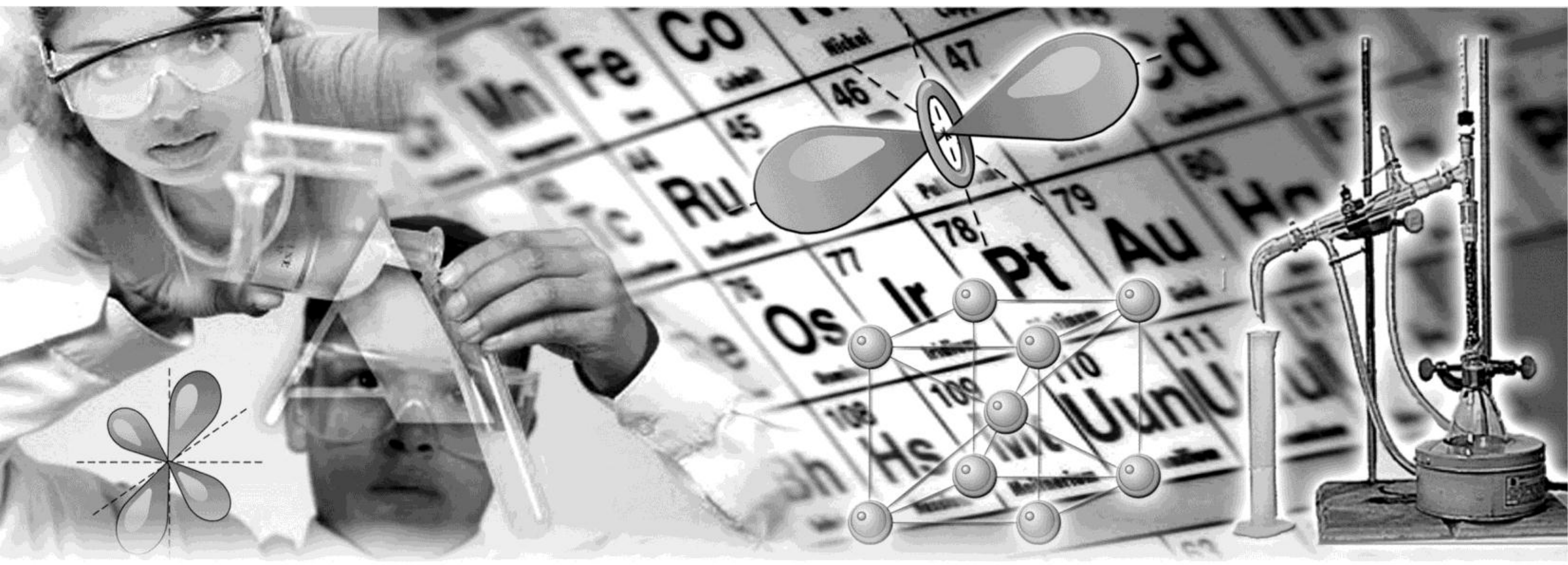


# Chapter 23

# General Organic Chemistry

Carbon is an essential element of organic compounds, it has four electrons in its outer most shell.

According to the ground state electronic configuration of carbon, it is divalent. Tetravalency of carbon can be explained by promoting one of the $2s^2$ - electrons to the unocupied $2p_{z^1}$ atomic orbital.

The four valencies of carbon atom are similar and they are symmetrically arranged around the carbon atom. According to **Le Bell 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 centre and the angle between any two valencies is 109°28′.

## Hybridisation in Organic Compounds

(1) The process of mixing atomic orbitals to form a set of new equivalent orbitals is termed as ***hybridisation***. There are *three types* of hybridisation,

(i) $sp^3$ ***hybridisation*** (involved in saturated organic compounds containing only single covalent bonds),

(ii) $sp^2$ ***hybridisation*** (involved in organic compounds having carbon atoms linked by double bonds) and

(iii) $sp$ ***hybridisation*** (involved in organic compounds having carbon atoms linked by a triple bonds).

