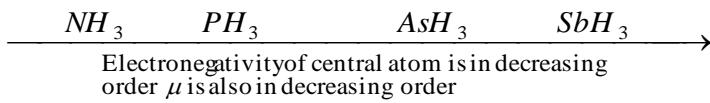
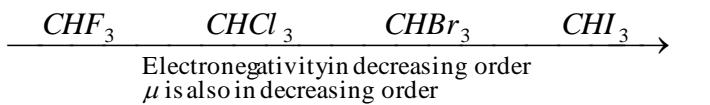
(ii) Central atom should have no lone pair of electrons.

Examples: CCl_4, CH_4, BH_3, CO_2 $H_2 O, H_2 S$
Symmetrical molecules Unsymmetrical molecules

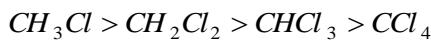


Note: Compounds which have regular tetrahedral structure has no dipole moment.

(3) $\mu \propto$ electronegativity of central atom or surrounding atoms present on the central atom of the molecule.



Note: Decreasing order of dipole moment in CH_3Cl , CH_2Cl_2 , $CHCl_3$ and CCl_4 is

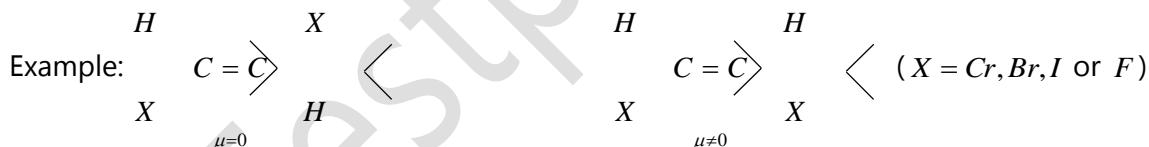


$$\mu = 1.86 \text{ D} \quad 1.62 \text{ D} \quad 1.03 \quad 0$$

Alkynes has larger dipole moment because the electronegativity of $sp - C$ is more than that of $sp^2 - C$.

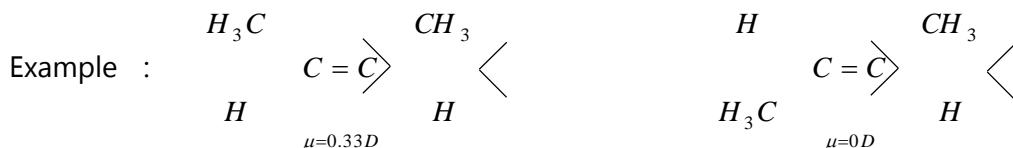
(4) $\mu_{\text{cis}} > \mu_{\text{trans}}$ in geometrical isomers.

(5) Dipole moment of the trans derivative of the compound $(a)(b)C = C(a)(b)$ will only be zero if both a and b will be in the form of atoms.



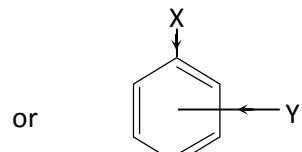
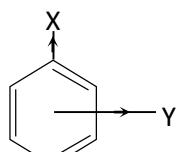
If both will not be atoms then μ_{trans} may or may not be zero.

If group have non-linear moments, then the dipole moment of the trans isomer will not be zero. If group have linear moments, then the dipole moment of the trans isomer will be zero.



(6) Dipole moment of disubstituted benzene

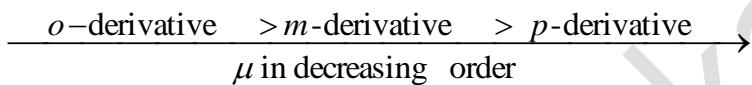
(i) When both groups X and Y are electron donating or both groups are electron with drawing



$$\text{Then, } \mu = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos\theta}$$

Where, μ_1 = dipole moment of bond $C - X$, μ_2 = dipole moment of bond $C - Y$, θ = angle between X and Y .

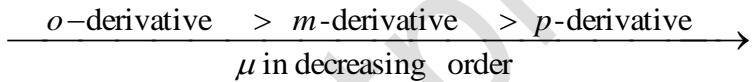
If value of θ will be more, then $\cos\theta$ will be less. Hence, dipole moment will be as,



(ii) When one group is electron with drawing and the other group is electron donating then,

$$\mu = \sqrt{\mu_1^2 + \mu_2^2 - 2\mu_1\mu_2 \cos\theta}$$

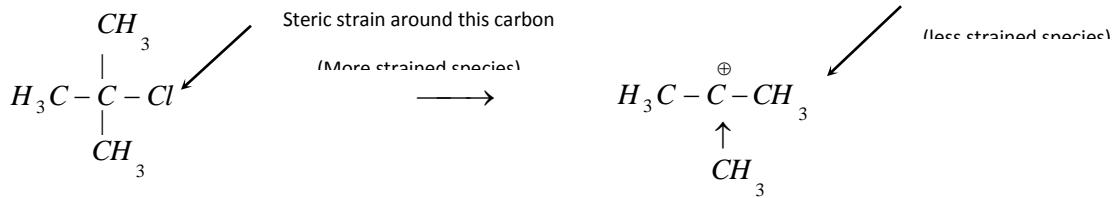
Hence, dipole moment is as follows,



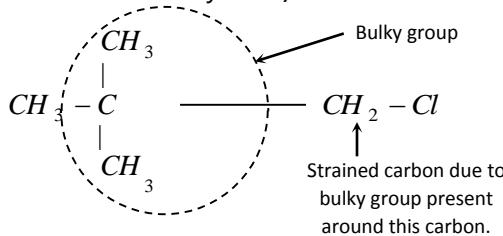
4. Steric effect

On account of the presence of bulkier groups at the reaction center, they cause mechanical interference and with the result that the attacking reagent finds it difficult to reach the reaction site and thus slows down the reaction. This phenomenon is called **steric hindrance or steric effect**.

(1) Tertiary alkyl halides having bulky groups form tertiary carbocation readily when hydrolyzed because of the presence of the three bulky groups on the carbon having halogen.



(2) Primary alkyl halide having quaternary β -carbon does not form transition state because of the steric strain around α -carbon by the β -carbon. To release the strain it converts into carbocation.



(3) Steric strain inhibits the resonance. This phenomenon is known as **steric inhibitions of resonance**.

5. Intermolecular forces.

In an ionic compound, the structural units are ions. These ions are held together by very powerful electrostatic forces are known as inter ionic forces. On the other hand, in non-ionic (covalent) compounds, the structural units are molecules. These molecules are held together by very weak forces are known as **intermolecular forces or secondary forces**. Secondary forces are of the following types,

- (1) Dipole – dipole forces.
- (2) Van der Waal's forces.
- (3) Hydrogen bond.

(1) **Dipole – Dipole Forces:** These forces exist between polar molecules which have permanent dipoles. The interactions of the **permanent dipole** in different molecules are called **dipole-dipole forces (DF)**. Magnitude of DF depends on the dipole moment (μ) of the bond of the compound and intermolecular distance (d), $DF \propto \mu \propto \frac{1}{d^4}$ (i.e. these forces are effective only over short distance)

Example – CH_3-Cl, CH_3-Br, CH_3-I
 d in increasing order, μ in decreasing order and DF also in decreasing order \rightarrow

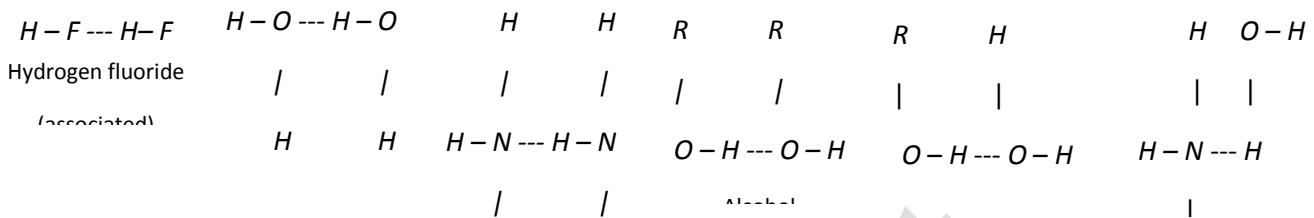
(2) **Vander Waal's forces:** These forces exist between non-polar molecules. The intermolecular electrostatic attractions between nuclei of one molecule and electrons of the other molecule are called **Vander Waal's forces (VF)**. Magnitude of VF depends on the number of electrons (e^-) and protons (p) in the molecule as well as on the intermolecular distance (d),

$VF \propto$ number of e^- and $p; \propto 1/d^7; \propto MW; \propto$ Surface area of the molecule and
 \propto Symmetry of the molecule (symmetry of molecule decreases intermolecular distance (d)).



(3) **Hydrogen bonding:** An electrostatic attractive force between the covalently bonded hydrogen atom of one molecule and an electronegative atom (such as *F, O, N*) of the other molecule is known as **hydrogen bonding**.

Examples of H-bonding in between the two molecules of same or different compounds are



Nature and Importance of Hydrogen bonding

- Hydrogen bond is merely an electrostatic force rather than a chemical bond.
- Hydrogen bond never involves more than two atoms.
- Bond energy of hydrogen bond is in the range of 3 to 10 kcal/mol or 10 to 40 kJ/mol, i.e., about 1/10th the energy of a covalent bond.
- With the increase of electronegativity of the atom to which hydrogen is covalently linked, the strength of the hydrogen bond increases.
- All the three atoms in $X - H - - X$ lie in a straight line.
- The bond length of hydrogen bond is of the order of 250 to 275 pm.

The relative order of these intermolecular forces is,

Hydrogen bonding > dipole-dipole forces > Vander Waal's forces.

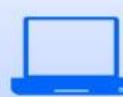
6. Mechanism of organic reactions.

When a chemical reaction takes place between two or more chemical species, new products are formed. This change is represented by a chemical equation. In a chemical equation, reactants are written on the left hand side while the products are written on the right hand side. The two are separated by an arrow (\rightarrow). The reactants normally consists of two species,

- Substrate:** The species, which is attacked by some other chemical species, is called a substrate.
- Reagent:** The species, which attacks the substrate in order to get the major product, is called a reagent.

Thus, Substrate + Reagent \rightarrow Products.

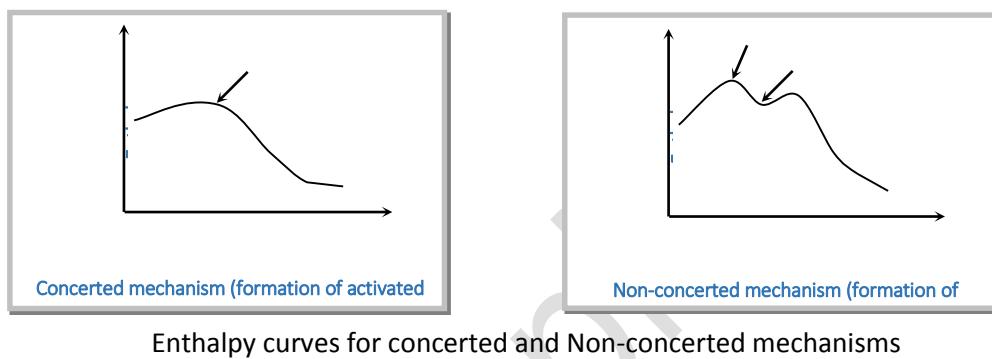
Normally, a substance and a chemical reagent form a highly energetic species, called **activated complex**, before it changes into the product. In certain cases, a relatively energetically more stable species than the activated complex may also be formed. It is called **reaction intermediate**. Thus, a chemical reaction, in general, may follow either of the following two paths,



Path I: Substrate + Reagent → Activated complex → Products

Path II: Substrate + Reagent → Activated complex → Intermediate → Products.

The detailed step by step description of a chemical reaction is called mechanism of a reaction which is only a hypothesis. If the reaction mechanism involves the breaking and making of bonds simultaneously without the formation of any intermediate, it is called **concerted mechanism**. On the other hand, if the reaction mechanism involve the formation of intermediates before the formation of products, it is called **non-concerted mechanism**.



Enthalpy curves for concerted and Non-concerted mechanisms

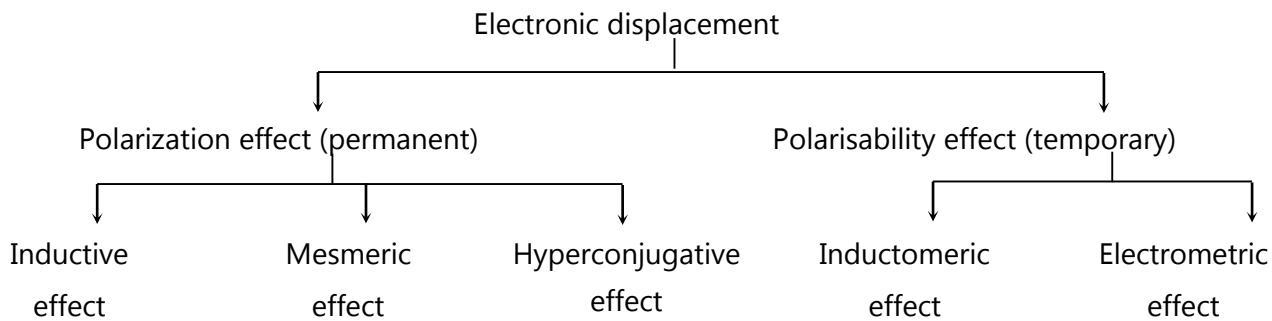
To understand clearly the mechanism of various organic reactions, it is essential to have knowledge about the following concepts:

- Electronic displacements in covalent bonds,
- Cleavage (fission or breaking) of covalent bonds,
- Nature of attacking reagents.

7. Electronic displacement in covalent bonds.

It is observed that most of the attacking reagents always possess either a positive or a negative charge, therefore for a reaction to take place on the covalent bond the latter must possess oppositely charged centers. This is made possible by displacement (partial or complete) of the bonding electrons. The electronic displacement in turn may be due to certain effects, some of which are **permanent** and others are **temporary**. The former effects are permanently operating in the molecule and are known as **polarization effects**, while the latter are brought into play by the attacking reagent and as soon as the attacking reagent is removed, the electronic displacement disappears; such effects are known as the **polarisability effects**.





Inductive effect or Transmission effect

(1) When an electron with drawing (X) or electron-releasing (Y) group is attached to a carbon chain, polarity is induced on the carbon atom and on the substituent attached to it. This permanent polarity is due to electron displacement due to difference in electronegativities. This is called inductive effect or simply as I - effect.



(2) **Important features of Inductive effect**

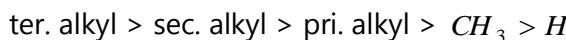
- (i) It is a permanent effect in the molecule or ion.
- (ii) It operates through σ bonds.
- (iii) It is generally observed in saturated compounds.
- (iv) The shared pair of electrons although permanently shifted towards more electronegative atom, yet remains in the same valence shell.
- (v) As a result of electron shifting, the more electronegative end acquires partial negative charge and the other acquires partial positive charge.
- (vi) The inductive effect is not confined to the polarization of one bond but is transmitted along a chain of carbon atoms through σ bonds. However, the effect is insignificant beyond second carbon in the chain.
- (vii) Inductive effect brings changes in physical properties such as dipole moment, solubility, etc. It affects the rates of the reaction.
- (viii) Carbon-hydrogen bond is taken as a standard of inductive effect. Zero effect is assumed for this bond. Atoms or groups which have a greater electron withdrawing capacity than hydrogen are said to



have- I effect whereas atoms or groups which have a greater electron releasing power are said to have + I effect.



- I power of groups in decreasing order with respect to the reference H



+ I power in decreasing order with respect to the reference H

+ I power \propto number of carbons in same type of alkyl groups



+ I power in decreasing order in same type of alkyl groups

(3) Application of Inductive effect

(i) **Magnitude of positive or negative charge:** Magnitude of +ve charge on cations and magnitude of -ve charge on anions can be compared by + I or - I groups present in it.

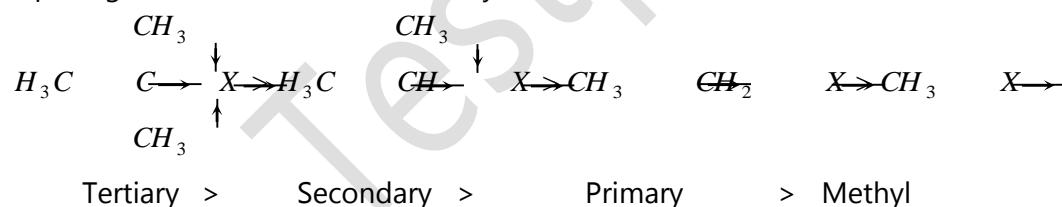
$$\text{Magnitude of +ve charge} \propto \frac{1}{+I \text{ power of the group}}$$

$$\text{Magnitude of +ve charge} \propto -I \text{ power of the group}$$

$$\text{Magnitude of -ve charge} \propto \frac{1}{-I \text{ power of the group}}$$

$$\text{Magnitude of -ve charge} \propto +I \text{ power of the group}$$

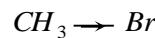
(ii) **Reactivity of alkyl halide:** + I effect of methyl group enhances - I effect of the halogen atom by repelling the electron towards tertiary carbon atom.



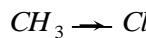
(iii) **Dipole moment:** As the inductive effect increases, the dipole moment increases.



1.64 D



1.79 D



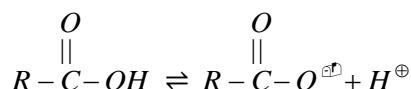
1.83 D

Inductive effect increases

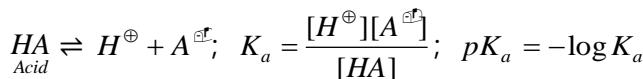


(iv) **Relative strength of the acids** (Acidic nature of – COOH)

(a) An acid may be defined as a species that has the tendency to lose proton. Furthermore, the strength of an acid depends on the tendency to release proton when the acid is dissolved in water.



(b) The relative strength of acids are measured in their ionization constants (K_a or pK_a values).



Greater the value of K_a or lower the value of pK_a stronger will be the acid.

(c) Any group or atom showing +I effect decreases the acid strength as it increases the negative charge on the carboxylate ion which holds the hydrogen firmly. Alkyl groups have + I effect.

Thus, acidic nature is, $\text{HCOOH} > \text{CH}_3\text{COOH} > \text{C}_2\text{H}_5\text{COOH} > \text{C}_3\text{H}_7\text{COOH} > \text{C}_4\text{H}_9\text{COOH}$

(→ + Inductive effect increases, so acid strength decreases)

Formic acid, having no alkyl group, is the most acidic among these acids.

(d) The group or atom having – I effect increases the strength as it decreases the negative charge on the carboxylate ion. Greater is the number of such atoms or groups (having – I effect), greater is the acid strength.

Thus, acidic nature is, $\text{CCl}_3\text{COOH} > \text{CHCl}_2\text{COOH} > \text{CH}_2\text{ClCOOH} > \text{CH}_3\text{COOH}$

(← Trichloro acetic acid Dichloro acetic acid Monochloro acetic acid Acetic acid
– Inductive effect increases, so acid strength increases)

(e) Strength of aliphatic carboxylic acids and benzoic acid



Hence benzoic acid is stronger acid than aliphatic carboxylic acids but exception is formic acid. Thus,

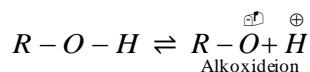
$\text{HCOOH} < \text{C}_6\text{H}_5\text{COOH} < \text{RCOOH}$
→ Acid strength in decreasing order

Note: Decreasing order of acids: $\text{NO}_2\text{CH}_2\text{COOH} > \text{FCH}_2\text{COOH} > \text{ClCH}_2\text{COOH} > \text{BrCH}_2\text{COOH}$.

$\text{F}_3\text{C}-\text{COOH} > \text{Cl}_3\text{C}-\text{COOH} > \text{Br}_3\text{C}-\text{COOH} > \text{I}_3\text{C}-\text{COOH}$.

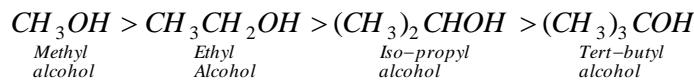
(v) **Acidity of alcohols:** Acidity of alcohol depends on the stability of alkoxide ion (i.e., conjugate base of alcohol) which is obtained by the dissociation of alcohols.



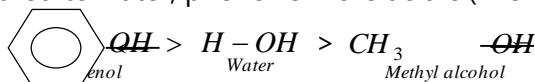


Acid strength of alcohol \propto stability of alkoxide ion

The decreasing order of acid strength of acid strength in alcohols is also due to +I effect of alkyl groups.



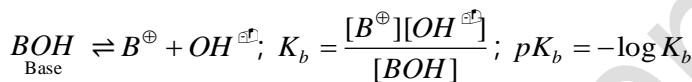
As compared to water, phenol is more acidic (-I effect) but methyl alcohol is less acidic (+I effect).



(vi) Relative strength of the bases (Basic nature of $-NH_2$)

(a) A base may be defined as a species which is capable of accepting a proton. Base strength is defined as the tendency to donate an electron pair for sharing.

(b) The relative strength of bases are measured in their ionization constants (K_b or pK_b values).



Greater the value of K_b or lower the value of pK_b stronger will be the base.

(c) The difference in base strength in various amines can be explained on the basis of inductive effect. The +I effect increases the electron density while -I effect decreases. The amines are stronger bases than NH_3 as the alkyl groups increase electron density on nitrogen due to + I effect while $C_6H_5NH_2$ is less basic due to -I effect. "So more is the tendency to donate electron pair for coordination with proton, the more is basic nature, i.e., more is the negative charge on nitrogen atom (due to +I effect of alkyl group), the more is basic nature".

Thus, the basic nature decreases in the order; $(C_2H_5)_2NH > CH_3CH_2NH_2 > CH_3NH_2 > NH_3 > C_6H_5NH_2$

Diethyl amine Ethyl amine Methyl amine Ammonia Chloro amine

The order of basicity is as given below:

Alkyl groups (R-) Relative base strength

CH_3 $R_2NH > RNH_2 > R_3N > NH_3$

C_2H_5 $R_2NH > RNH_2 > NH_3 > R_3N$

$(CH_3)_2CH$ $RNH_2 > NH_3 > R_2NH > R_3N$

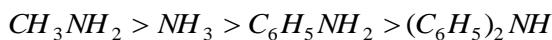
$(CH_3)_3C$ $NH_3 > RNH_2 > R_2NH > R_3N$



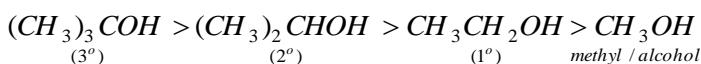
Note: The relative basic character of amines is not in total accordance with inductive effect ($t > s > p$) but it is in the following order: Secondary > Primary > Tertiary. The reason is believed to be steric factor.

In gas phase or in non-aqueous solvents such as chlorobenzene etc., the solvation effect, i.e., the stabilization of the conjugate acid due to H -bonding are absent and hence in these media the basicity of amines depends only on the +I effect of the alkyl group thus the basicity of amines follows the order : $3^\circ > 2^\circ > 1^\circ > NH_3$.

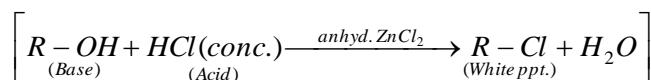
(d) As compared to ammonia, methylamine is more basic (+I effect) but aniline is less basic and diphenylamine is still weaker (-I effect).



(vii) **Basicity of alcohols:** The decreasing order of base strength in alcohols is due to +I effect of alkyl groups.



In Lucas test of making distinction between three types ($1^\circ, 2^\circ$ and 3°) of monohydric alcohols,

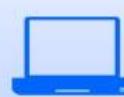


The basic character of alcohols is in the order, benzyl $> 3^\circ > 2^\circ > 1^\circ$ and hence, the strongest base (3°) will be reacting fastest with conc. HCl in presence of anhydrous $ZnCl_2$ (Lucas reagent) and gives white turbidity immediately.

(viii) **Stability of carbonium ion:** +I effect tends to decrease the (+ve) charge and -I effect tends to increases the +ve charge on carbocation.



(ix) **Stability of carbanion:** Stability of carbanion increases with increasing -I effect.

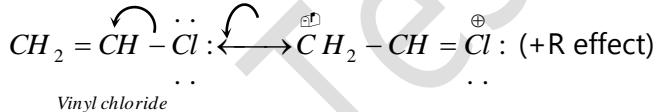


Resonance effect or mesomeric effect

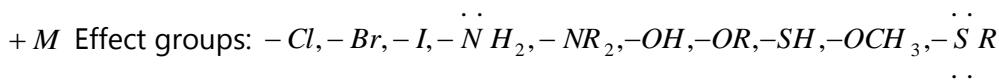
(1) The effect in which π electrons are transferred from a multiple bond to an atom, or from a multiple bond to a single covalent bond or lone pair (s) of electrons from an atom to the adjacent single covalent bond is called mesomeric effect or simply as M-effect. In case the compound in question is having conjugated system of double bonds, the mesomeric effect is transmitted through whole of the conjugated system and thus the effect may better be known as **conjugative effect**.

(2) Important features of mesomeric effect

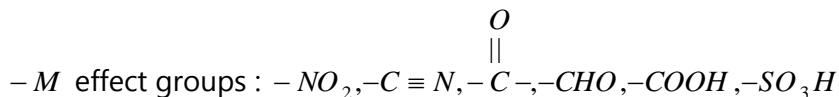
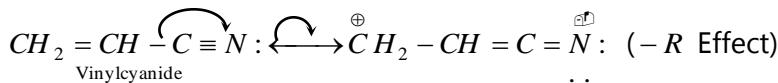
- (i) It is a permanent effect present in the molecule in the ground state.
- (ii) It is operative in unsaturated compounds especially having conjugated systems.
- (iii) It involves electrons of π -bonds or lone pair of electrons. This effect operates through conjugative mechanism.
- (iv) In this effect the electron pair is completely transferred and thus full positive and negative charges are developed.
- (v) It affects the physical properties such as dipole moment, solubility etc. Rate of reaction of the substance is also affected.
- (vi) Groups which have the capacity to increase the electron density of the rest of the molecule are said to have $+M$ effect. Such groups possess lone pairs of electrons. Groups which decrease the electron density of the rest of the molecule by withdrawing electron pairs are said to have $-M$ effect, e.g.,
- (a) The groups which donate electrons to the double bond or to a conjugated system are said to have $+M$ effect or $+R$ effect.



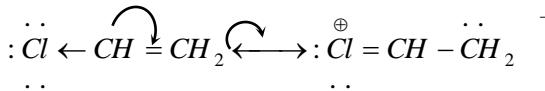
In vinyl chloride $C - Cl$ bond has double bond character due to resonance.



(b) The groups which withdraw electrons from the double bond or from a conjugated system towards itself due to resonance are said to have $-M$ effect or $-R$ effect.



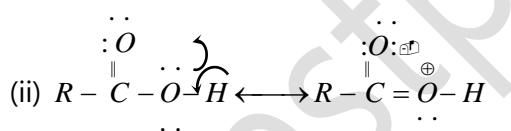
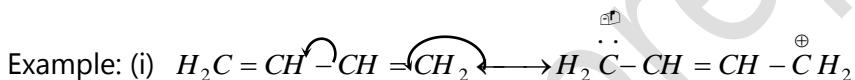
(vii) The inductive and mesomeric effects, when present together, may act in the same direction or oppose each other. The mesomeric effect is more powerful than the former. For example, in vinyl chloride due to $-I$ effect the chlorine atom should develop a negative charge but on account of mesomeric effect it has positive charge.



(3) **Application of mesomeric effect:** It explains,

- (i) Low reactivity of aryl and vinyl halides,
- (ii) The acidic nature of carboxylic acids,
- (iii) Basic character comparison of ethylamine and aniline,
- (iv) The stability of some free radicals, carbocations and carbanions.

(4) **Difference between Resonance and Mesmerism:** Although both resonance and mesmerism represent the same phenomenon, they differ in the following respect: Resonance involves all types of electron displacements while mesmerism is noticeable only in those cases where a multiple bond is in conjugation with a multiple bond or electron pair.



Both (i) and (ii) are the examples of mesmerism and resonance effect. Let us consider the following example

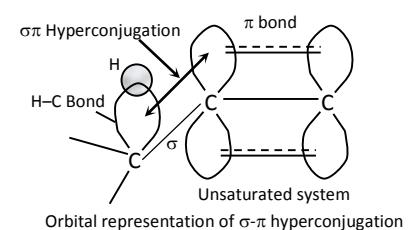
$H \rightarrow \ddot{C}l : \longleftrightarrow H\dot{C}l^+$. Such an electron displacement is the example of resonance only (not the mesmerism).



Hyperconjugative effect

(1) When a $H - C$ bond is attached to an unsaturated system such as double bond or a benzene ring, the sigma (σ) electrons of the $H - C$ bond interact or enter into conjugation with the unsaturated system. The interactions between the electrons of π systems (multiple bonds) and the adjacent σ bonds (single $H - C$ bonds) of the substituent groups in organic compounds is called hyper conjugation. The concept of hyper conjugation was developed by Baker and Nathan and is also known as Baker and Nathan effect. In fact hyper conjugation effect is similar to resonance effect. Since there is no bond between the α -carbon atom and one of the hydrogen atoms, the hyper conjugation is also called no-bond resonance.

(2) **Orbital concept of hyper conjugation:** The orbital concept of hyper conjugation may be explained with the help of propene. In this, the electron pair of $C - H$ bond (σ -bond) is involved in conjugation with the π -electron pair of the double bond. Therefore, hyper conjugation involves delocalization of σ -electrons of $H - C$ bond through overlapping of p -orbitals of double bond as shown in figure.



(3) Structural requirement for hyper conjugation

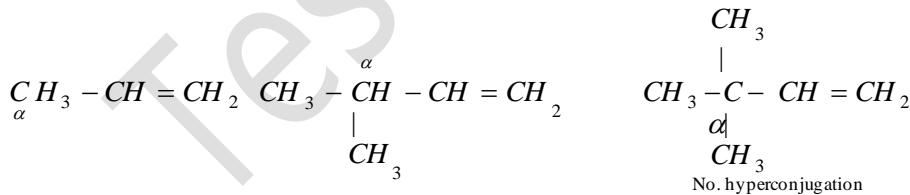
(i) Compound should have at least one sp^2 -hybrid carbon of either alkene alkyl carbocation or alkyl free radical.

(ii) α -carbon with respect to sp^2 hybrid carbon should have at least one hydrogen.

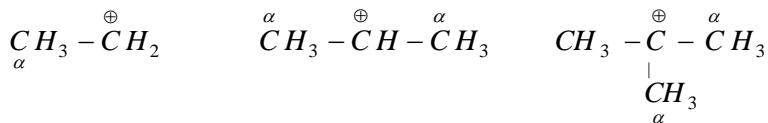
If both these conditions are fulfilled then hyper conjugation will take place in the molecule.

(iii) Hyper conjugation is of three types

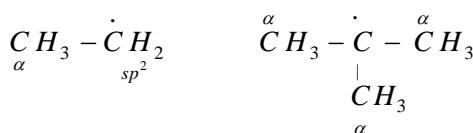
(a) σ ($C - H$), π conjugation: This type of conjugation occurs in alkenes.



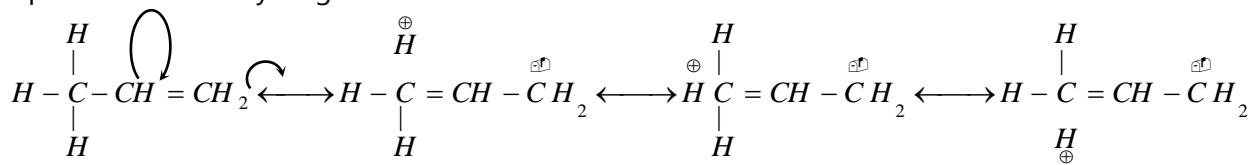
(b) σ ($C - H$), positive charge conjugation: This type of conjugation occurs in alkyl carbocations.



(c) σ ($C - H$), odd electron conjugation: This type of conjugation occurs in alkyl free radicals.



(iv) Resonating structures due to hyper conjugation may be written involving "no bond" between the alpha carbon and hydrogen atoms.



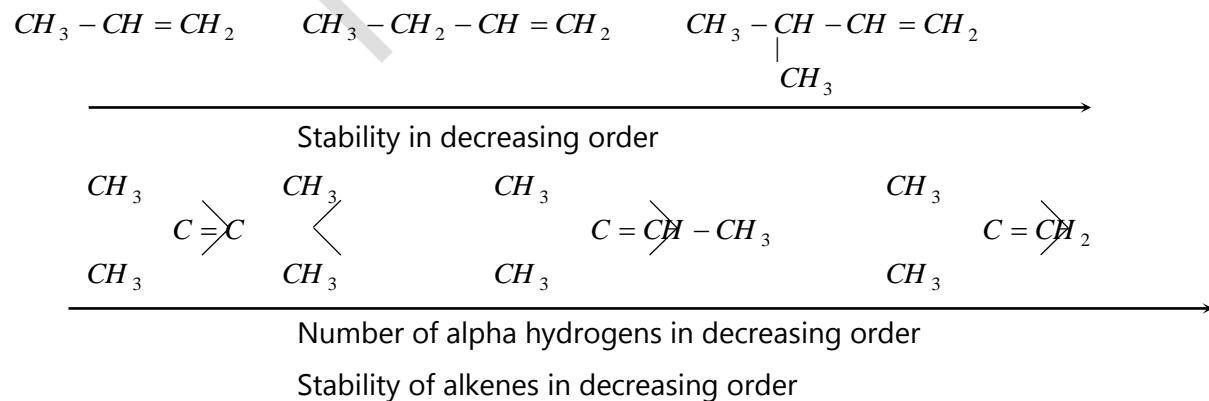
(v) Number of resonating structures due to the hyper conjugation = Number of α -hydrogens + 1.

Structure	Number of α -hydrogens	Number of resonating structures
$CH_3 - CH = CH_2$	3	4
$CH_3 - CH_2 - CH = CH_2$	2	3
$CH_3 - CH = CH - CH_3$	6	7
$CH_3 - \overset{\oplus}{C}H_2$	3	4
$CH_3 - \overset{\oplus}{C} - CH_3$	6	7
$CH_3 - \overset{\oplus}{C} - CH_3$ CH_3	9	10

(4) Applications of hyper conjugation

(i) **Stability of alkenes:** Hyper conjugation explains the stability of certain alkenes over other alkenes.

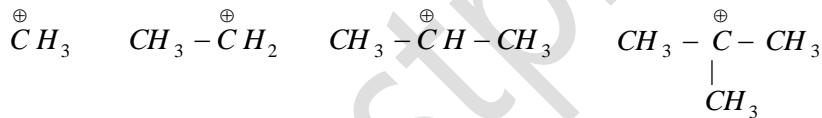
Stability of alkenes \propto Number of alpha hydrogens \propto Number of resonating structures



(ii) **Carbon-carbon double bond length in alkenes:** As we know that the more is the number of resonating structures, the more will be single bond character in carbon-carbon double bond. Thus, bond length between carbon double bond \propto numbers of resonating structures. Examples:

Structure	Number of α -hydrogens	Number of resonating structures	Carbon-carbon double bond length in Å
$CH_2 = CH_2$	Zero	Zero	1.34 Å
$CH_3 - CH = CH_2$	3	4	1.39 Å
$CH_3 - CH_2 - CH = CH_2$	2	3	1.37 Å
$CH_3 - \begin{matrix} CH \\ \\ CH_3 \end{matrix} - CH = CH_2$	1	2	1.35 Å
$CH_3 - \begin{matrix} CH_3 \\ \\ C - C H \\ \\ CH_3 \end{matrix} = CH_2$	Zero	Zero	1.34 Å

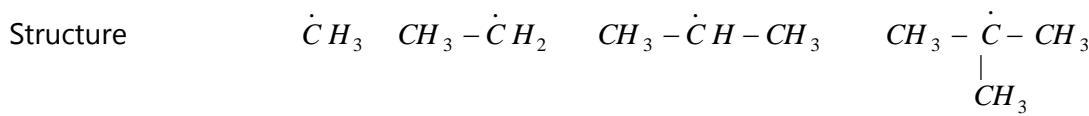
(iii) **Stability of alkyl carbocations:** Stability of alkyl carbocations \propto number of resonating structures \propto number of resonating structures \propto number of alpha hydrogens.



Number of α -hydrogens in increasing order

Stability in increasing order

(iv) **Stability of alkyl free radicals:** Stability of alkyl free radicals can be explained by hyper conjugation. Stability depends on the number of resonating structures.



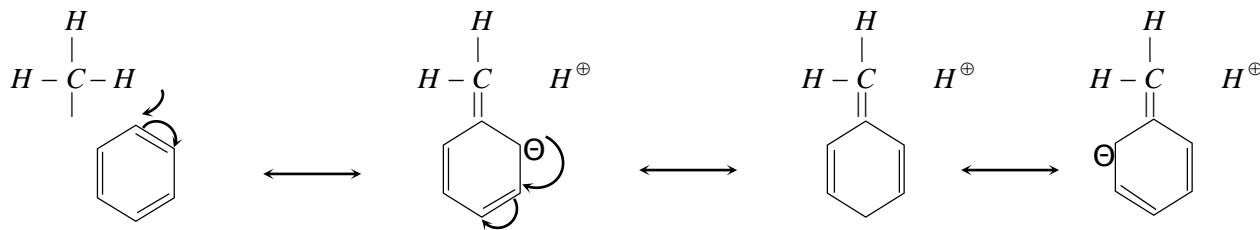
No. of resonating structures 0 4 7 10

Number of resonating structures in increasing order

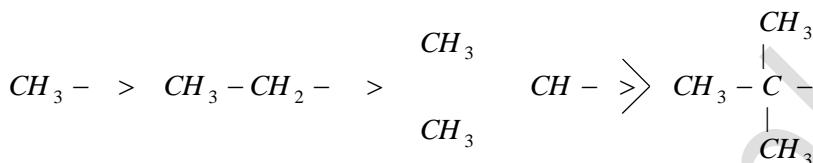
Stability is in increasing order



(v) **Electron releasing (or donating) power of R in alkyl benzenes:** CH_3- (or alkyl group) is $+R$ group, ortho-para directing group and activating group for electrophilic aromatic substitution reaction because of the hyper conjugation.



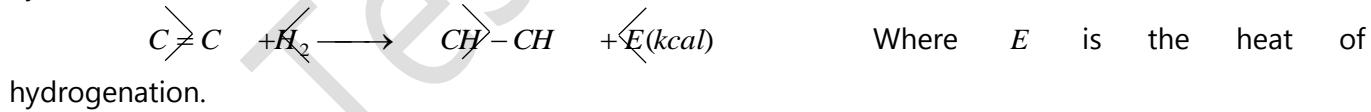
The electron donating power of alkyl group will depends on the number of resonating structures, this depends on the number of hydrogens present on α -carbon. The electron releasing power of some groups are as follows,



Increasing inductive effect

Electron donating power in decreasing order due to the hyper conjugation.

(vi) **Heat of hydrogenation:** It is the heat evolved/mol in the addition of hydrogen to form a saturated hydrocarbon.

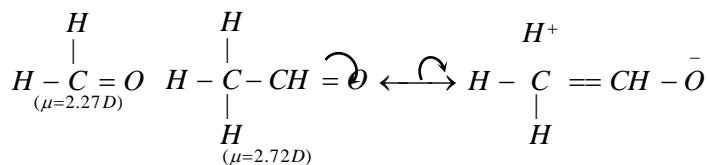


Lesser the heat of hydrogenation, lesser is the internal energy and more is stability of the system. Hyper conjugation decreases the heat of hydrogenation. For ethylene it is 32.8 kcal/mol and for propylene, 30.1 kcal/mol respectively.

(vii) **Dipole moment:** Since hyper conjugation causes the development of charges, it also affects the dipole moment in the molecule.

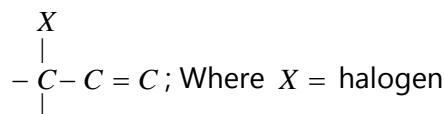
The increase in dipole moment, when hydrogen of formaldehyde ($\mu = 2.27D$) is replaced by methyl group, i.e., acetaldehyde ($\mu = 2.72D$) can be referred to hyper conjugation, which leads to development of charges.



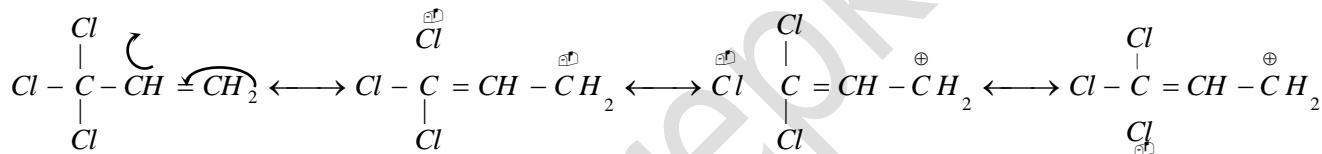


(viii) **Orienting influence of alkyl group in *o*, *p* -positions and of $-CCl_3$ group in *m* -position:** Ortho-para directing property of methyl group in toluene is partly due to $+I$ effect and partly due to hyper conjugation.

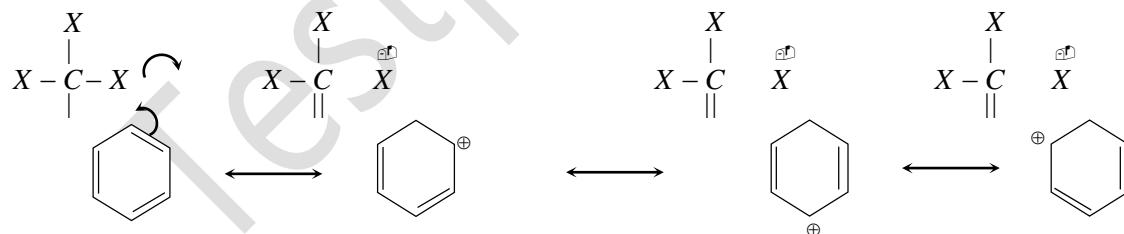
(5) **Reverse Hyper conjugation:** The phenomenon of hyper conjugation is also observed in the system given below,



In such system the effect operates in the reverse direction. Hence the hyper conjugation in such system is known as reverse hyper conjugation.

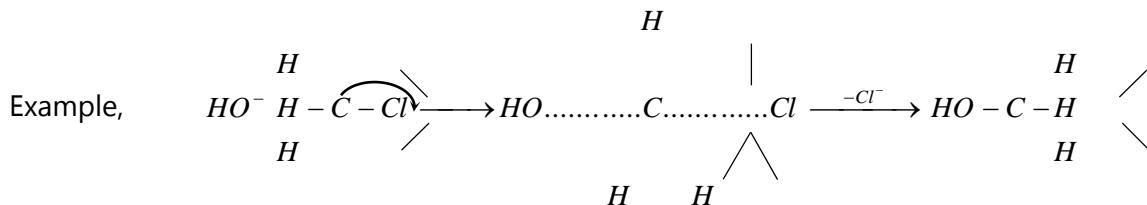


The meta directing influence and deactivating effect of CX_3 group for electrophilic aromatic substitution reaction can be explained by this effect.



Inductomeric effect

Inductomeric effect is the temporary effect which enhances the inductive effect and it accounts only in the presence of an attacking reagent.



In methyl chloride the $-I$ effect of Cl group is further increased temporarily by approach of hydroxyl ion.

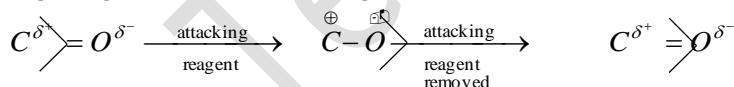
Electrometric effect

(1) The phenomenon of movement of electrons from one atom to another in multibonded atoms at the demand of attacking reagent is called electrometric effect. It is denoted as E-effect and represented by a curved arrow (\curvearrowright) showing the shifting of electron pair.



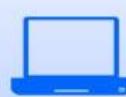
(2) Important features of electrometric effect

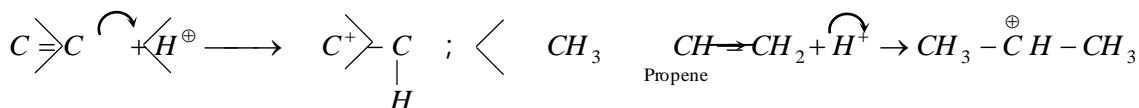
- (i) It is a temporary effect
- (ii) It is brought into play instantaneously at the demand of the attacking reagent. However as soon as the attacking reagent is removed, original electronic condition is restored.