**Table : 23.1**

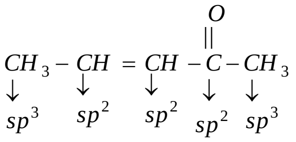
| **Type of hybridisation** | $sp^3$ | $sp^2$ | $sp$ |
|---|---|---|---|
| **Number of orbitals used** | 1*s* and 3*p* | 1*s* and 2*p* | 1*s* and 1*p* |
| **Number of unused *p*-orbitals** | Nil | One | Two |
| **Bond** | Four -σ | Three -σ<br>One -π | Two -σ<br>Two -π |
| **Bond angle** | 109.5° | 120°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

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

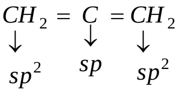
(i) ***First method*** **:** In this method hybridisation can be know by the number of $\pi-$ bonds present on that particular atom.

| *Number of $\pi$– bond/s* | 0 | 1 | 2 |
|---|---|---|---|
| *Type of hybridisation* | $sp^3$ | $sp^2$ | $sp$ |

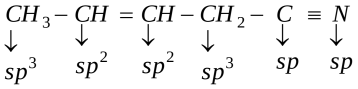
*Examples* **:**

(i) 

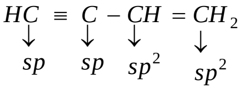
$$\underset{sp^3}{\underset{\downarrow}{CH_3}}-\underset{sp^2}{\underset{\downarrow}{CH}}=\underset{sp^2}{\underset{\downarrow}{CH}}-\underset{sp^2}{\underset{\downarrow}{\overset{\overset{O}{||}}{C}}}-\underset{sp^3}{\underset{\downarrow}{CH_3}}$$

(ii) 

$$\underset{sp^2}{\underset{\downarrow}{CH_2}}=\underset{sp}{\underset{\downarrow}{C}}=\underset{sp^2}{\underset{\downarrow}{CH_2}}$$

(iii) 

$$\underset{sp^3}{\underset{\downarrow}{CH_3}}-\underset{sp^2}{\underset{\downarrow}{CH}}=\underset{sp^2}{\underset{\downarrow}{CH}}-\underset{sp^3}{\underset{\downarrow}{CH_2}}-\underset{sp}{\underset{\downarrow}{C}}\equiv\underset{sp}{\underset{\downarrow}{N}}$$

(iv) 

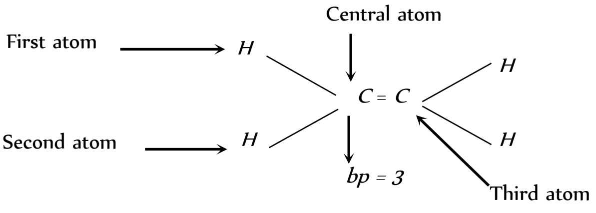
$$\underset{sp}{\underset{\downarrow}{HC}}\equiv\underset{sp}{\underset{\downarrow}{C}}-\underset{sp^2}{\underset{\downarrow}{CH}}=\underset{sp^2}{\underset{\downarrow}{CH_2}}$$

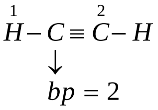
❑ In diamond carbon is $sp^3$ hybridised and in graphite carbon is $sp^2$ hybridised.

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

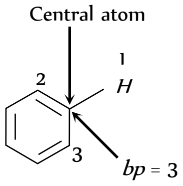
*ep* = *bp* + *lp;* where *ep* = electron pair present in hybrid orbitals , *bp* = bond pair present in hybrid orbitals

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





$$\overset{1}{H}-\underset{bp\,=\,2}{\underset{\downarrow}{C}}\equiv\overset{2}{C}-H$$



Number of *lp*'s can be determined as follows,

(a) If carbon has $\pi$ - bonds or positive charge or odd electron, than *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 hybridisation as follows,

| *ep* | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|
| *Type of hybridisation* | $sp$ | $sp^2$ | $sp^3$ | $sp^3d$ | $sp^3d^2$ |

*Example :*

(i) $CH_2 = \overset{\oplus}{C}H \downarrow$ $\quad bp = 2,\ lp = 0,\ ep = 2, sp$

(ii) $CH_2 = \overset{\ominus}{C}H \downarrow$ $\quad bp = 2,\ lp = 1,\ ep = 3, sp^2$

(iii) $CH_2 = \overset{\bullet}{C} - CH_3$ with $CH_3$ below $\quad bp = 3,\ lp = 0,\ ep = 3, sp^2$

(iv) $CH \equiv \overset{\ominus}{C} \downarrow$ $\quad bp = 1,\ lp = 1,\ ep = 2, sp$