(iii) The electrometric effect is of common occurrence during addition of polar reagents on $C=C$, $C=O$ and $C \equiv N$ bonds etc.

- (iv) The effect involves the complete transference of π electrons.
- (v) In this effect the displaced electrons leave their orbitals and take a new position.
- (vi) In this there is complete charge separation and ions are formed.
- (vii) There are two types of electrometric effects, i.e., $+E$ effect or $-E$ effect.
- (a) When the transfer of electrons take place towards the attacking reagent, the effect is called $+E$ effect. The addition of acids to alkenes.

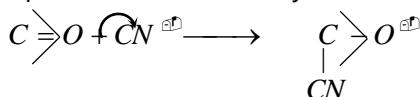




Since, $-CH_3$ group is electron repelling, the electrons are transferred in the direction shown.

The attacking reagent is attached to that atom on which electrons have been transferred.

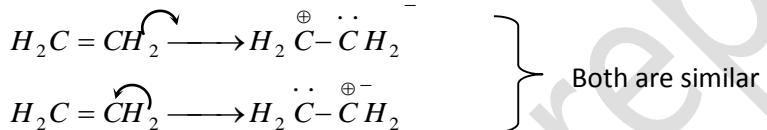
(b) When the transfer of electrons takes place away from the attacking reagent, the effect is called $-E$ effect. Example, the addition of cyanide ion to carbonyl compounds.



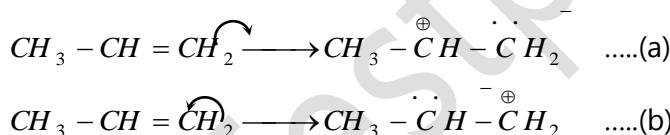
The attacking reagent does not attach to that atom on which electrons have been transferred.

(3) **Direction of the shift of electron pair:** The direction of the shift of electron pair can be decided on the basis of following points.

(i) When the groups linked to a multiple bond are similar, the shift can occur to either direction. For example, in ethylene the shift can occur to any one of the carbon atoms.

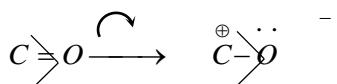


(ii) When the dissimilar groups are linked on the two ends of the double bond, the shift is decided by the direction of inductive effect. For example, in propylene the shift can be shown in the following ways,

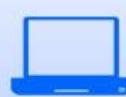


Due to electron repelling nature of methyl group, the electronic shift occurs according to Eq. (a) way and not by Eq. (b) way.

In the case of carbonyl group, the shift is always towards oxygen, i.e., more electronegative atom.



Note: In cases where inductive effect and electromeric effect simultaneously operate, usually electromeric effect predominates.

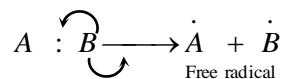


7. Cleavage (fission or breaking) of covalent bonds.

Breaking of covalent bond of the compound is known as **bond fission**. A bond can be broken by two ways,

(1) Homolytic bond fission or Homolysis

(i) In homolysis, the covalent bond is broken in such a way that each resulting species gets its own electron. This leads to the formation of odd electron species known as **free radical**.



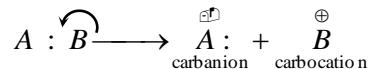
(ii) The factor which favors homolysis is zero or a small difference in electronegativity between A and B .

(iii) Homolysis takes place in gaseous phase or in the presence of non-polar solvents (CCl_4 , CS_2), peroxide, UV light, heat ($\geq 500^\circ C$), electricity and free radical.

(iv) Mechanism of the reaction in which homolysis takes place is known as homolytic mechanism or free radical mechanism.

(2) Heterolytic bond fission or heterolysis

(i) In heterolysis, the covalent bond is broken in such a way that one species (i.e., less electronegative) is deprived of its own electron, while the other species gains both the electrons.

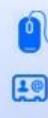


Thus formation of opposite charged species takes place. In case of organic compounds, if positive charge is present on the carbon then cation is termed as **carbocation**. If negative charge is present on the carbon then anion is termed as **carbonion**.

(ii) The factor which favors heterolysis is a greater difference of electronegativity between A and B .

(iii) Mechanism of the reaction in which heterolysis takes place is known as Heterolytic mechanism or ionic mechanism.

(iv) The energy required for heterolysis is always greater than that for homolysis due to electrostatic force of attraction between ions.

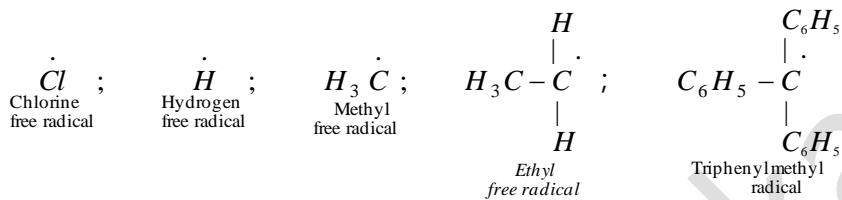


8. Reaction Intermediates.

Short lived fragments called reaction intermediates result from homolytic and Heterolytic bond fission. The important reaction intermediates are free radicals, carbocations, carbonions, carbenes, benzene and nitrenes.

Free radicals

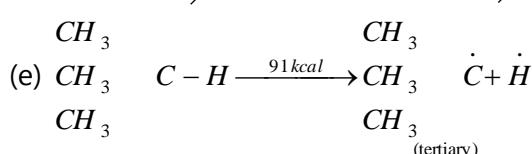
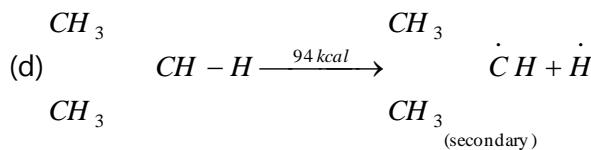
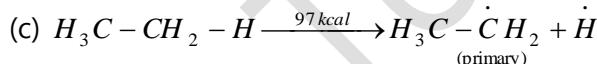
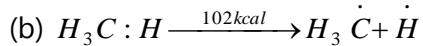
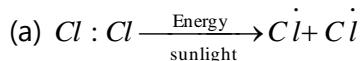
A free radical may be defined as an atom or group of atoms having an odd or unpaired electron. These result on account of homolytic fission of a covalent bond and are denoted by putting a dot (.) against the symbol of atom or group of atoms.

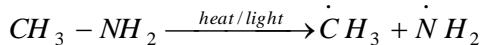
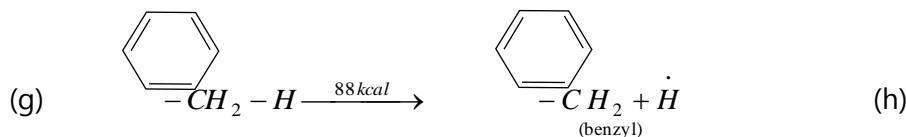
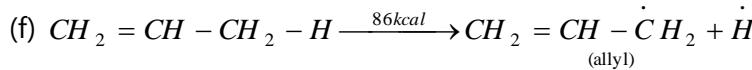


The first stable organic free radical was triphenyl methyl radical and it was prepared by **Gomberg**.

(1) Characteristics of free radical.

(i) The formation of free radical is initiated by heat, light or catalysts.





(ii) Free radicals are generally electrically neutral.

(iii) There are seven electrons in the outermost orbit of carbon of carbon free radicals.

(iv) Owing to the presence of an odd electron; a carbon radical is paramagnetic in nature. Due to this reason free radicals are highly reactive.

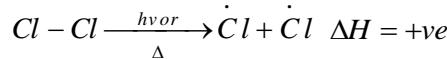
(v) Free radicals are neutral electrophiles.

(vi) Chemical reactions which take place with the formation of free radical as an intermediate are known as free radical reactions. These reactions take place in three steps,

- (a) Initiation
- (b) Propagation and
- (c) Termination

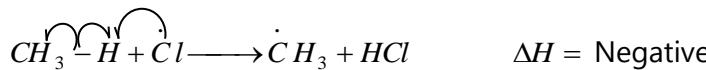
Each of these steps, in turn, may involve two or more steps.

(a) **Initiation step:** In this step, homolytic bond fission takes place in the presence of initiator, i.e., peroxide, $h\nu$, heat etc. The process is always endothermic.

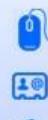


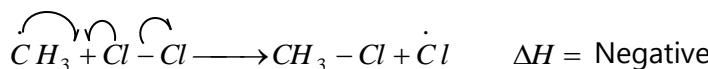
(b) **Propagation step:** Propagation step is always two or more than two step process and **all propagation steps should be exothermic, otherwise free radical reactions would not take place.**

Propagation step I: In this step, formation of free radical as reaction intermediate takes place. For example,

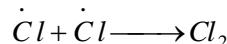


Propagation step II: Reaction intermediate reacts with reagent to give the product.





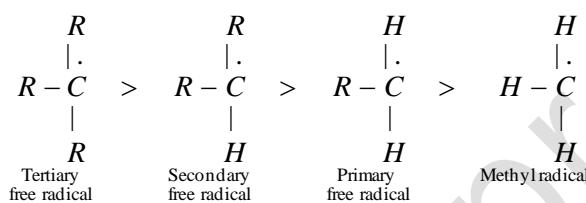
(c) Termination step : In this step, free radical formed in the last propagation step (generally propagation step II) is destroyed by the addition of free radical or by the addition of some impurities like $CHCl_3$ or CCl_4 .



Reaction velocity of free radical reaction is very-very high.

Note: Certain compounds, known as inhibitor, retard velocity of free radical reactions. Common inhibitors are O_2 , I_2 , p-benzoquinone and diphenylamine.

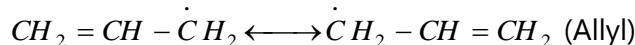
(2) **Relative stabilities of free radicals:** The tertiary alkyl free radicals are most stable and methyl free radical is least stable, i.e., the free radical formed easily has greater stability.



Benzyl and allyl free radicals are resonance stabilized hence are more stable than alkyl free radicals.



Benzyl free radical



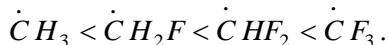
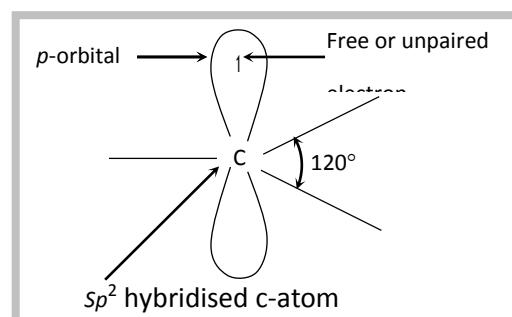
Relative stability of free radicals are: Benzyl > allyl > 3° > 2° > 1° > methyl, vinyl

The stability of various free radicals can be compared from their bond dissociation energies (the energy required for the homolytic cleavage of the covalent bond in the molecule to form two radicals). In general, the smaller the amount of energy required for bond breaking, the more stable is the radical.



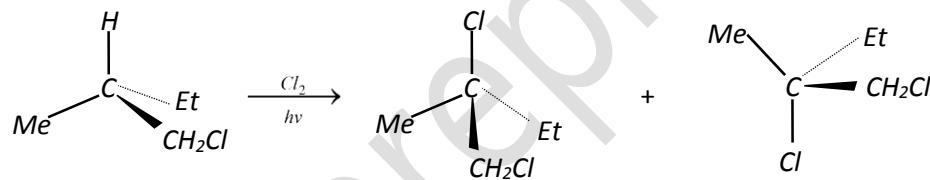
(3) **Structure of alkyl free radicals:** The carbon atom of alkyl free radicals which is bonded to only three atoms or groups of atoms is sp^2 hybridized. Thus, free radicals have a planar structure with odd electron situated in the unused p -orbital at right angles to the plane of hybrid orbitals.

However, in the substituted alkyl radicals the 's' character of these orbitals has been found to increase, thus, tending to the pyramidal shape.

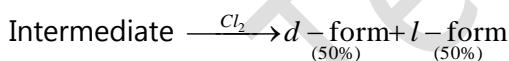


So, CF_3 is essentially pyramidal in shape.

(4) **Stereochemistry of free radicals:** To learn about the stereochemistry of free radical reaction. We choose the reaction, chlorination of 1-chloro-2-methyl butane. The reaction products are,

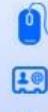


If we review the insight of the reaction, it is clear that the reaction involves racemization at the reaction center. The free radical should have the sp^2 hybridization. Obviously a Cl_2 molecule could attack either the upper or lower lobe of the p -orbital with equal chances, leading to racemic mixture.



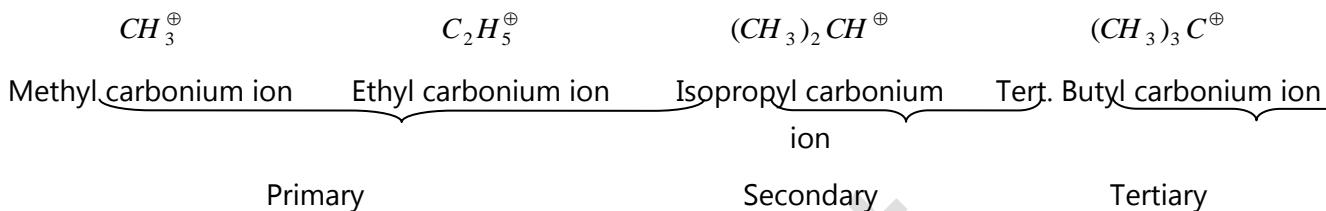
(5) Reactions involving free radicals,

- (i) Chlorination of alkanes
- (ii) Pyrolysis of alkanes
- (iii) Wurtz reaction
- (iv) Anti-markownikoff rule
- (v) Kolbe electrolytic synthesis
- (vi) Polymerization initiated by free radical.



Carbonium ions (carbocations)

Carbocation is defined as a group of atoms which contain positively charged carbon having only six electrons. It is obtained by Heterolytic fission of a covalent bond involving carbon atom. It is denoted by putting a positive charge (+) against the symbol of group of atoms.



(1) Characteristics of carbocations

(i) The formation of carbocations can be done,



(ii) Carbocations are not electrically neutral.

(iii) There are six electrons in the outermost orbit of carbon of carbocation i.e., 2 electrons less than octet.

(iv) A carbocation is diamagnetic in nature due to all paired electrons.

(v) Carbocations are charged electrophiles i.e., they react with nucleophilic reagents. The order of reactivity of carbocations is, Primary (1°) > Secondary (2°) > Tertiary (3°)

(2) Types of carbocations:

Carbocations can be classified into the following types,

(i) Alkyl carbocations

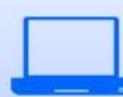
(a) When positive charge is present on the alkyl carbon, carbocation is known as alkyl carbocation.

(b) Alkyl carbocation is of four types

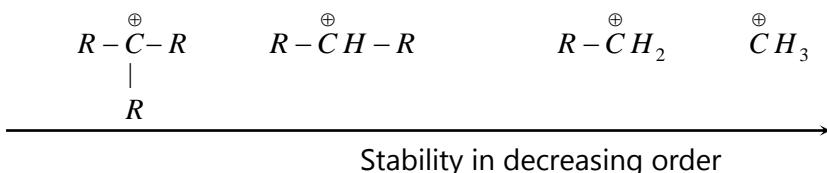


(c) Stability of alkyl carbocations can be explained by

Inductive effect and hyper conjugation.

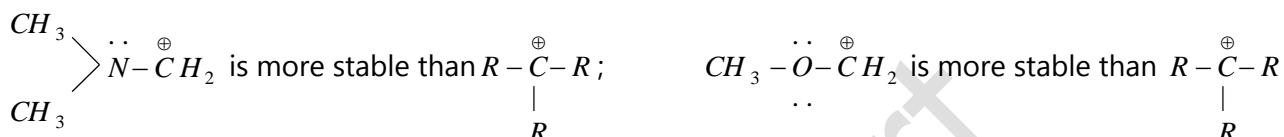


(d) According to these two effects the stability order is as follows:



(e) If α -atom with respect to carbocationic carbon has one or more than one lone pair of electrons then lone pair of electrons strongly stabilizes a carbocation due to the delocalization.

Alkoxy and amino groups are important substituents for such type of carbocations.



(ii) **Vinyl carbocation:** When positive charge is present on vinylic carbon then carbocation is known as vinyl carbocation, $CH_2 = \overset{\oplus}{C} H$

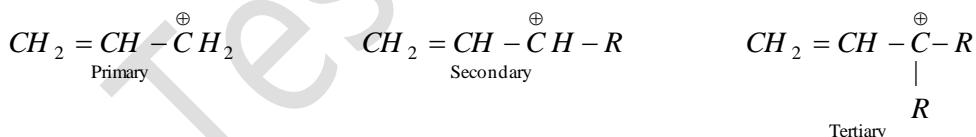
This carbocation is the least stable because positive charge is present on the electronegative carbon.

(iii) **Allyl carbocation:** ($CH_2 = CH - \overset{\oplus}{C} H_2$)

(a) When positive charge is present on the allylic carbon of the allyl group, the carbocation is known as allyl carbocation.

(b) Allyl carbocations are more stable than the alkyl carbocations due to the resonance. Allyl carbocations are stabilized by delocalization (or resonance).

(c) Allyl carbocations are of the following types,



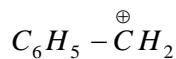
(d) Stability of primary, secondary and tertiary allyl carbocations can be compared by, Inductive effect and Hyper conjugation. Thus, tertiary is more stable than secondary which is more stable than primary allyl carbocation.

(iv) **Phenyl methyl carbocations**

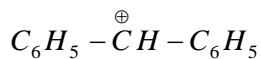
(a) When positive charge is present on benzyl carbon, carbocation is known as phenyl methyl carbocation.



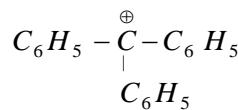
(b) Phenyl methyl carbocations are of three types,



Benzyl carbocation
or
Phenyl methyl carbocation
(1°-carbocation)



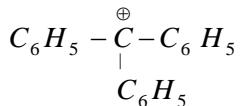
Diphenyl methyl
carbocation
(2°-carbocation)



Triphenyl methyl
carbocation
(3°-carbocation)

(c) Stability of phenyl methyl carbocations can be explained by resonance.

Structure :

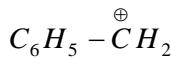


No. of resonating
structures :

10



7



4

- (i) Number of resonating structures in decreasing order
- (ii) Stability in decreasing order.

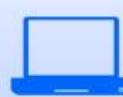
(d) Phenyl methyl carbocations are more stable than allyl carbocations due to the number of resonating structures.

(v) **Aromatic carbocations**

(a) Cations in which positive charge is present on carbon of aromatic system is known as aromatic carbocation.

(b) Aromatic carbocations are so stable that even their solid states are known. For example tropolium carbocation as tropolium bromide is a yellow solid. It fact tropolium carbocation is about 10^{11} times more stable than triphenyl methyl carbocation.

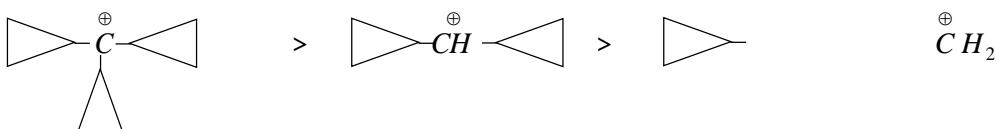
(c) Cations obeying Huckel ($4n+2$) rule are stable because they are aromatic and there is complete delocalization of positive charge.



(vi) Cyclopropyl methyl carbocations

(a) These carbocations are very stable carbocations. They are more stable than benzyl carbocations.

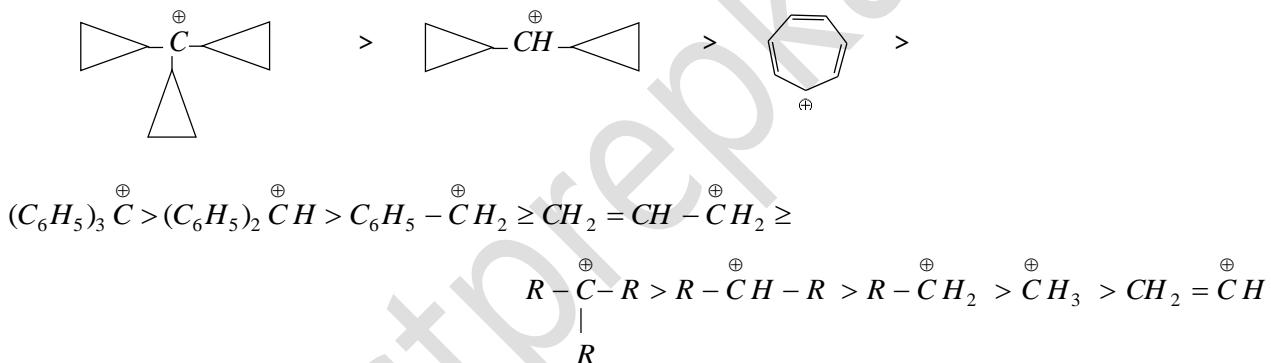
(b) Stability of Cyclopropyl methyl carbocations increases with every Cyclopropyl group. Thus additional Cyclopropyl group has cumulative additive effect on the stability. Thus,



Stability in decreasing order

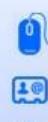
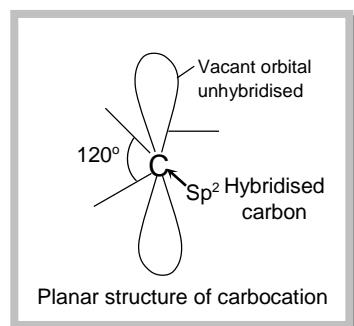
(c) The special stability is a result of conjugation between the bent orbitals of the Cyclopropyl ring and the vacant- p -orbital of the cationic carbon.

(3) **Relative:** Stability of different types of carbocations in decreasing order



Note: More stable is a carbocation, the more easily it is formed.

(4) **Structure of carbocation:** The carbon atom in carbocation is sp^2 hybridized. The three sp^2 hybrid orbitals form three σ bonds with hydrogen or other carbon atoms of alkyl groups. The unhybridised p -orbital of carbon remains vacant. Since it involves sp^2 hybridization, its structure is planar with a bond angle of 120° .



(5) Reactions involving carbocations

- (i) Electrophilic addition reactions
- (ii) S_N^1 Reactions
- (iii) Electrophilic substitution reactions
- (iv) Molecular rearrangement reactions, e.g., Pinacole-Pinacolone rearrangement.

(6) Rearrangement in carbocations

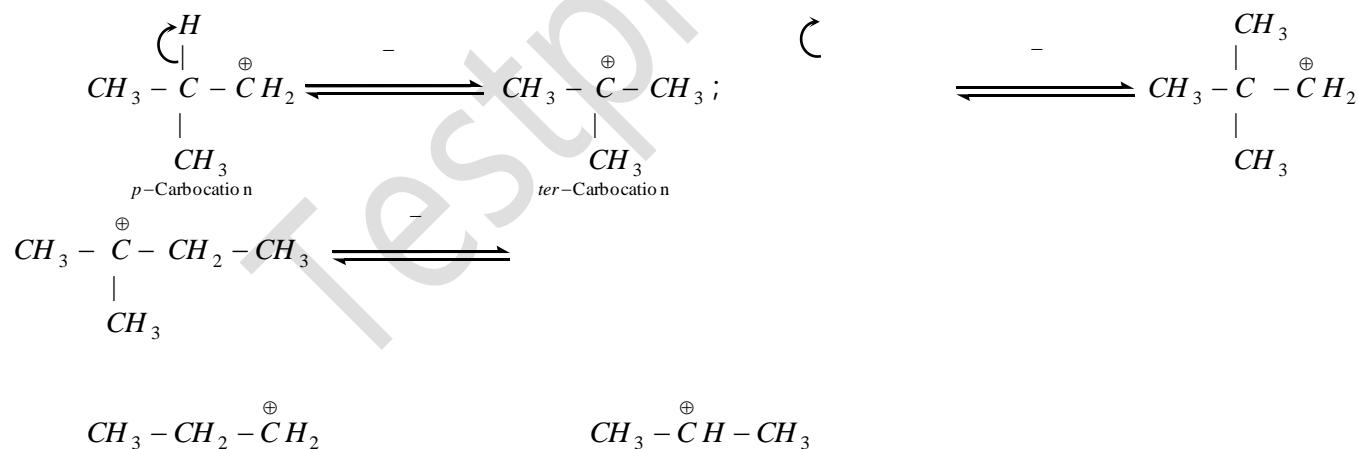
- (i) Rearrangement takes place in primary and secondary carbocations.



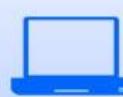
Driving force for rearrangement is the stability factor (Less stable species wants to convert into more stable species).

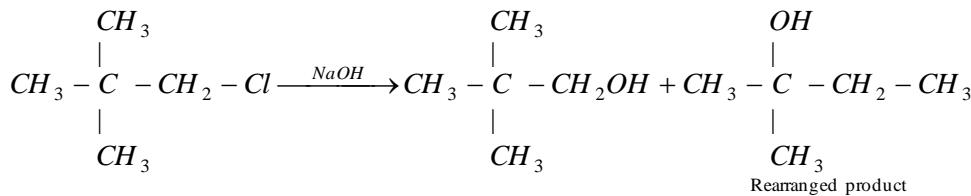
- (ii) For rearrangement, carbocation should have at least three carbons. (α , β and γ).

(iii) If β -carbon has hydrogen as well as alkyl group then rearrangement is due to the migration of hydrogen in the form of hydride ion from β to α -carbon. If β -carbon has only hydrogens then hydrogen migrates. If β -carbon has only alkyl groups then alkyl group migrates from β to α -carbon.



Note: If the number of products of the reaction is more than the expected products then product formation takes place by formation of carbocation and there is rearrangement in carbocation.

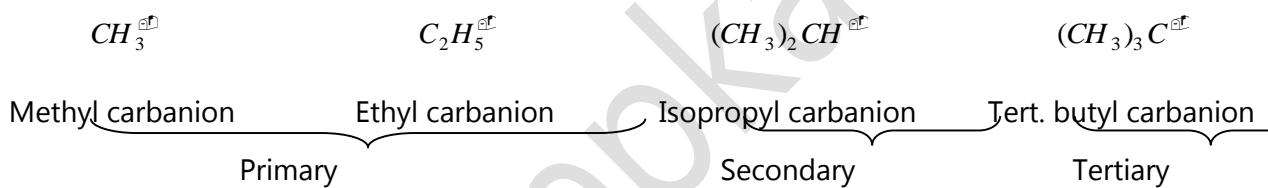




Carbanions

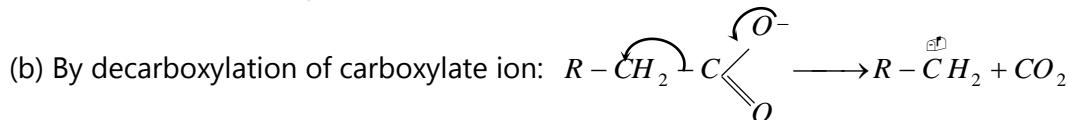
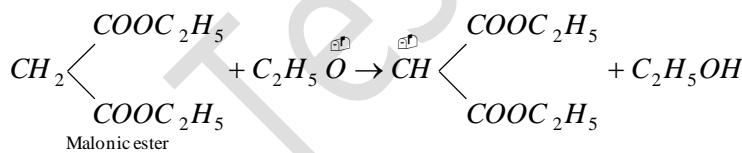
A carbanion may be defined as a species containing a carbon atom carrying a negative charge. These are generated by the Heterolytic fission of covalent bond involving carbon atom in which the atom linked to carbon goes without the bonding electrons.

It is denoted by putting a negative charge (–) against the symbol of group of atoms.



(1) Characteristics of carbanions,

- (i) The formation of carbanions can be done,
 - (a) By attack of base on hydrogen atom : Organic compounds which possess a labile or acidic hydrogen have the tendency to produce carbanions as in the case of reactive methylene compounds which lose proton in presence of sodium ethoxide (C_2H_5ONa).



- (c) By the formation of organometallic compound;
- $$CH_3 - Cl \xrightarrow{Mg / ether} CH_3MgCl \longrightarrow CH_3 + Mg^+Cl^-$$

(ii) Carbanions are not electrically neutral.

(iii) There are eight electrons in the outermost orbit of carbanionic carbon hence its octet is complete.



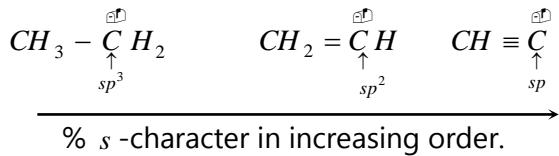
- (iv) A carbanion is diamagnetic in nature due to all paired electrons.

(v) Carbanions are charged nucleophiles i.e., they react with electrophilic reagents. The order of reactivity of carbanions is, Tertiary (3°) > Secondary (2°) > Primary (1°) (Decreasing order)

(2) **Stability of carbanions:** The stability of carbanion may be explained by

(i) Electronegativity of carbanionic carbon

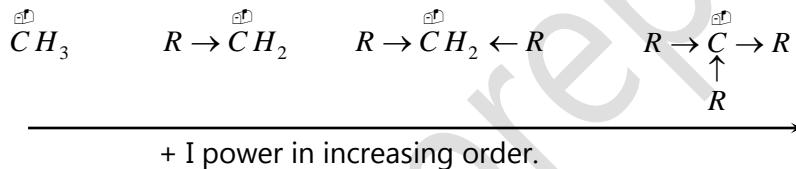
Stability \propto Electronegativity of carbanionic carbon \propto % *s*-character of carbanionic carbon



Stability in increasing order.

(ii) **Inductive effect:** Stability of carbanions depends on the +I or -I group as follows:

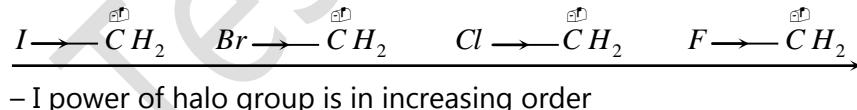
$$(a) \text{Stability} \propto \frac{1}{+I \text{ power of the group}}$$



Stability in decreasing order.

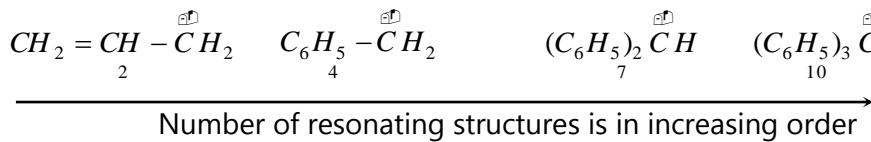
(b) Stability of carbanions $\propto -I$ power of the group.

For example:



Stability is in increasing order

(iii) **Delocalization or Resonance:** Allyl and benzyl carbanions are stabilized by delocalization of negative charge.



Stability is in increasing order.



Preparation Classes



Counseling Sessions



Online Test



Free Trial Classes



www.testprepkart.com



info@testprepkart.com

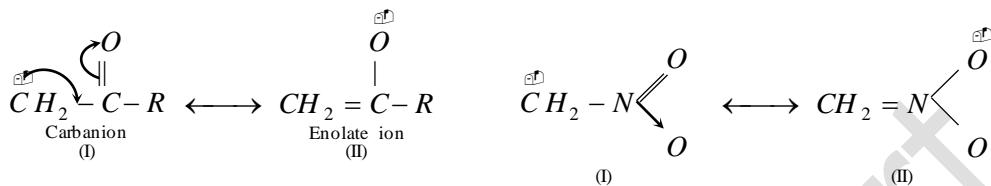


+91 - 8800 1234 92

(iv) **Stabilization by sulphur and phosphorous:** Attachment of carbanionic carbon of a sulphur and phosphorus atom causes an increase in carbanion stability.

The cause of stability is due to the delocalization of negative charge of carbanion by vacant d -orbital ($p\pi - d\pi$ bonding) of phosphorus and sulphur.

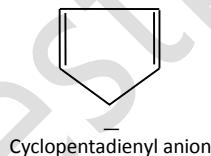
(v) **Stabilization by $>C=O$, $-NO_2$ and CN groups present on carbanionic carbon:** These groups stabilize carbanion by resonance effect.



Contribution of structure (II) will be more than (I) because in (II) negative charge is present on electronegative oxygen.

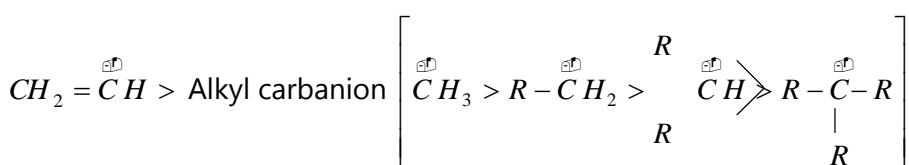
(vi) Stability of Aromatic carbanions

- (a) Anions in which negative charge is present on carbon of aromatic system is known as aromatic carbanions.
- (b) Aromatic carbanions are most stable carbanions.
- (c) Anions obeying Huckel rule are stable because they are aromatic and there is complete delocalization of negative charge.

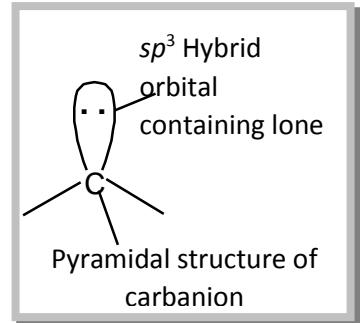


(3) Relative stability of different types of carbanions in decreasing order

Aromatic carbanion > Benzyl carbanion > Allyl carbanion > $CH \equiv C^- >$



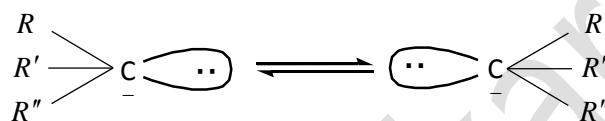
(4) **Structure of carbanion:** The negatively charged carbon atom in carbanion is sp^3 hybridized. Therefore, it has a pyramidal structure. Three of the four sp^3 hybridized orbitals form 3σ bonds with hydrogen or carbon atom of the alkyl group. The fourth sp^3 hybrid orbital contains the lone pair of electrons.



Note: Geometry of allyl and benzyl carbanion is almost planar and hybridization is sp^2 .

Methyl anion is isostructural (pyramidal) and isoelectronic (eight valency electrons) with ammonia.

The carbanions having three different bulky groups are not optically active. It is due to pyramidal structure of carbanion which is not rigid and shows a rapid equilibrium between following two enantiomeric pyramidal structures.

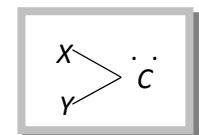


(5) Reactions involving carbanions

- (i) Condensation reactions of carbonyl compounds, i.e., Aldol condensation, Perkin reaction, Reformatsky reaction etc.
- (ii) Condensation reaction of ester; Claisen condensation.
- (iii) Wittig reaction.

Carbenes

A carbene may be defined as a species in which carbon atom has six electrons in the outer shell (electron deficient), out of which two constitute a lone pair and two are shared. So they are divalent carbon species containing two unpaired electrons and possess no charge.



The simplest carbene is $\dot{C}H_2$, which known as methylene. Substituted carbenes are simply named as

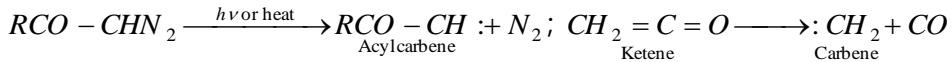
derivative of carbenes. For example, $C_6H_5-\dot{C}H$ Phenyl carbene $R-\dot{C}-R$ Dialkylcarbene $\dot{C}Cl_2$ Dichloro carbene



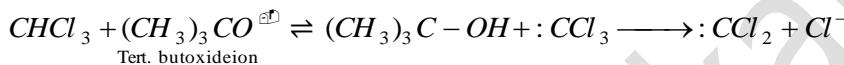
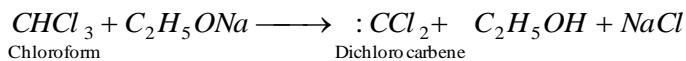
(1) Characteristics of carbnes

(i) Carbenes can be formed,

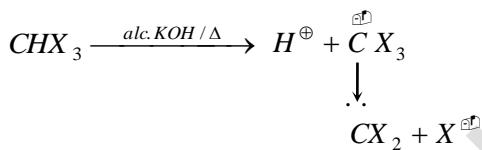
(a) By the photochemical decomposition or pyrolysis of aliphatic diazo compounds or ketenes.



(b) By the action of a base on suitable polyhalogen compound.



(ii) Carbenes are related to carbanions through the α -elimination reaction.

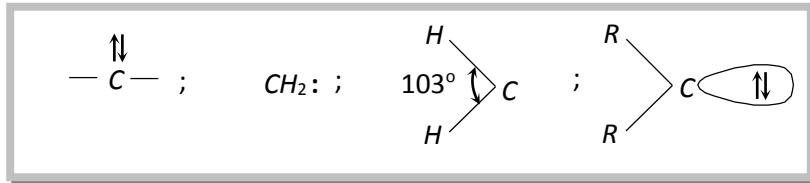


(iii) Carbenes are neutral, divalent, highly reactive carbon intermediates. They work as electrophiles.

(2) Types and stability of carbenes

Carbenes are of two types

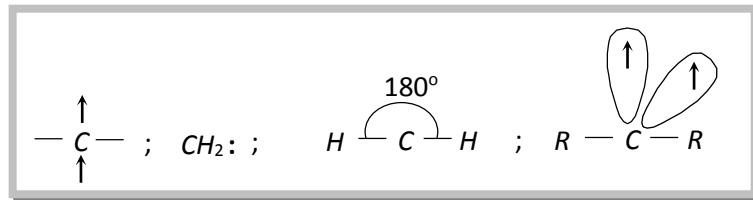
(i) **Singlet**: When both the electrons go into one orbital and have opposite spin (antiparallel), i.e., the unshared electrons are paired in one orbital and has a bent structure.



The singlet state is actually found to have $H - C - H$ bond angle 103° (between 90° to 120°) and a $C - H$ bond length of 1.12\AA . It is generally considered as the less stable.



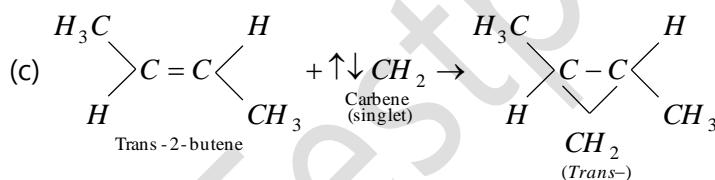
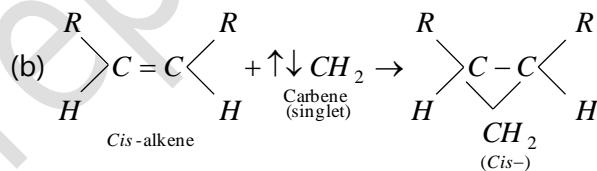
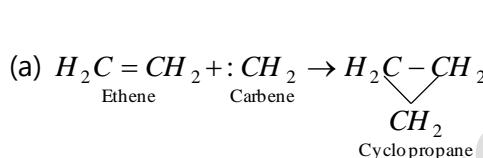
(ii) **Triplet:** When the two electrons go into different orbitals and have same spin (parallel), i.e., the unshared electrons are not paired. Such carbene would have a permanent magnetic moment and would exist in three closely grouped energy state, if it were placed in a magnetic field. Such a state is called triplet state and is believed to be a linear molecule.



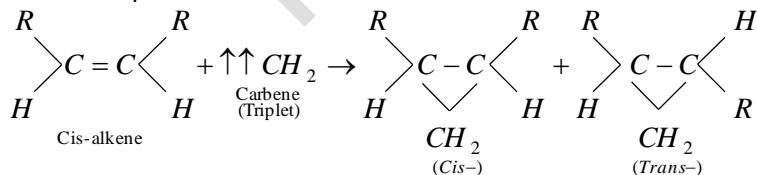
With $H - C - H$ bond angle 180° and a $C - H$ bond length of 1.03\AA , it might be considered as a free diradical and is more stable.

(3) Reactions involving carbenes

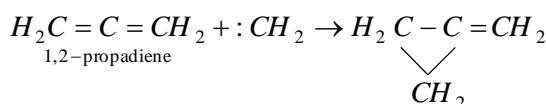
(i) **Addition to alkenes:** Formation of cyclo alkane derivatives, e.g.,

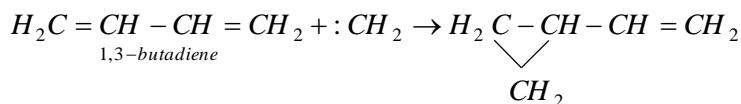


(d) Conversely, the triplet carbenes add on alkenes in a non-stereo specific manner to form both (cis- and trans-) products.

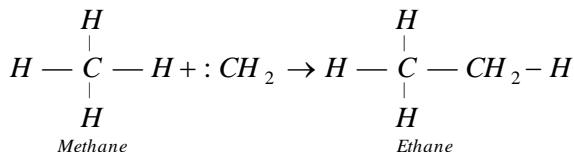


(e) In case of conjugated or cumulative, the addition always occurs exclusively at 1, 2-position.

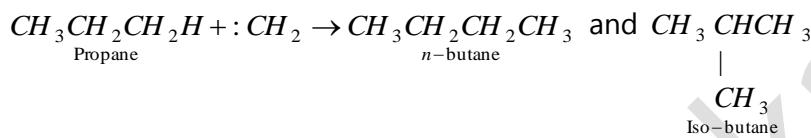




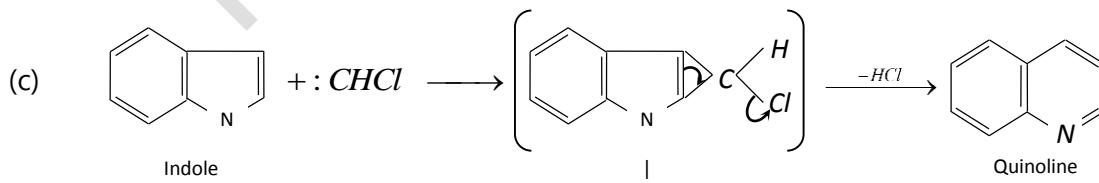
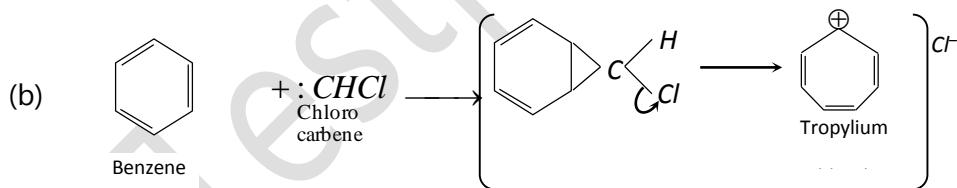
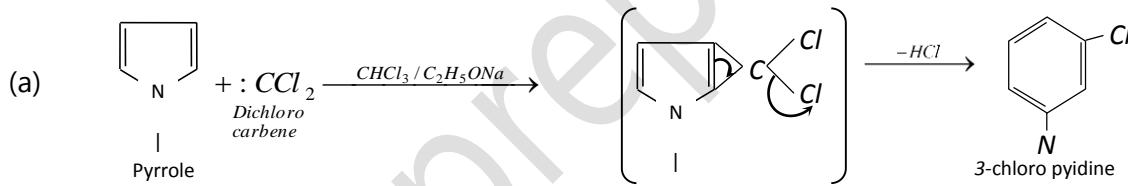
(ii) **Insertion reactions:** Carbenes are also used in its insertion between the $C-H$ bond, e.g.,



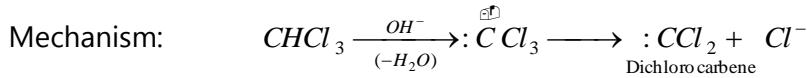
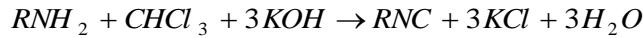
Further it can be inserted in all the possible positions (pri-, sec-, tert-).



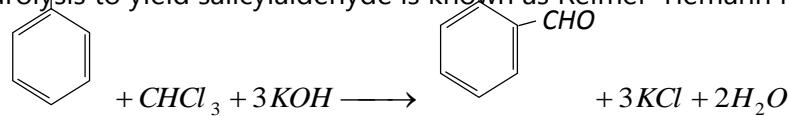
(iii) **Ring expansion reactions:** These involve the addition of a halogeno carbene across a double bond followed by rearrangement.