(v) $CH_3 - \overset{\ominus}{C}H - CH_3 \downarrow$ $\quad bp = 3,\ lp = 1,\ ep = 4, sp^3$

**(3) Applications of hybridisation**

(i) ***Size of the hybrid orbitals*** : Since $s$ - orbitals are closer to the 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***

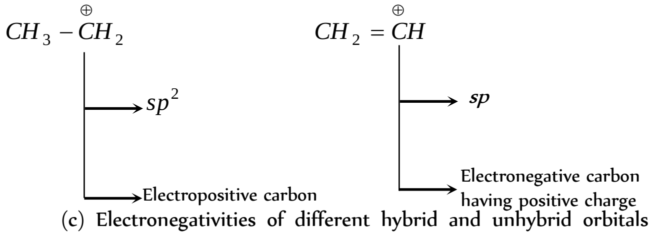
(a) Electronegativity of *s*-orbital is maximum.

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

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

$\longrightarrow$ *s*-character in decreasing order and electronegativity in decreasing order

Thus *sp*-hybrid carbon is always electronegative 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) Electronegativities of different hybrid and unhybrid orbitals in decreasing order is as follows

$$\xrightarrow{s > sp > sp^2 > sp^3 > p}$$

% s - character and electronegativity in decreasing order.

(iii) ***Bond length variation in hydrocarbons***

% of *s* orbital character

$$\propto \frac{1}{C - C \text{ bond length}} \propto \frac{1}{C - H \text{ bond length}}$$

**Table : 23.2**

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

(iv) ***Bond strength in hydrocarbons*** : *The shorter is the bond length, the greater is the compression between atomic nuclei and hence greater is the strength of that bond.*

**Table : 23.3**

| 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 nature.

(b) Acidity of hydrogen is directly proportional to the electronegativity of the atom on which hydrogen is present.

Thus

$$\xrightarrow{H-O-H \quad > \quad NH_3 \quad > \quad CH{\equiv}CH}$$

Electronegativity of the atoms
Acidity of compounds in decreasing order

(c) Acidity of hydrocarbon $\propto$ % of *s-character*

| | $CH \equiv CH$ | $CH_2 = CH_2$ | $CH_3 - CH_3$ |
|---|---|---|---|
| % *s*-character | 50 | 33.33 | 25 |
| $pKa$ | 25 | 44 | 50 |

$\longrightarrow$ *s*- character and acidity in decreasing order

Acidity $\propto Ka$ and Acidity $\propto \dfrac{1}{pKa} (pKa = -\log Ka)$

Order of acidic nature of alkynes is,

$$HC \equiv CH > HC \equiv C - CH_3$$

The relative acidic character follows the order;

$$H_2O > ROH > HC \equiv CH > NH_3 > CH_2 = CH_2 > CH_3 - CH_3$$

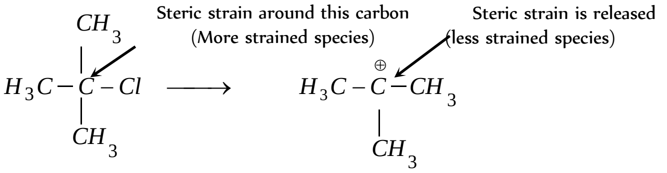
Obviously, the basic character of their conjugate bases follows the reverse order, *i.e.*,

$$CH_3CH_2^- > CH_2 = CH^- > NH_2^- > HC \equiv C^- > RO^- > HO^-$$

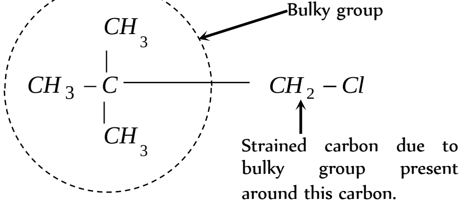
## Steric effect

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

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



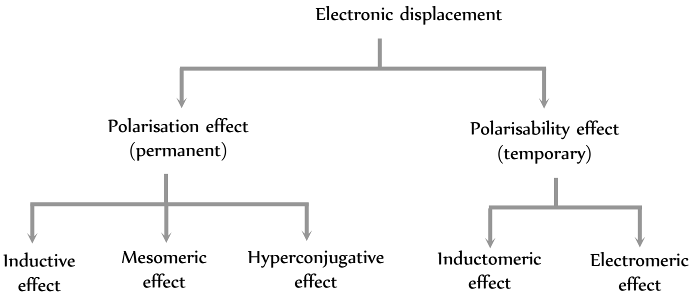
(2) Primary alkyl halide having quaternary $\beta$-carbon does not form transition state because of the steric strain around $\alpha$-carbon by the $\beta$-carbon. To release the strain it converts into carbocation.