(iv) **Carbylamine reaction:** By heating a mixture of primary amine and chloroform with ethanolic potassium hydroxide to form isocyanide (carbylamine) is known as carbylamine reaction.

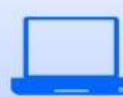


(v) **Reimer-Tiemann reaction:** Phenol on heating with chloroform and aqueous alkali followed by acid hydrolysis to yield salicylaldehyde is known as Reimer-Tiemann reaction.



Comparison of Free radical, Carbocation, Carbanion and Carbene

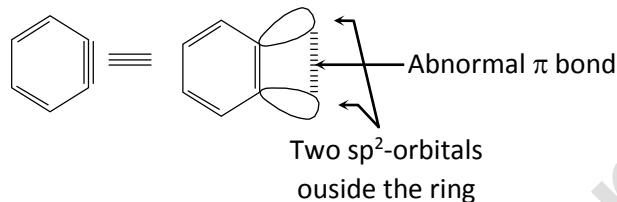
Characteristic	Free radical	Carbocation	Carbanion	Carbene
Nature	Neutral having odd electron	Positive charge on C	Negative charge on C	Neutral, divalent with 2 unshared electrons
Hybridization	sp^2	sp^2	sp^3 (non-conjugated) sp^2 (Conjugated)	(i) sp^2 (singlet) (ii) sp (triplet)
Structure	Planar	Planar	Pyramidal/Planar	(i) Planar (singlet) (ii) Linear (triplet)
Magnetism	Paramagnetic	Diamagnetic	Diamagnetic	(i) Diamagnetic (ii) Paramagnetic
Stability order	$\text{Ph}_3\dot{\text{C}} > \text{Ph}_2\dot{\text{CH}} > \text{Ph}\dot{\text{CH}}_2$ $\text{Ph}_3\dot{\text{C}} > \text{Ph}_2\dot{\text{CH}} > \text{Ph}\dot{\text{CH}}_2 > \text{CH}_2 = \text{CH} - \dot{\text{CH}}_2$ $\text{CH}_2 = \text{CH} - \dot{\text{CH}}_2 > 3^\circ > 2^\circ >$ $1^\circ > \dot{\text{CH}}_2 > \text{CH}_2 = \dot{\text{CH}}$	$\text{Ph}_3^+\text{C} > \text{Ph}_2^+\dot{\text{CH}} >$ $\text{Ph}\dot{\text{CH}}_2 > \text{CH}_2 = \text{CH} - \dot{\text{CH}}_2$ $\text{Ph}\dot{\text{CH}}_2 > \text{Allyl}$ $\text{CH}_2 > 1^\circ > 2^\circ > 3^\circ$	$\text{Ph}_3^+\text{C} > \text{Ph}_2^+\dot{\text{CH}} >$ $\text{Ph}\dot{\text{CH}}_2 > \text{CH}_2 = \text{CH} - \dot{\text{CH}}_2$ $\text{Ph}\dot{\text{CH}}_2 > \text{Allyl}$ $\text{CH}_2 > 1^\circ > 2^\circ > 3^\circ$	Triplet > singlet



Benzyne

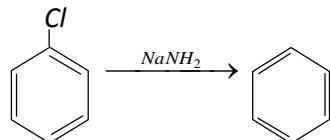
(1) 1, 2-Didehydrobenzene, C_6H_4 and its derivatives are called benzyne or arynes and the simplest member is benzyne.

(2) It is neutral reaction intermediate derived from benzene ring by removing two substituents, of ortho positions, one in the form of electrophile and other in the form of nucleophile leaving behind two electrons to be distributed between two orbitals.



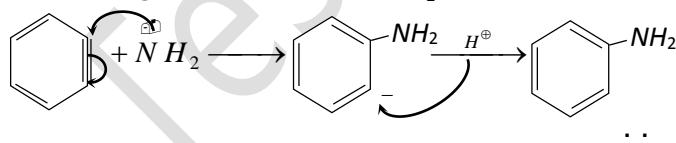
(3) Benzyne intermediate is aromatic in character.

(4) When halobenzene is heated with sodamide formation of benzyne takes place.



(5) (i) It behaves as dienophile and gives Diels-Alder reaction with diene.

(ii) It reacts with strong nucleophile like NH_2^-



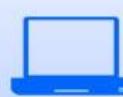
Nitrenes ($R - N :^-$)

(1) The nitrogen analogous of carbenes are called nitrenes.

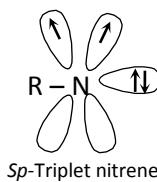
(2) There is possibility of two spin states for nitrenes depending on whether the two non-bonding electrons (the normal nitrogen lone pair remains paired) have their spins paired or parallel.

These two may be paired or unpaired

↑
These two are the pair of electrons

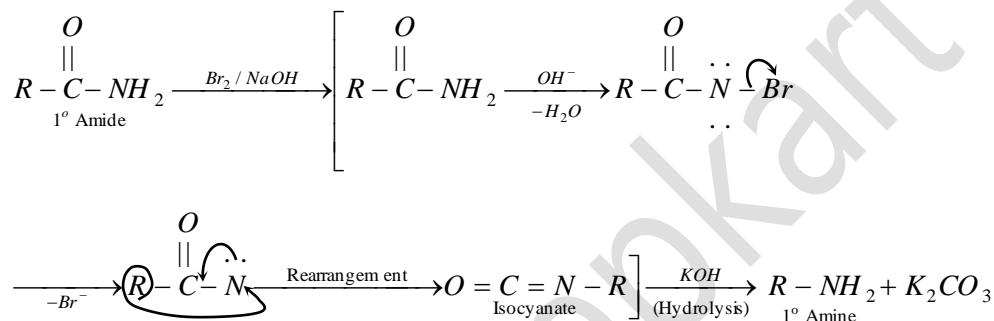


(3) In general nitrenes obey Hunds rule and are ground state triplet with two degenerate sp -orbitals containing a single electron each.



(4) Nitrenes can be generated, *in situ*, by the following methods,

(i) **By action of Br_2 in presence of a base on a 1° amide** (Hofmann-bromamide reaction),



(ii) **By decomposition of azides in presence of heat or light.**



(iii) Unsubstituted nitrene ($H-N\cdot$) can be obtained by photolysis of (or by passing electric discharge through) NH_3 , N_2H_4 or N_3H .



10. Attacking reagents.

Most of the attacking reagents carry either a positive or a negative charge. The positively charged reagents attack the regions of high electron density in the substrate molecule while the negatively charged reagents will attack the regions of low electron density in the substrate molecule. The fission of the substrate molecule to create centers of high or low electron density is influenced by attacking reagents. Most of the attacking reagents can be classified into two main groups.

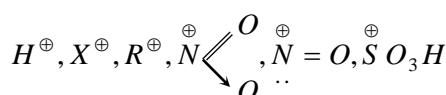
- (1) Electrophiles or electrophilic reagents.
- (2) Nucleophiles or nucleophilic reagents.

(1) **Electrophiles:** Electron deficient species or electron acceptor is electrophile.

It can be classified into two categories:

- (i) Charged electrophiles (E^\oplus), (ii) Neutral electrophiles (E)

(i) **Charged electrophiles:** Positively charged species in which central atom has incomplete octet is charged electrophile.



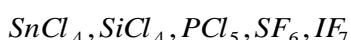
Note: All cations are charged electrophiles except cations of IA, IIA group elements, Al^{+++} and NH_4^\oplus

(ii) **Neutral electrophiles:** It can be classified into three categories,

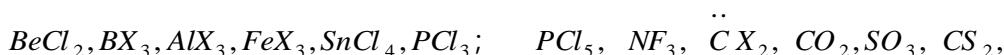
(a) Neutral covalent compound in which central atom has incomplete octet is neutral electrophile,



(b) Neutral covalent compound in which central atom has complete or expended octet and central atom has unfilled -d-sub-shell is neutral electrophile,



(c) Neutral covalent compound in which central atom is bonded only with two or more than two electronegative atoms is neutral electrophile.



Note: Cl_2, Br_2 and I_2 also behave as neutral electrophiles.

Electrophiles are Lewis acids.



Preparation Classes



Counseling Sessions



Online Test



Free Trial Classes



www.testprepkart.com



info@testprepkart.com



+91 - 8800 1234 92

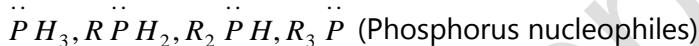
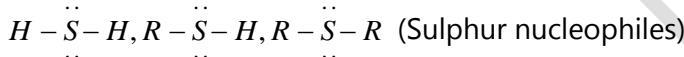
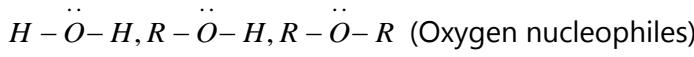
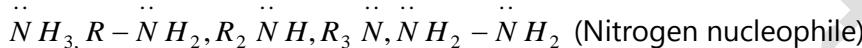
(2) **Nucleophiles:** Electron rich species or electron donor is nucleophiles. Nucleophiles can be classified into three categories:

(i) **Charged nucleophiles:** Negatively charged species are charged nucleophiles.



(ii) **Neutral nucleophiles:** It can be classified into two categories:

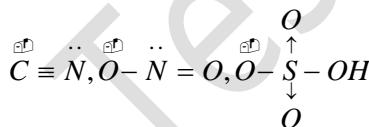
(a) Neutral covalent compound, in which central atom has complete octet, has at least one lone pair of electrons and all atoms present on central atom should not be electronegative, is neutral nucleophile.



(b) Organic compound containing carbon, carbon multiple bond/ bonds behaves as nucleophile.

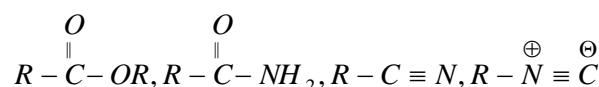
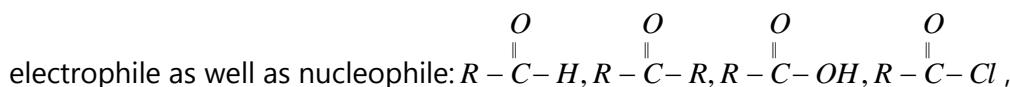
Alkenes, Alkynes, Benzene, $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2, \text{CH}_2 = \text{CH} - \text{C} \equiv \text{CH}$

(iii) **Ambident nucleophiles:** Species having two nucleophilic centers, one is neutral (complete octet and has at least one lone pair of electrons) and other is charged (negative charge) behaves as ambident nucleophile



Note: Organometallic compounds are nucleophiles. Nucleophiles are Lewis bases.

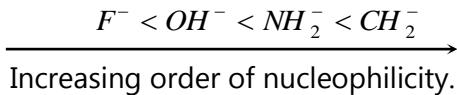
Organic compounds which behave as electrophile as well as nucleophile: Organic compound in which carbon is bonded with electronegative atom (O, N, S) by multiple bond/bonds behaves as



Note: During the course of chemical reaction electrophile reacts with nucleophile.

Strong Lewis acids stronger is electron phile $\text{CO}_2 < \overset{\oplus}{N} \text{O}_2 < \overset{\oplus}{S} \text{O}_3\text{H}$. Stronger is an acid weaker is its conjugated base or weaker is nucleophile.

Examples: $\text{HF} > \text{H}_2\text{O} > \text{NH}_3 > \text{CH}_4$



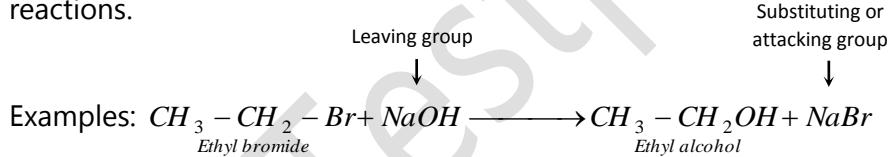
14. Types of organic reactions.

It is convenient to classify the numerous reactions of the various classes of organic compound into four types,

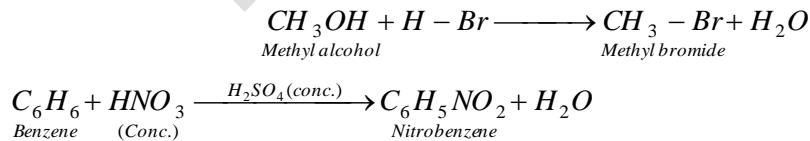
- Substitution reactions,
- Addition reaction,
- Elimination reactions,
- Rearranged reactions,

Substitution reactions

Replacement of an atom or group of the substrate by any other atom or group is known as substitution reactions.

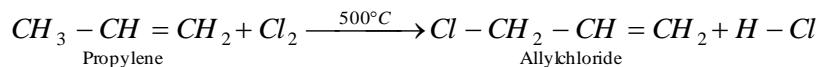


(Bromine atom is replaced by hydroxyl group)

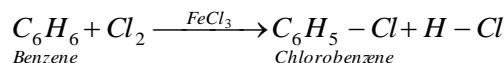


(Hydroxyl group is replaced by bromine)

(Hydrogen is replaced by NO_2 group)



(Hydrogen is replaced by chlorine)



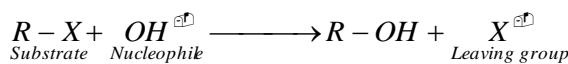
(Hydrogen is replaced by chlorine)

Types of substitution reactions: On the basis of the nature of attacking species substitution reactions are classified into following three categories:

- (1) Nucleophilic substitution reactions
- (2) Electrophilic substitution reactions,
- (3) Free radical substitution reactions

(1) Nucleophilic substitution reactions

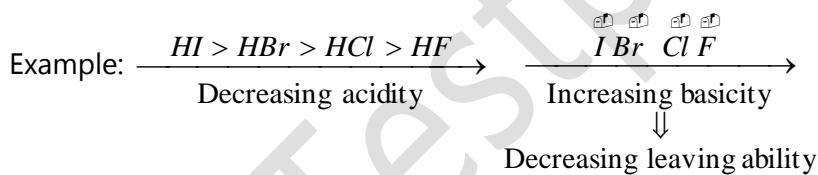
(i) Many substitution reactions, especially at the saturated carbon atom in aliphatic compounds such as alkyl halides, are brought about by nucleophilic reagents or nucleophiles.



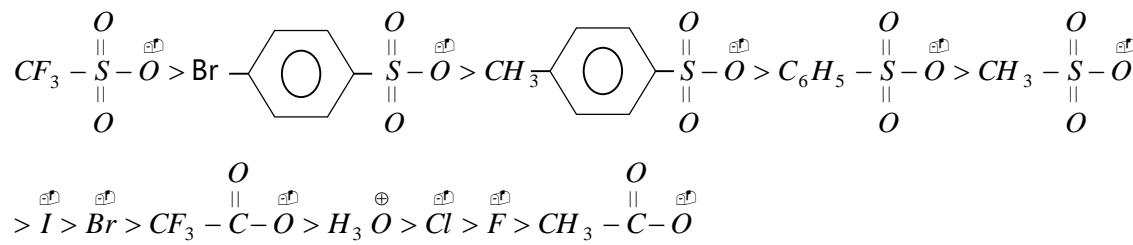
Such substitution reactions are called nucleophilic substitution reactions, i.e., S_N reactions (S stands for substitution and N for nucleophile).

(ii) The weaker the basicity of a group of the substrate, the better is its leaving ability.

$$\text{Leaving power of the group} \propto \frac{1}{\text{Basicity of the group}}$$



(iii) The leaving power of some nucleophilic groups are given below in decreasing order,



(iv) In these reactions leaving group of the substrate is replaced by another nucleophile. If reagent is neutral than leaving group is replaced by negative part of the reagent. Negative part of the reagent is always nucleophilic in character.



Preparation Classes



Counseling Sessions



Online Test



Free Trial Classes



www.testprepkart.com

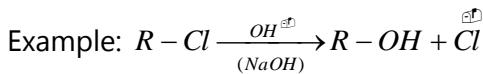


info@testprepkart.com

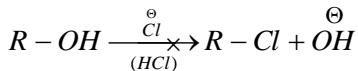


+91 - 8800 1234 92

(v) In S_N reactions basicity of leaving group should be less than the basicity of incoming nucleophilic group. Thus strongly basic nucleophilic group replaces weakly basic nucleophilic group of the substrate.



Basicity of OH^- is more than Cl^- hence OH^- replaces Cl as Cl^-



Basicity of Cl^- is less than OH^- hence Cl^- will not replace OH^- as OH^- .

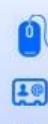
(vi) Unlike aliphatic compounds having nucleophilic group as leaving group, aromatic compounds having same group bonded directly with aromatic ring do not undergo nucleophilic substitution reaction under ordinary conditions.

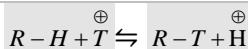
The reason for this unusual reactivity is the presence of lone pair or π bond on key atom of the functional group. Another factor for the low reactivity is nucleophilic character of aromatic ring.

(vii) The S_N reactions are divided into two classes, S_{N^2} and S_{N^1} reactions.

Distinction between S_N^2 and S_N^1 reactions

Factors	S_N^2 Reactions	S_N^1 Reactions
Number of steps	One: $R : L + : Nu \xrightarrow{\Theta} R : Nu + : L^\Theta$	Two: (i) $R : L \xrightarrow{Slow} R^+ + : L^\delta^-$ (ii) $R^+ + : Nu^- \xrightarrow{Fast} R : Nu$
Reaction rate and order	Second order: Rate \propto [Substrate] [Nucleophile] or Rate = $K_2[RL][:Nu^\delta^-]$	First order: Rate \propto [Substrate] or Rate = $K_1[RL]$
Molecularity	Bimolecular	Unimolecular
TS of slow step	$:Nu^\delta^- \cdots C \cdots L^\delta^-$	$:Nu^\delta^- \cdots C^\delta^+ \cdots L^\delta^- \cdots Nu^\delta^-$
Reacting nucleophile	The nucleophile attacks the carbon of the substrate exclusively from the back side.	The nucleophile can attack the carbon of the substrate both on the back and front sides although the back side attack predominates.
Stereochemistry	Complete inversion of configuration takes place.	Inversion and retention takes place.
Reactivity order of alkyl halides	Methyl > 1° > 2° > 3° halides. $(I > Br > Cl > F)$	3° > 2° > 1° > methyl halides. $(I > Br > Cl > F)$





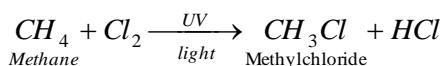
Step 3. Carbonium ion loses the proton to form substitution product.

The bromination of benzene in the presence of $FeBr_3$ is an example of electrophilic substitution.

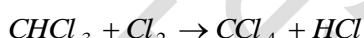
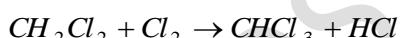
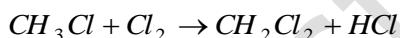
Similarly, Nitration, sulphonation and Friedel-Crafts reaction....etc., in benzene nucleus are the other examples of electrophilic substitution.

3) **Free radical substitution reactions:** Free radical substitution reactions involve the attack by a free radical. These reactions occur by free radical mechanism which involves: Initiation, Propagation and Termination steps. Examples,

(i) **Chlorination of methane:** The chlorination of methane in the presence of ultraviolet light is an example of free radical substitution (HOMOLYSIS).

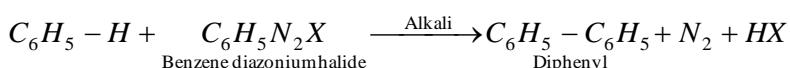


The reaction does not stop with the formation of methyl chloride (CH_3Cl) but the remaining hydrogen atoms are replaced one by one with chlorine atoms to give rise to chain reaction.

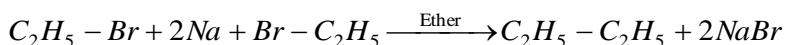


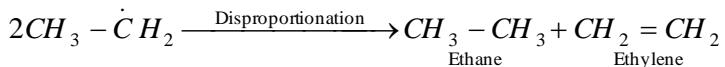
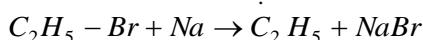
Reactivity of the halogens for free radical substitution is in the order: $F_2 > Cl_2 > Br_2 > I_2$

(ii) **Arylation of aromatic compounds** (Gomberg reaction): The reaction of benzene diazonium halide with benzene gives diphenyl by a free radical substitution reaction.

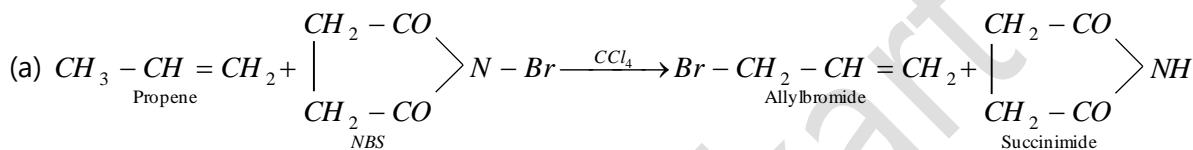


(iii) **Wurtz reaction:** Ethyl bromide on treatment with metallic sodium forms butane, ethane and ethylene by involving free radical mechanism.





(iv) **Allylic bromination by NBS** (N-Bromosuccinimide): NBS is a selective brominating agent and it normally brominates the ethylenic compounds in the allylic ($CH_2 = CH - CH_2 -$) position. This type of reaction involving substitution at the alpha carbon atom with respect to the double bond is termed Allylic substitution. It is also used for benzylic bromination. Some examples are:



Note: Halogenation of alkanes occurs by a free radical mechanism and is catalyzed by radical initiators like $(C_6H_5COO)_2$, $Pb(CH_3)_4$, $Pb(C_2H_5)_4$ etc.

Addition reactions

These reactions are given by those compounds which have at least one π bond,

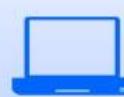
i.e., ($>C=C<$, $-C\equiv C-$, $-C-C-$, $C\equiv N$). in this reaction there is loss of one π bond and gain of two σ bonds. Thus product of the reaction is generally more stable than the reactant. The reaction is a spontaneous reaction.

Types of addition reactions: Addition reactions can be classified into three categories on the basis of the nature of initiating species.

(1) Electrophilic additions (2) Nucleophilic additions and (3) Free radical additions

(1) Electrophilic addition reactions

- (i) This reaction is mainly given by alkenes and alkynes.
- (ii) Electrophilic addition reactions of alkenes and alkynes are generally two step reactions.
- (iii) Alkenes and alkynes give electrophilic addition with those reagents which on dissociation gives electrophile as well as nucleophile.
- (iv) If the reagent is a weak acid then electrophilic addition is catalyzed by strong acids (Generally H_2SO_4).
- (v) Unsymmetrical alkenes and alkynes give addition reactions with unsymmetrical reagents according to



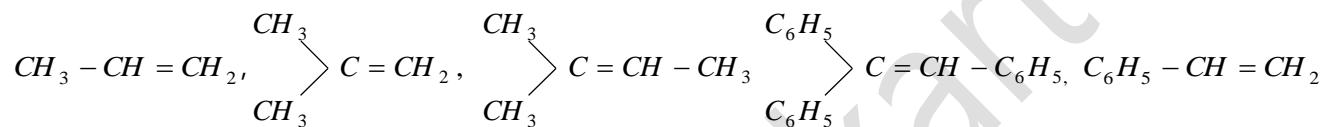
Markownikoff's rule.

The negative part of the reagent adds on that doubly bonded carbon of the alkene which has least number of hydrogen (s).

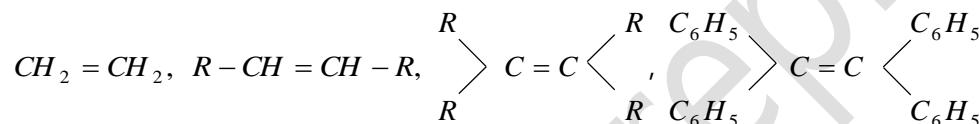
This rule can be used only in those alkenes which fulfil the following conditions:

- (a) Alkene should be unsymmetrical.
- (b) Substituent/substituents present on doubly bonded carbon/(s) should only be +I group.
- (c) If phenyl group is present on doubly bonded carbon, then both doubly bonded carbons should be substituted by phenyl groups.

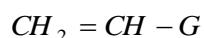
For example, the following alkenes will give addition according to the Markownikoff's rule.



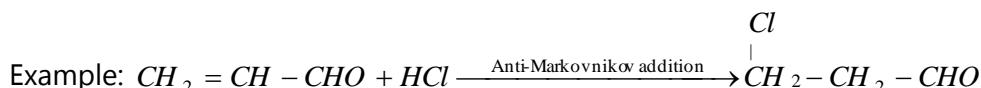
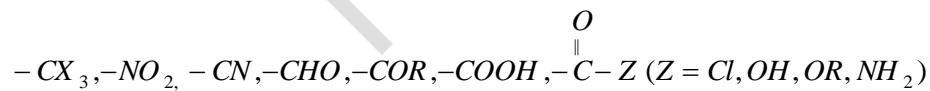
Following alkenes will not give addition reaction according to Markownikoff's rule.



- (vi) Unsymmetrical alkenes having the following general structure give addition according to anti Markownikoff's rule.



Where G is a strong -I group such as



Preparation Classes



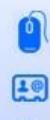
Counseling Sessions



Online Test



Free Trial Classes



www.testprepkart.com

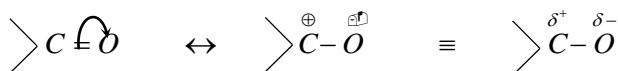


info@testprepkart.com

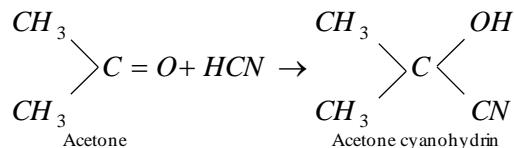


+91 - 8800 1234 92

(2) Nucleophilic addition reactions: When the addition reaction occurs on account of the initial attack of nucleophile, the reaction is said to be a nucleophilic addition reaction. Due to presence of strongly electronegative oxygen atom, the π -electrons of the carbon-oxygen double bond in carbonyl group ($C = O$) get shifted towards the oxygen atom and thereby such bond is highly polarized. This makes carbon atom of the carbonyl group electron deficient.

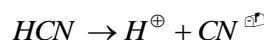


Example: The addition of HCN to acetone is an example of nucleophilic addition.

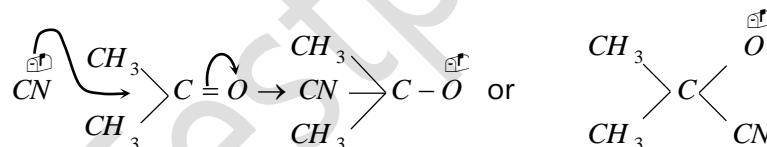


The mechanism of the reaction involves the following steps:

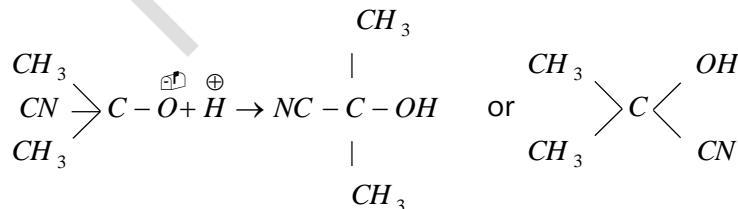
Step 1. HCN gives a proton (H^+) and nucleophile, a cyanide ion (CN^-).



Step 2. The nucleophile (CN^-) attacks the positively charged carbon as to form an anion [H^+ does not attack the negatively charged oxygen as anion is more stable than cation].



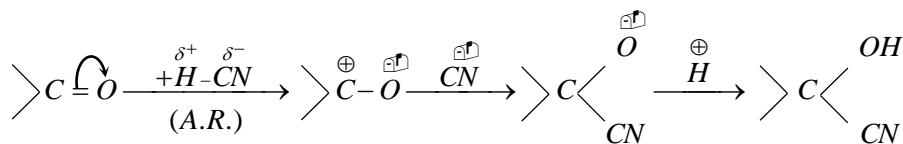
Step 3. The proton (H^+) combines with anion to form the addition product.



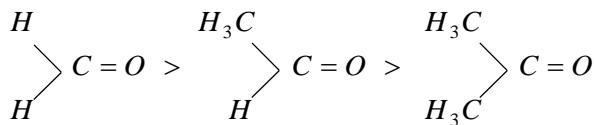
In $\text{C}=\text{O}$ compounds, the addition of liquid HCN gives cyanohydrin and the addendum is CN^-

ion (addition is catalyzed by bases or salts of weak acids and retarded by acids or unaffected by neutral compounds) and not HCN directly.

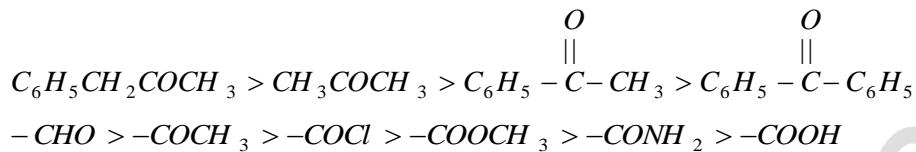




Nucleophilic addition (A_N) reactions on carbonyl compounds will be in order:

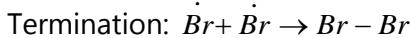
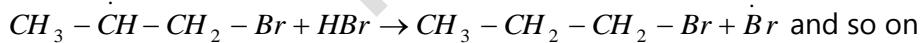
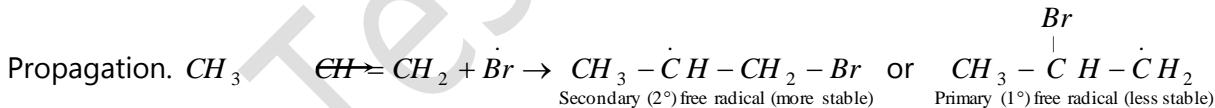
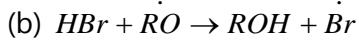


Note: Decreasing order of nucleophilic addition in some species.

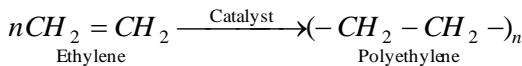


(3) **Free radical addition reactions:** Those reactions which involve the initial attack by a free radical are known as free radical reactions. Addition of hydrogen bromide to alkenes (say, propylene) in the presence of peroxide (radical initiator) follows free radical mechanism. Free radical reactions generally take place in non-polar solvents such as CCl_4 , high temperature, in presence of light or a free radical producing substance like O_2 and peroxides. The essential steps of the reactions are as follows.

Initiation (Formation of free radical)



Polymerization of ethylene to polyethylene and vinyl monomers to polyvinyl polymers are free radical addition reactions.



Preparation Classes



Counseling Sessions



Online Test



Free Trial Classes



www.testprepkart.com



info@testprepkart.com

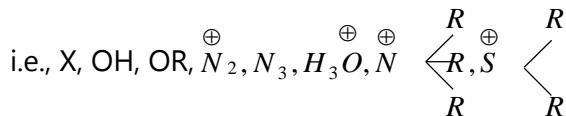


+91 - 8800 1234 92

Elimination reactions

Elimination reactions are formally the reverse of addition reactions and consist in removing the two groups (Generally, one being a proton) from one or two carbon atoms of a molecule to form an unsaturated linkage or center.

Elimination reaction is given by those compounds which have a nucleophilic group as leaving group,

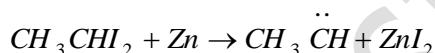


Elimination reactions are generally endothermic and take place on heating.

Elimination reactions are classified into two general types,

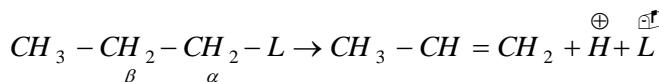
- (I) α - elimination reactions or 1, 1-elimination reactions.
- (II) β - elimination reaction or 1, 2-elimination reactions.

(I) α - elimination reactions or 1, 1-elimination reactions: A reaction in which both the groups or atoms are removed from the same carbon of the molecule is called α - elimination reaction. This reaction is mainly given by gem dihalides and gem trihalides having at least one α - hydrogen.



Product of the reaction is halocarbenes or dihalocarbenes. Carbenes are key intermediates in a wide variety of chemical and photochemical reactions.

(II) β - elimination reactions or 1, 2-elimination reactions: Consider the following reactions,



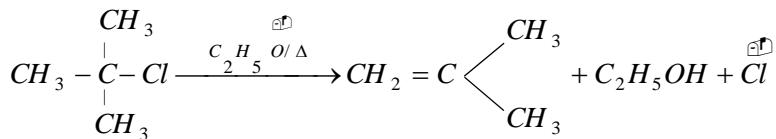
A reaction in which functional group (i.e., leaving group) is removed from α - carbon and other group (Generally hydrogen atom) from the β - carbon is called β - elimination reaction. In this reaction there is loss of two σ bonds and gain of one π bond. Product of the reaction is generally less stable than the reactant.



(1) **Types of β - elimination reactions:** In analogy with substitution reactions, β - elimination reactions are divided into three types:

(i) E₁ (Elimination unimolecular) reaction, (ii) E₂ (Elimination bimolecular) reaction and (iii) E_{1cb} (Elimination unimolecular conjugate base) reaction

(i) **E₁ (Elimination unimolecular) reaction:** Consider the following reaction,



(a) Reaction velocity depends only on the concentration of the substrate; thus reaction is unimolecular reaction.

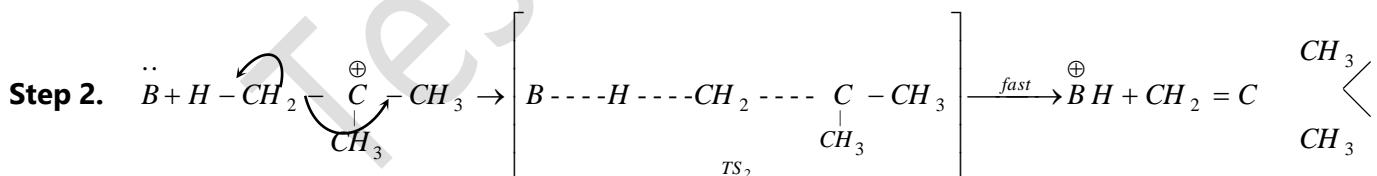
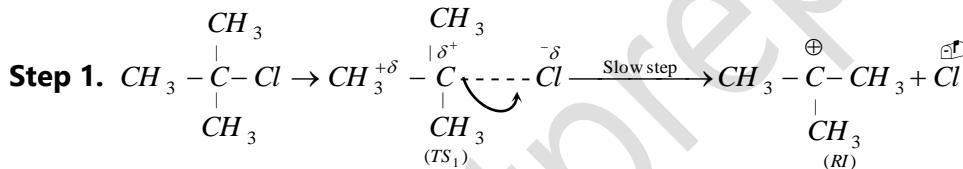
Rate \propto [Substrate]

(b) Product formation takes place by formation of carbocation as reaction intermediate (RI).

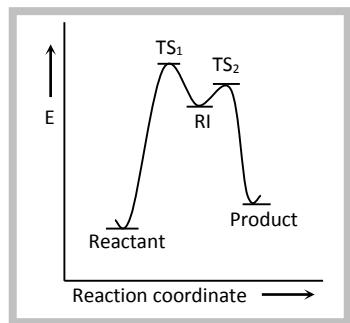
(c) Since reaction intermediate is carbocation, rearrangement is possible in E₁ reaction.

(d) Reaction is carried out in the presence of polar protic solvent.

(e) The E₁ reaction occurs in two steps,



(f) Energy profile diagram for E₁ reaction is,



Preparation Classes



Counseling Sessions



Online Test



Free Trial Classes



www.testprepkart.com

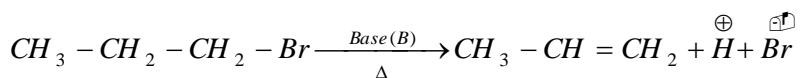


info@testprepkart.com

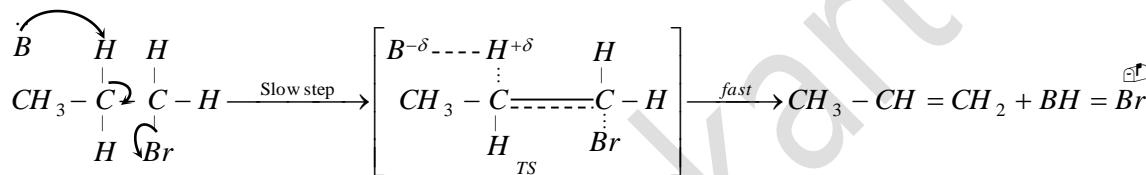


+91 - 8800 1234 92

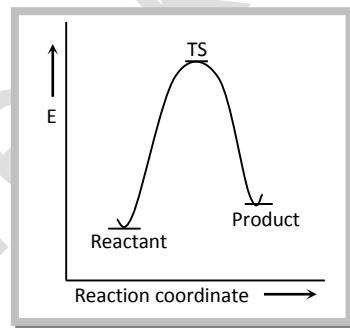
(ii) **E₂** (Elimination bimolecular) **reaction**: Consider the following reaction,



- (a) Reaction velocity depends only on the concentration of the substrate and the base used; thus reaction is bimolecular reaction. Rate \propto [Substrate] [Base]
- (b) Since the reaction is a bimolecular reaction, the product formation will take place by formation of transition state (TS).
- (c) Rearrangement is not take place in E₂ reaction but in case of allylic compound rearrangement is possible.
- (d) Reaction is carried out in the presence of polar aprotic solvent.
- (e) The E₁ reaction occurs in one step,



(f) Energy profile diagram for E₂ reaction is,

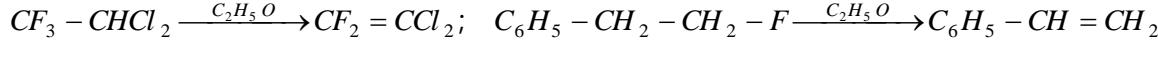


(iii) **E_{1cb}** (Elimination unimolecular conjugate base) **reaction**

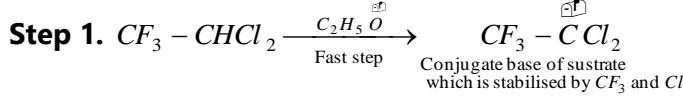
- (a) E_{1cb} mechanism is limited to substrates with substituents which can stabilize the carbanion as reaction intermediate.

Thus β - carbon should contain strong $-I$ group, e.g., $-C\equiv N$, $-NO_2$, $-C\equiv N$ or other carbanion stabilizing group.

- (b) This reaction is given by those compounds, which have poor leaving group, otherwise carbanion will not be formed.
- (c) β - hydrogen should be highly acidic so that it can easily be removed as proton to give carbanion.



(d) The E_{1cb} reaction occurs in two step,



Preparation Classes



Counseling Sessions



Online Test



Free Trial Classes



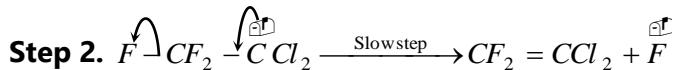
www.testprepkart.com



info@testprepkart.com

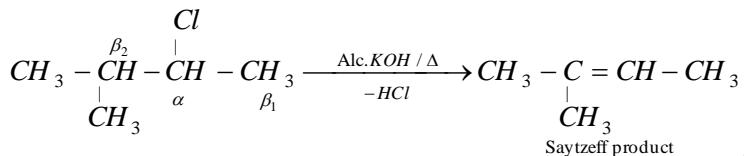


+91 - 8800 1234 92

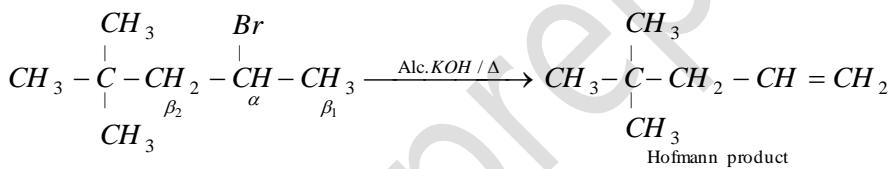


(2) **Orientation in β - elimination reactions:** If substrate is unsymmetrical, then this will give more than one product. Major product of the reaction can be known by two empirical rules.

(i) **Saytzeff rule:** According to this rule, major product is the most substituted alkene i.e., major product is obtained by elimination of H^+ from that β - carbon which has the least number of hydrogen. Product of the reaction in this case is known as Saytzeff product.



(ii) **Hofmann rule:** According to this rule, major product is always least substituted alkene i.e., major product is formed from β - carbon which has maximum number of hydrogen. Product of the reaction in this case is known as Hofmann product.



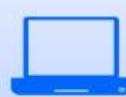
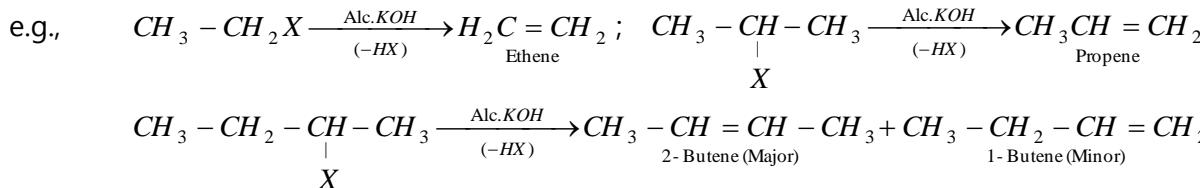
Note: In E₁ reactions, product formation always takes place by Saytzeff rule.

In E_{1cb} reactions, product formation always takes place by Hofmann rule.

In E_2 reactions, product formation takes place by Saytzeff as well as Hofmann rule. In almost all E_2 reactions product formation take place by Saytzeff rule.

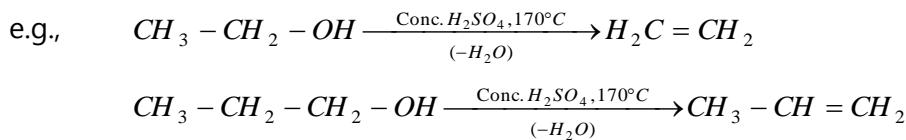
(3) Examples of β - elimination reactions

(i) **Dehydrohalogenation** is removal of HX from alkyl halides with alcoholic KOH or KNH_2 or OK - ter-Bu (Potassium tertiary butoxide) and an example of α - β elimination,



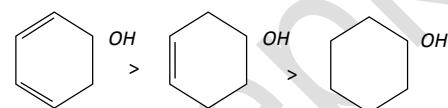
(ii) **Dehydration** of alcohol is another example of elimination reaction. When acids like conc. H_2SO_4 or H_3PO_4 are used as dehydrating agents, the mechanism is E₁. The proton given by acid is taken up by alcohol.

Dehydration is removal of H_2O from alcohols,

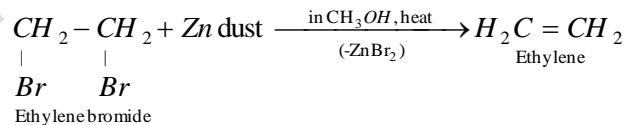


Note: Dehydration of alcohols is in the order: Tertiary > Secondary > Primary
 (3°) (2°) (1°)

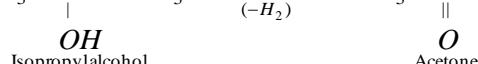
2° and 3° alcohol by E₁ process and 1° alcohol by E₂ process. Alcohols leading to conjugated alkenes are more easily dehydrated than the alcohols leading to non-conjugated alkenes. $CH_2 = CH - CH - CH_3$ is easily dehydrated than $CH_3 - CH_2 - CH - CH_3$ and so



(iii) **Dehalogenation:** It is removal of halogens, e.g.



(iv) **Dehydrogenation:** It is removal of hydrogen, e.g., $CH_3 - CH - CH_3 \xrightarrow[(-H_2)]{Cu, 300^\circ C} CH_3 - C - CH_3$



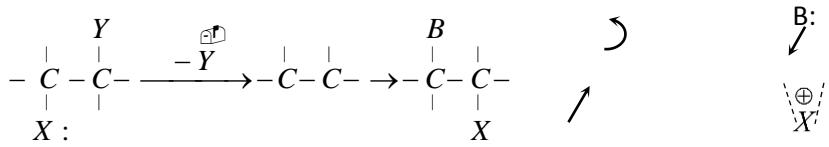
Rearrangement reactions

The reactions, which involve the migration of an atom or group from one site to another within the molecule (nothing is added from outside and nothing is eliminated) resulting in a new molecular structure, are known as rearrangement reactions. The new compound is actually the structural isomer of the original one.