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

## 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 centres. 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 **polarisation 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 withdrawing ($X$) 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 displacement of shared electron of a covalent bond towards a more electronegative atom. This is called *inductive effect or simply as I – effect.*

$C - C - C - C$ *Non polar*

$$C^{\delta\delta\delta\delta^+} \longrightarrow C^{\delta\delta\delta^+} \longrightarrow C^{\delta\delta^+} \longrightarrow C^{\delta^+} \longrightarrow X^{\delta^-}$$

$$C^{\delta\delta\delta\delta^-} \longleftarrow C^{\delta\delta\delta^-} \longleftarrow C^{\delta\delta^-} \longleftarrow C^{\delta^-} \longleftarrow Y^{\delta^+}$$

(2) 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.

$$\overset{\oplus}{N}H_3 > NO_2 > CN > SO_3H > CHO > CO > COOH > COCl > COOR$$
$$> CONH_2 > F > Cl > Br > I > OH > OR > NH_2 > C_6H_5 > H$$

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

*ter.* alkyl > *sec.* alkyl > *pri.* alkyl > $CH_3 > H$

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

+ I power ∝ number of carbon in the same type of alkyl groups

$$CH_3 - CH_2 - CH_2 - CH_2 - > CH_3 - CH_2 - CH_2 - >$$
$$CH_3 - CH_2 -$$

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

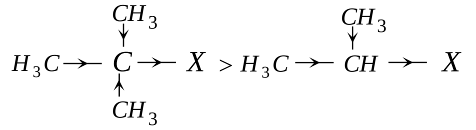
(3) **Applications of Inductive effect**

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

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

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



$$H_3C \rightarrow \overset{\overset{CH_3}{\downarrow}}{\underset{\underset{CH_3}{\uparrow}}{C}} \rightarrow X > H_3C \rightarrow \overset{\overset{CH_3}{\downarrow}}{CH} \rightarrow X$$

$$> CH_3 \rightarrow CH_2 \rightarrow X > CH_3 \rightarrow X$$

Tertiary > Secondary > Primary > Methyl

(iii) **Relative strength of the acids :**

(a) 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,

$$\underrightarrow{HCOOH > CH_3COOH > C_2H_5COOH > C_3H_7COOH > C_4H_9COOH}$$

+*I* effect increases, so acid strength decreases

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

(b) The group or atom having – *I* effect increases the acid 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,

$$\underleftarrow{\underset{\text{Trichloro aceticacid}}{CCl_3COOH} > \underset{\text{Dichloro aceticacid}}{CHCl_2COOH} > \underset{\text{Monochloro aceticacid}}{CH_2ClCOOH} > \underset{\text{Aceticacid}}{CH_3COOH}}$$

(– Inductive effect increases, so acid strength increases)

(c) Strength of aliphatic carboxylic acids and benzoic acid

$$\underset{+I\,group}{\overset{\uparrow}{R}} \rightarrow COOH \qquad \underset{-I\,group}{\overset{\uparrow}{C_6H_5}} \leftarrow COOH$$

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

$$\underrightarrow{HCOOH \;>\; C_6H_5COOH \;>\; RCOOH}$$

Acid strength in decreasing order

❑ Decreasing order of acids :

$$NO_2CH_2COOH > FCH_2COOH > ClCH_2COOH > BrCH_2COOH\,.$$

$$F_3C-COOH > Cl_3C-COOH > Br_3C-COOH > I_3C-COOH\,.$$

$$\underset{\text{Methyl alcohol}}{CH_3OH} > \underset{\text{Ethyl Alcohol}}{CH_3CH_2OH} > \underset{\text{Iso-propyl alcohol}}{(CH_3)_2CHOH} > \underset{\text{Tert-butyl alcohol}}{(CH_3)_3COH}$$

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

$$\underset{\text{Phenol}}{C_6H_5\leftarrow OH} > \underset{\text{Water}}{H-OH} > \underset{\text{Methyl alcohol}}{CH_3 \rightarrow OH}$$