It is convenient to divide rearrangement reactions into following types:



(1) Rearrangement or migration to electron deficient atoms (Nucleophilic rearrangement): Those rearrangement reactions in which migrating group is nucleophilic and thus migrates to electron deficient center which may be carbon, nitrogen and oxygen.



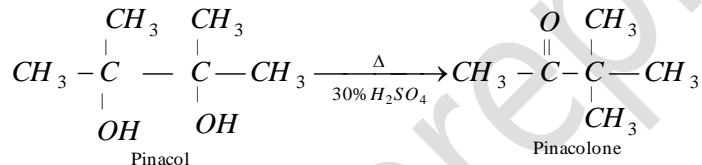
Bridged or

Non-classical carbocation

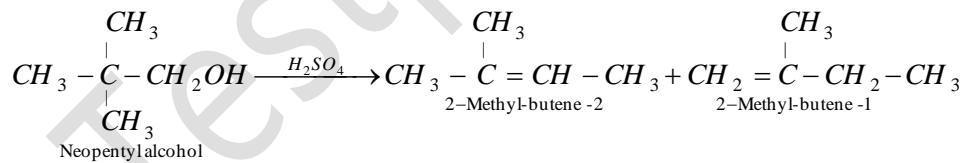
X= Nucleophilic species, Y = Electronegative group, B = another nucleophile.

Examples:

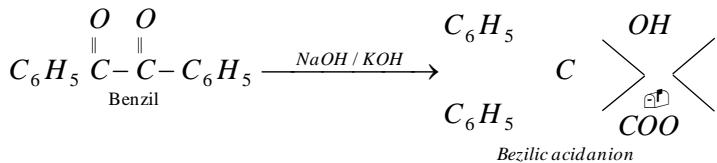
(i) Pinacol – pinacolone rearrangement



(ii) Wagner – Meerwein rearrangement



(iii) Benzilic acid rearrangement



Preparation Classes



Counseling Sessions



Online Test



Free Trial Classes



www.testprepkart.com

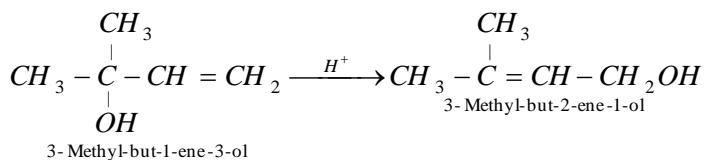


info@testprepkart.com

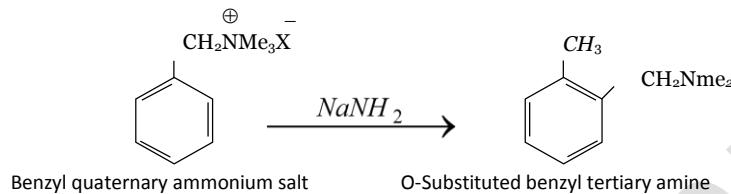


+91 - 8800 1234 92

(v) **Allylic rearrangement**



(vi) **Sommelet – Hauser rearrangement**



(vii) **Hofmann rearrangement:** $RCONH_2 + Br_2 + 4KOH \rightarrow RNH_2 + 2KBr + K_2CO_3 + 2H_2O$

(viii) **Curtius rearrangement:** $RCO\text{N}_3 \xrightarrow[\text{Acid azide}]{\Delta} RNCO + N_2$

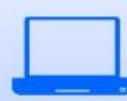
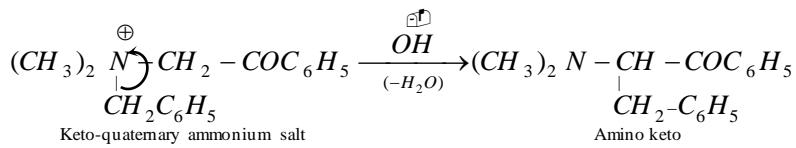
(ix) **Schimdt rearrangement:** $RCOOH + HN_3 \xrightarrow{H_2SO_4} R - NH_2 + CO_2 + N_2$

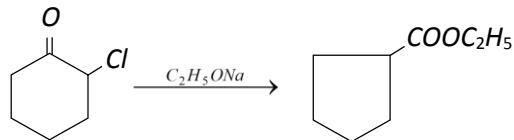
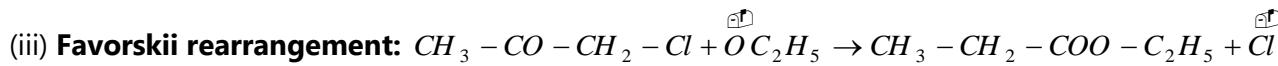
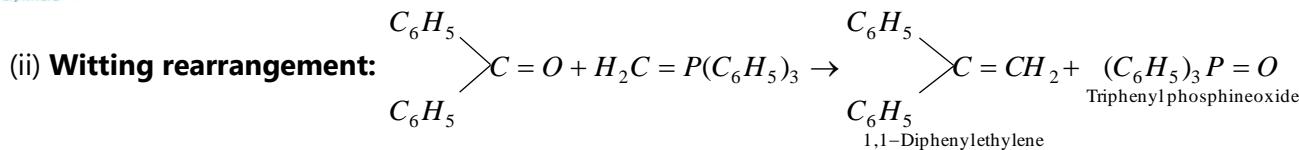
(x) **Baeyer Villiger reaction:** $CH_3 - CO - CH_3 + CH_3 - COOOH \xrightarrow{H_2SO_4} CH_3 - COO - CH_3 + H_3CCOOH$

(2) **Rearrangement or migration to electron rich atoms (Electrophilic rearrangement):** Those rearrangement reactions in which migrating group is electrophile and thus migrates to electron rich center.

Examples:

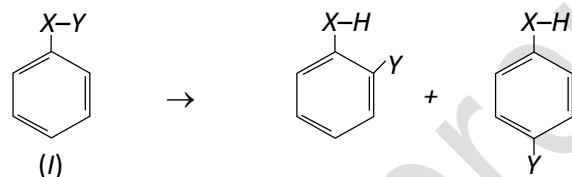
(i) **Stevens rearrangement:**





(3) **Rearrangement or migration to free radical species** (Free radical rearrangement): Those rearrangement reactions in which the migrating group moves to a free radical center. Free radical rearrangements are comparatively rare.

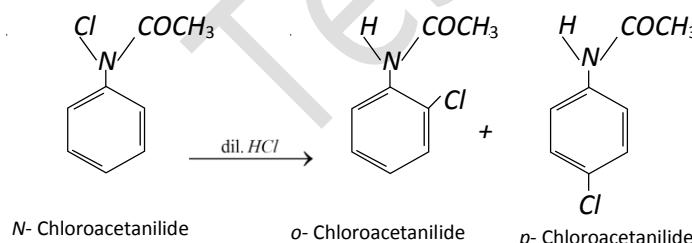
(4) **Aromatic rearrangement:** Those rearrangement reactions in which the migrating group moves to aromatic nucleus. Aromatic compounds of the type (I) undergo rearrangements in the manner mentioned below,



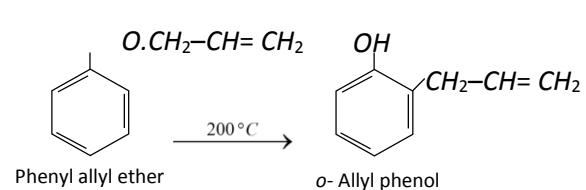
The element X from which group Y migrates may be nitrogen or oxygen.

Examples:

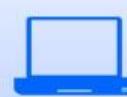
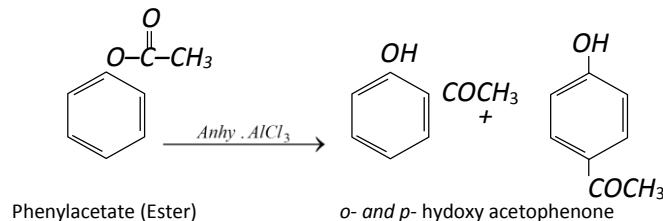
(i) **Orton rearrangement**



(ii) **Claisen rearrangement**



(iii) **Fries rearrangement**

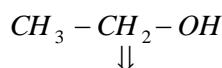


15. Isomerism.

Compounds having same molecular formula but differing from each other at least in some physical or chemical properties or both are known as isomers (Berzelius) and the phenomenon is known as isomerism.

For example,

Ethyl alcohol (C_2H_6O)



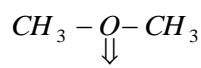
It is liquid.

Its boiling point is $78^{\circ}C$

It reacts vigorously with sodium and evolves hydrogen.

It reacts with HI and forms ethyl iodide, C_2H_5I .

Dimethyl ether (C_2H_6O)



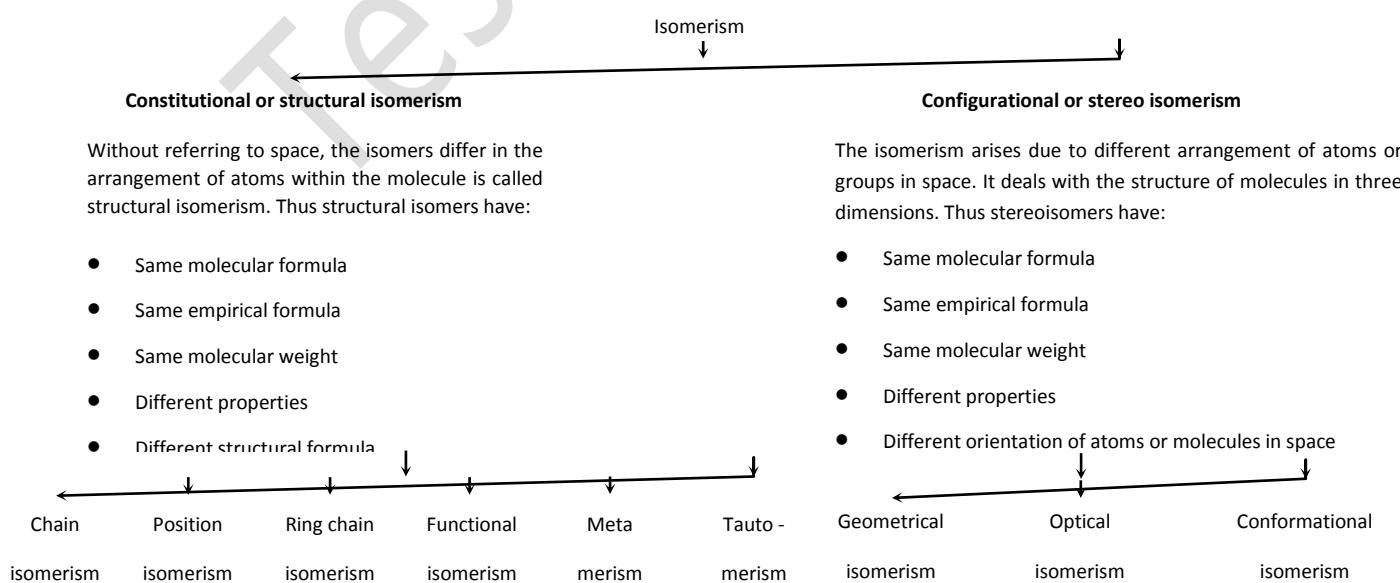
It is a gas.

Its boiling point is $-24^{\circ}C$.

It does not react with sodium.

It reacts with HI and forms methyl iodide, CH_3I

The difference in properties of isomers is due to the difference in the relative arrangements of various atoms or groups present in their molecules. Isomerism can be classified as follows:



Preparation Classes



Counseling Sessions



Online Test



Free Trial Classes



www.testprepkart.com



info@testprepkart.com

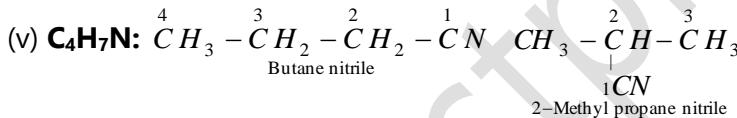
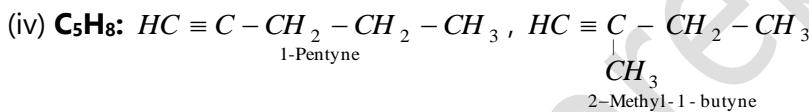
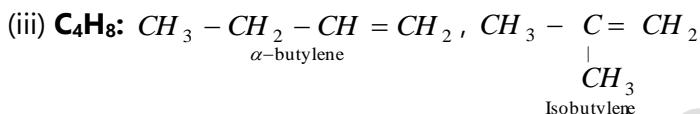
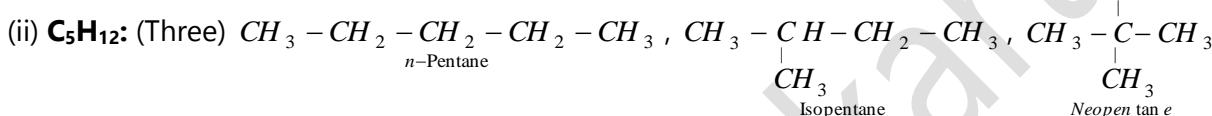
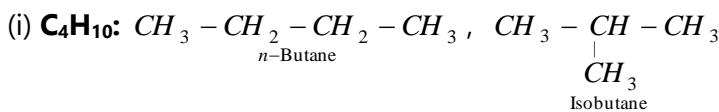


+91 - 8800 1234 92

16. Constitutional or structural isomerism.

(1) **Chain, nuclear or skeleton isomerism:** This type of isomerism arises due to the difference in the nature of the carbon chain (i.e., straight or branched) which forms the nucleus of the molecule.

Examples:



Note: Except alkynes chain isomerism is observed when the number of carbon atoms is four or more than four. Chain isomers differ in the nature of carbon chain, i.e., in the length of carbon chain.

The isomers showing chain isomerism belong to the same homologous series, i.e., functional group, class of the compound (Cyclic or open) remains unchanged.

Chain and position isomerism cannot be possible together between two isomeric compounds. If two compounds are chain isomers then these two will not be positional isomers.

(2) **Position isomerism:** It is due to the difference in the position of the substituent atom or group or an unsaturated linkage in the same carbon chain.

Examples:



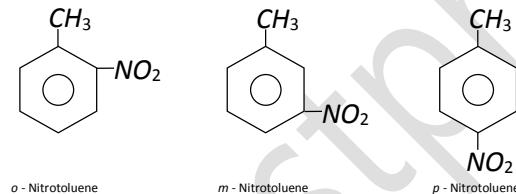
(ii) **C₃H₆Cl₂**: CH₃—CCl₂—CH₃, CH₃—CH₂—CH—Cl₂, CH₃— $\begin{array}{c} \text{CH} \\ | \\ \text{Cl} \end{array}$ —CH₂, CH₂—CH₂— $\begin{array}{c} \text{CH}_2 \\ | \\ \text{Cl} \end{array}$
 2,2-Dichloro propane, 1,1-Dichloro propane 1,2-Dichloro propane 1,3-Dichloro propane
 [Gem-two, vic-one and α , ω -one]

(iii) **C₄H₈**: CH₃ - CH₂ - CH = CH₂, CH₃ - CH = CH - CH₃
 1-Butene 2-Butene

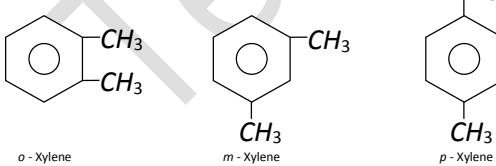
(iv) **C₄H₆**: CH₃ – CH₂ – C ≡ CH , CH₃ – C ≡ C – CH₃ , CH₂ = C = CH – CH₃ , CH₂ = CH – CH = CH₂
 1-Butyne 2-Butyne 1,2-Butadiene 1,3-Butadiene

(v) **C₃H₆O₂** : CH₃ - C(H-OH) - CHO , CH₂ - CH₂ - CHO
 2-Hydroxy propanal 3-Hydroxy propanal

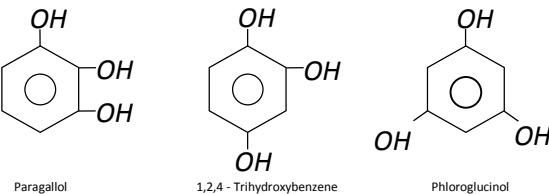
(vi) **C₇H₇NO₂ (Three aromatic):**



(vii) **C₈H₁₀ (Three aromatic):**



(viii) **C₆H₃(OH)₃** (Three aromatic):



Preparation Classes



Counseling Sessions



Online Test



Free Trial Classes



www.testprepkart.com

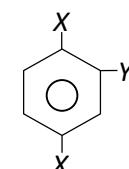
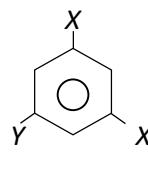
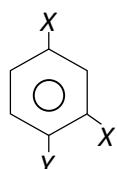
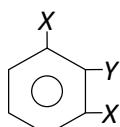
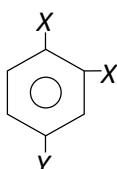
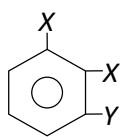


info@testprepkart.com

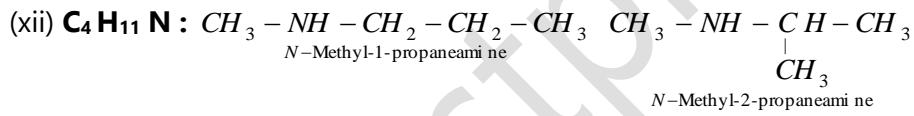
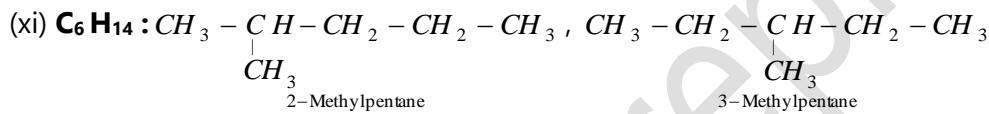
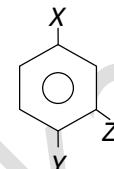
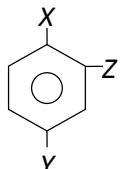
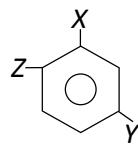
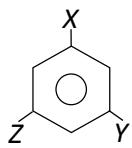
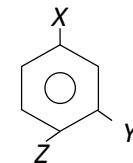
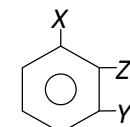
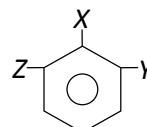
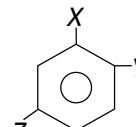
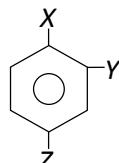
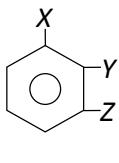


+91 - 8800 1234 92

(ix) **C₆H₃X₂Y (Six aromatic):**



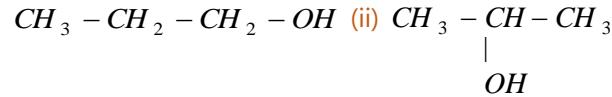
(x) **C₆H₃XYZ (Ten aromatic):**



Note: Aldehydes, carboxylic acids (and their derivatives) and cyanides do not show position isomerism.

Monosubstituted alicyclic compounds and aromatic compounds do not show position isomerism.

Structural isomers which differ in the position of the functional group are called regiomers. For example, (i)

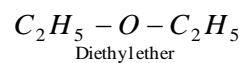
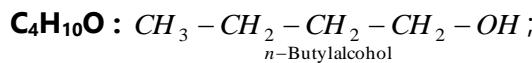
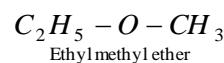
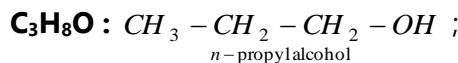
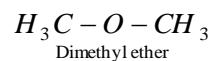
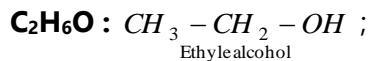


(3) **Functional isomerism:** This type of isomerism is due to difference in the nature of functional group present in the isomers. The following pairs of compounds always form functional isomers with each other.

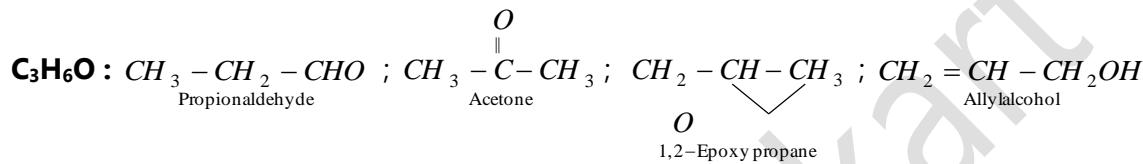


Examples:

(i) **Alcohols and ethers ($C_n H_{2n+2}O$)**



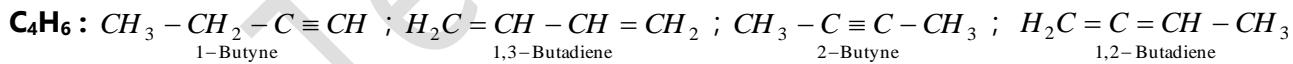
(ii) **Aldehydes, ketones and unsaturated alcohols ...etc. ($C_n H_{2n}O$)**



(iii) **Acids, esters and hydroxy carbonyl compounds ...etc. ($C_n H_{2n}O_2$)**



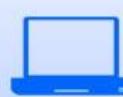
(iv) **Alkynes and alkadienes ($C_n H_{2n-2}$)**

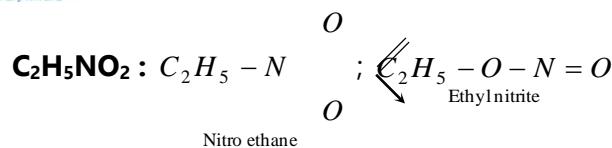


(v) **Cyanides and isocyanides ($-CN$ and $-NC$)**

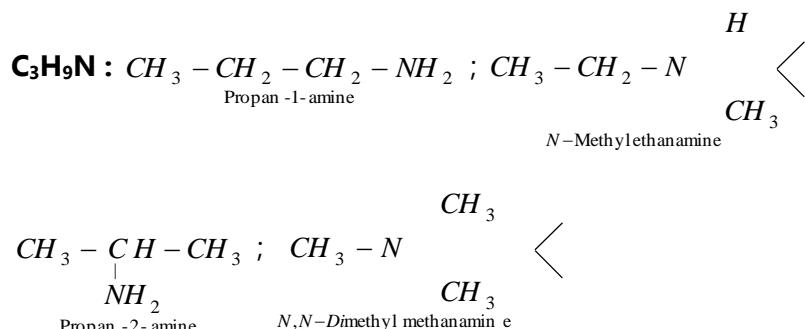


(vi) **Nitro alkanes and alkyl nitrites ($-NO_2$ and $-O - N = O$)**

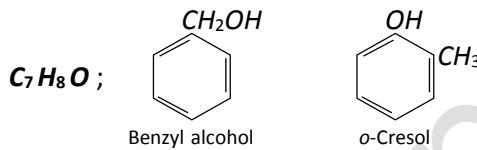




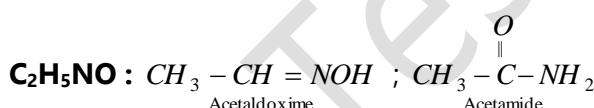
(vii) Amines (Primary, secondary and tertiary)



(viii) Alcohols and phenols



(ix) Oximes and amides



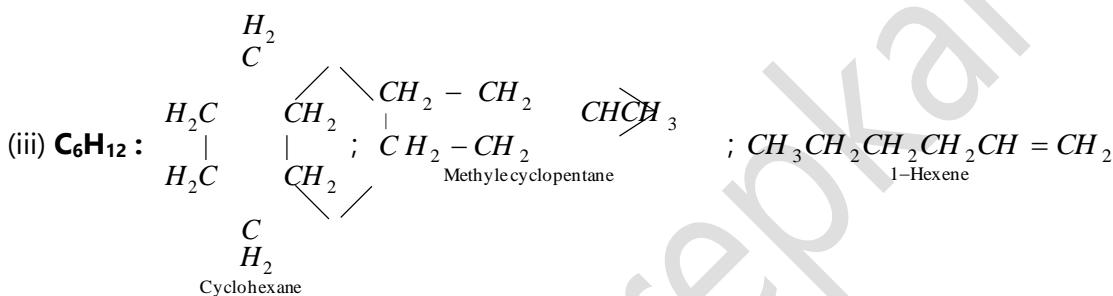
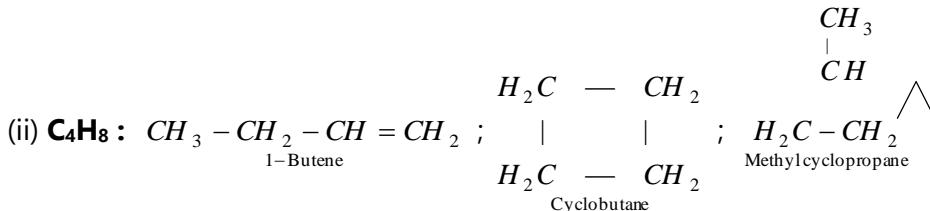
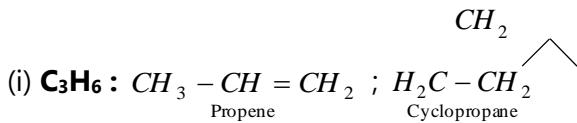
(x) Thio alcohols and thio ethers



Knowledge... Everywhere

(4) **Ring-chain isomerism:** This type of isomerism is due to different modes of linking of carbon atoms, i.e., the isomers possess either open chain or closed chain structures.

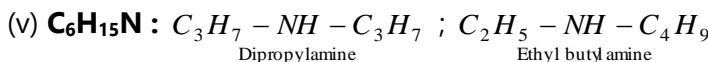
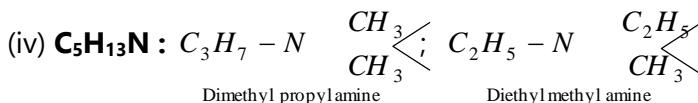
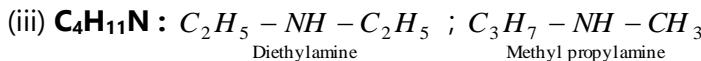
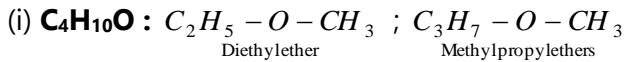
Examples:



Note: Ring – chain isomers are always functional isomers.

(5) **Metamerism** : This type of isomerism is due to the difference in the nature of alkyl groups attached to the polyvalent atoms or functional group. Metamers belong to the same homologous series. Compounds like ethers, thio-ethers ketones, secondary amines, etc. show metamerism.

Examples:



Preparation Classes



Counseling Sessions



Online Test



Free Trial Classes



www.testprepkart.com

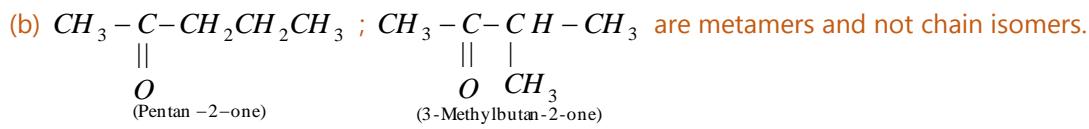
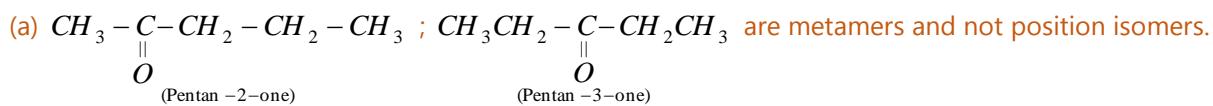


info@testprepkart.com



+91 - 8800 1234 92

Note: If same polyvalent functional group is there in two or more organic compounds, then never write chain or position isomerism, it will be metamerism e.g.,



Alkenes does not show metamerism.

(6) Tautomerism

(i) The type of isomerism in which a substance exist in two readily interconvertible different structures leading to dynamic equilibrium is known as tautomerism and the different forms are called **tautomers** (or tautomerides).

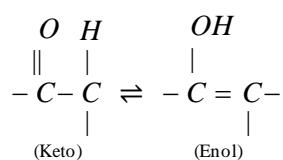
The term **tautomerism** (Greek: tauto = same; meros = parts) was used by **Laar** in 1885 to describe the phenomenon of a substance reacting chemically according to two possible structures.

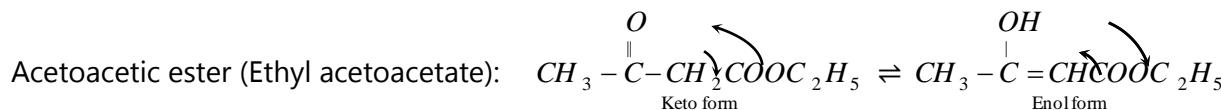
(ii) It is caused by the wandering of hydrogen atom between two polyvalent atoms. It is also known as **Desmotropism** (Desmos = bond and tropos = turn). If the hydrogen atom oscillates between two polyvalent atoms linked together, the system is a **dyad** and if the hydrogen atom travels from first to third in a chain, the system is a **triad**.

(a) Dyad system: Hydrocyanic acid is an example of dyad system in which hydrogen atom oscillates between carbon and nitrogen atoms. $H - C \equiv N \rightleftharpoons C \equiv N - H$

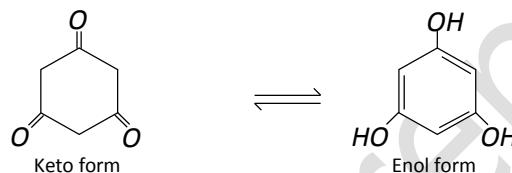
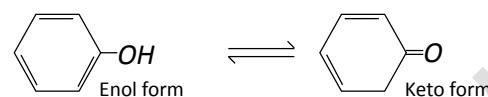
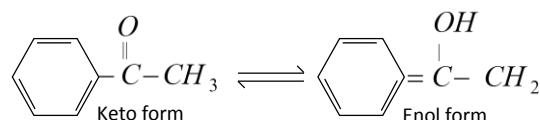
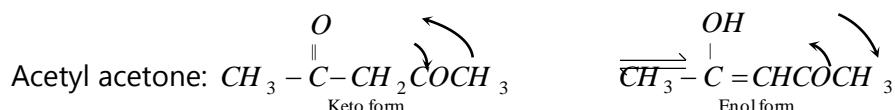
(b) Triad system Keto-enol system: Polyvalent atoms are oxygen and two carbon atoms.

Examples:

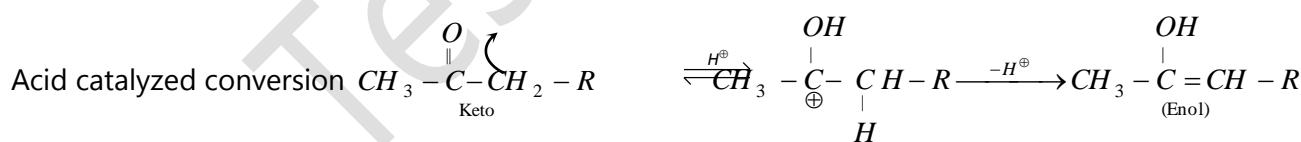
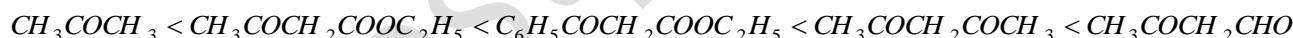




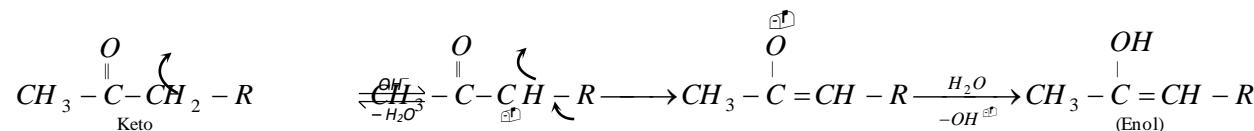
Acetoacetic ester gives certain reactions showing the presence of keto group (Reactions with HCN , H_2NOH , $\text{H}_2\text{NNHC}_6\text{H}_5$, etc.) and certain reactions showing the presence of enolic group (Reactions with Na , CH_3COCl , NH_3 , PCl_5 , Br_2 water and color with neutral FeCl_3 , etc.).



Enolisation is in order



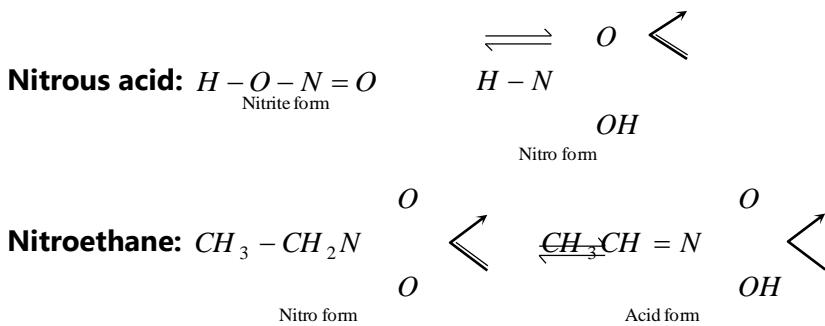
Base catalyzed conversion



Triad system containing nitrogen



Examples:



(iii) Characteristics of tautomerism

- (a) Tautomerism (cationotropy) is caused by the oscillation of hydrogen atom between two polyvalent atoms present in the molecule. The change is accompanied by the necessary rearrangement of single and double bonds.
 - (b) It is a reversible intramolecular change.
 - (c) The tautomeric forms remain in dynamic equilibrium. Hence, their separation is a bit difficult. Although their separation can be done by special methods, yet they form a separate series of stable derivatives.
 - (d) The two tautomeric forms differ in their stability. The less stable form is called the labile form. The relative proportion of two forms varies from compound to compound and also with temperature, solvent etc. The change of one form into another is also catalyzed by acids and bases.
 - (e) Tautomers are in dynamic equilibrium with each other and interconvertible (\rightleftharpoons).
 - (f) Two tautomers have different functional groups.
 - (g) Tautomerism has no effect on bond length.
 - (h) Tautomerism has no contribution in stabilizing the molecule and does not lower its energy.
 - (i) Tautomerism may occur in planar or nonplanar molecules.

Note: Keto=enol tautomerism is exhibited only by such aldehydes and ketones which contain at least one α -hydrogen. For example CH_3CHO , CH_3CH_2CHO , CH_3COCH_3 , $COCH_3$.

Tautomerism is not possible in benzaldehyde (C_6H_5CHO), benzophenone ($C_6H_5COC_6H_5$), tri methyl acetaldehyde, $(CH_3)_2C-CHO$ and chloral CCl_3-CHO as they do not carry $\alpha - H$.



Number of structural isomers

Molecular formula	Number of isomers
Alkanes	
C_4H_{10}	Two
C_5H_{12}	Three
C_6H_{14}	Five
C_7H_{16}	Nine
C_8H_{18}	Eighteen
C_9H_{20}	Thirty five
$C_{10}H_{22}$	Seventy five
Alkenes and cycloalkanes	
C_3H_6	Two (One alkene + one cycloalkane)
C_4H_8	Six (Four alkene + 2 - cycloalkane)
C_5H_{10}	Nine (Five alkenes + 4 – cycloalkanes)
Alkynes	
C_3H_4	Two
C_4H_6	Six
Monohalides	
C_3H_7X	Two
C_4H_9X	Four
$C_5H_{11}X$	Eight
Dihalides	
$C_2H_4X_2$	Two
$C_3H_6X_2$	Four
$C_4H_8X_2$	Nine
$C_5H_{10}X_2$	Twenty one
Alcohols and ethers	
C_2H_6O	Two (One alcohol and one ether)
C_3H_8O	Three (Tow alcohols and one ether)
$C_4H_{10}O$	Seven (Four alcohols and three ethers)
$C_5H_{12}O$	Fourteen (Eight alcohols and six ethers)
Aldehydes and ketones	
C_3H_6O	Two (One aldehyde and one ketone)



Preparation Classes



Counseling Sessions



Online Test



Free Trial Classes



www.testprepkart.com



info@testprepkart.com



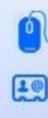
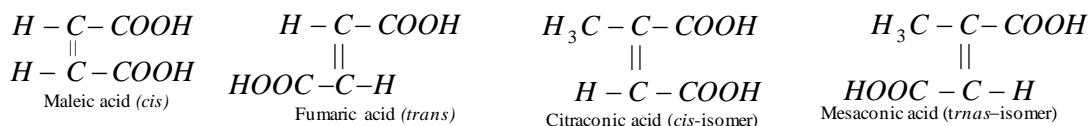
+91 - 8800 1234 92

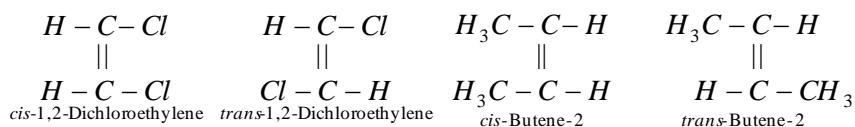
C_4H_8O	Three (Two aldehydes and one ketone)
$C_5H_{10}O$	Three (Four aldehydes and three ketone)
Monocarboxylic acids and esters	
$C_2H_4O_2$	Two (One acid and one ester)
$C_3H_6O_2$	Three (One acid and two esters)
$C_4H_8O_2$	Six (Two acids and four esters)
$C_5H_{10}O_2$	Thirteen (Four acids and nine esters)
Aliphatic amines	
C_2H_7N	Two (One 1°-amine and one 2°-amine)
C_3H_9N	Four (Two 1°-amines, one 2°-amine and one 3°-amine)
$C_4H_{11}N$	Eight (Four 1°-amines, three 2°-amines and one 3°-amines)
Aromatic compounds	
C_8H_{10}	Four
C_9H_{12}	Nine
C_7H_8O	Five

17. Geometrical or cis-trans isomerism.

The compounds which have same molecular formula but differ in properties due to different spatial arrangement of atoms or groups in space are known as geometrical isomers and the phenomenon is known as geometrical isomerism. The isomer in which same groups or atoms are on the same side is known as cis form and the isomer in which same groups or atoms are on the opposite side is called trans-isomer.

Examples:

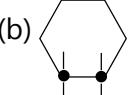


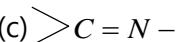


(1) Conditions for geometrical isomerism: Compound will show geometrical isomerism if it fulfils the following two conditions

(i) There should be frozen rotation about two adjacent atoms in the molecule.

(a)  Frozen rotation about carbon, carbon double bond in alkenes.

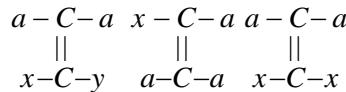
(b)  Frozen rotation about carbon, carbon single bond in cycloalkanes.

(c)  Frozen rotation about carbon, nitrogen double bond in oxime and imine.

(ii) Both substituents on each carbon should be different about which rotation is frozen.

If these two conditions are fulfilled, then compound will show geometrical isomerism.

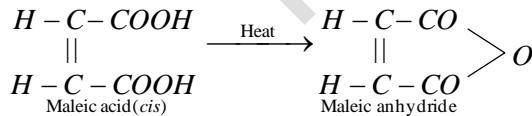
Note: The compounds of the following type will not show geometrical isomerism.



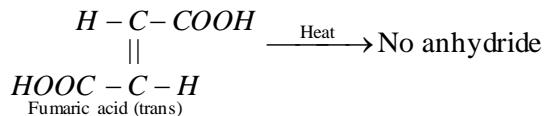
Note the similar atoms (Groups) on one or both of the carbon atoms.

(2) Distinction between cis- and trans- isomers

(i) **By cyclization method:** Generally, the cis-isomer (e.g. maleic acid) cyclizes on heating to form the corresponding anhydride while the trans-isomer does not form its anhydride at all.



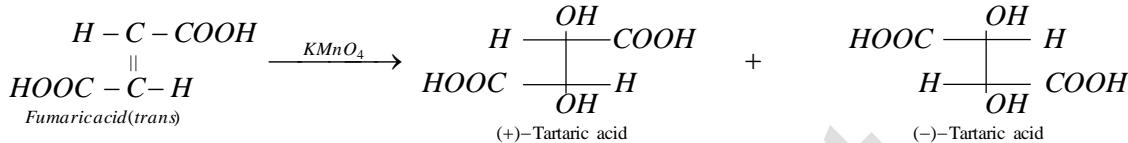
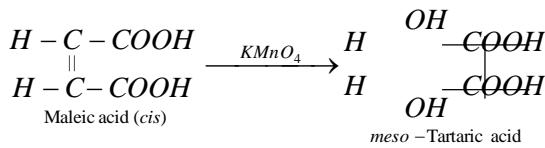
Note: Note that the two reacting groups (-COOH) are near to each other.



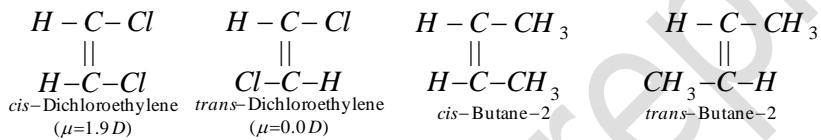
Note: Note that the two reacting groups (-COOH) are quite apart from each other, hence cyclisation is not possible.



(ii) **By hydroxylation** (Oxidation by means of $KMnO_4$, OsO_4 or H_2O_2 in presence of OsO_4): Oxidation (Hydroxylation) of alkenes by means of these reagents proceeds in the cis-manner. Thus the two geometrical isomers of an alkene leads to different products by these reagents. For example,



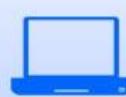
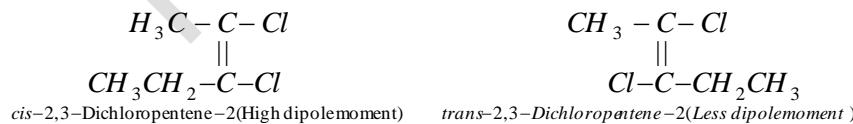
(iii) **By studying their dipole moments:** The cis-isomer of a symmetrical alkene (Alkenes in which both the carbon atoms have similar groups) has a definite dipole moment, while the trans-isomer has either zero dipole moment or less dipole moment than the cis-isomer. For example, 1, 2-dichloroethylene and butene-2.



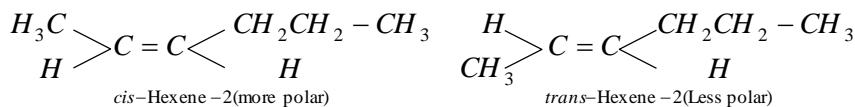
In trans-isomer of the symmetrical alkenes, the effect produced in one half of the molecule is cancelled by that in the other half of the molecule.

In case of unsymmetrical alkenes, the cis-isomer has higher dipole moment than the corresponding trans-isomer.

For Example,

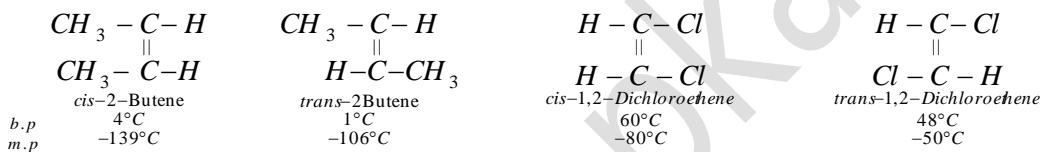


Similar is the case with hexene-2.



Note: Note that the $-CH_2CH_2 - CH_3$ has more +I effect than the $-CH_3$ group, hence dipole moment of the two polar bonds do not cancel each other in the trans isomer. Thus trans-isomer is also polar, but less than the corresponding cis-isomer.

(iv) **By studying other physical properties:** (a) The cis-isomer of a compound has higher boiling point due to higher polarity, higher density and higher refractive index than the corresponding trans-isomer (Auwers-skita rule).



(b) The trans-isomer has higher melting point than the cis-isomer due to symmetrical nature and more close packing of the trans-isomer.

(v) **Stability:** Trans-isomer is more stable than cis-isomer due to steric hindrance.

Note: Terminal alkenes such as propene, 1-butene and 2-methyl propene do not show geometrical isomerism.

Cis-trans isomers are configurational isomers but not mirror images, hence cis and trans isomers are always diastereomers.

Non-terminal alkenes with the same atoms or groups either on one or both the carbon atoms of the double bond such as 2-methyl-2-butene, 2,3-dimethyl –2 – butene etc. do not show geometrical isomerism.