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

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 it. The amines are stronger bases than $NH_3$ as the alkyl groups increase electron density on nitrogen due to + *I* effect while $ClNH_2$ 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;

$$\underset{\text{Diethyl amine}}{(C_2H_5)_2NH} > \underset{\text{Ethyl amine}}{CH_3CH_2NH_2} > \underset{\text{Methyl amine}}{CH_3NH_2} > \underset{\text{Ammonia}}{NH_3} > \underset{\text{Chloro amine}}{ClNH_2}$$

The order of basicity is as given below;

| **Alkyl groups (*R*– )** | **Relative base strength** |
|---|---|
| $CH_3$ | $R_2NH > RNH_2 > R_3N > NH_3$ |
| $C_2H_5$ | $R_2NH > RNH_2 > NH_3 > R_3N$ |
| $(CH_3)_2CH$ | $RNH_2 > NH_3 > R_2NH > R_3N$ |
| $(CH_3)_3C$ | $NH_3 > RNH_2 > R_2NH > R_3N$ |

❑ 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 the steric hindrance existing in the *t*-amines.

❑ In gas phase or in 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 : $3^o > 2^o > 1^o > NH_3$.

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

$$\underset{(3^o)}{(CH_3)_3COH} > \underset{(2^o)}{(CH_3)_2CHOH} > \underset{(1^o)}{CH_3CH_2OH} > CH_3OH$$

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

$$(CH_3)_3C^{\oplus} > (CH_3)_2CH^{\oplus} > CH_3CH_2^{\oplus} > CH_3^{\oplus}$$

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

$$CH_3^- > CH_3CH_2^- > (CH_3)_2CH^- > (CH_3)_3C^-$$

## Resonance effect or mesomeric effect

(1) The effect in which $\pi$ 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 of the compound with 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) 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.,

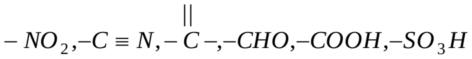
(a) The groups which donate electrons to the double bond or to a conjugated system are said to have $+M$ *effect or* $+R$ *effect.*

$+M$ *effect groups* :

$$-Cl,-Br,-I,-\overset{..}{N}H_2,-NR_2,-OH,-OR,-SH,-OCH_3,-\underset{..}{\overset{..}{S}}R$$

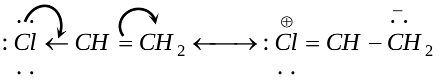
(b) The groups which withdraw electrons from the double bond or from a conjugated system towards itself due to resonance are said to have $-M$ effect or $-R$ effect.

$-M$ effect groups :



$$-NO_2,-C\equiv N,-\overset{\overset{\large O}{||}}{C}-,-CHO,-COOH,-SO_3H$$

(3) 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.



$$:\ddot{Cl} \leftarrow CH = CH_2 \longleftrightarrow :\overset{\oplus}{Cl} = CH - \overset{\ominus}{\ddot{C}}H_2$$

**Application of mesomeric effect** : It explains,

(1) Low reactivity of aryl and vinyl halides,

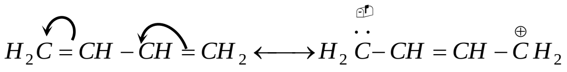
(2) The acidic nature of carboxylic acids,

(3) Basic character comparison of ethylamine and aniline,

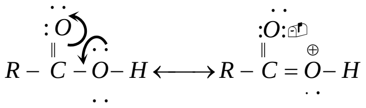
(4) The stability of some free radicals, carbocations and carbanions.

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

Example :

(i) 

$$H_2C = CH - CH = CH_2 \longleftrightarrow H_2\overset{\ominus}{\ddot{C}} - CH = CH - \overset{\oplus}{C}H_2$$

(ii) 

$$R - \underset{\Vert}{\overset{:\ddot{O}}{C}} - \ddot{O} - H \longleftrightarrow R - \overset{:\ddot{O}:^{\ominus}}{\underset{}{C}} = \overset{\oplus}{\ddot{O}} - H$$

Both (i) and (ii) are the examples of mesomerism and resonance effect. Let us consider the following example $H \rightarrow \ddot{Cl}: \longleftrightarrow \overset{\oplus}{H}\overset{\ominus}{Cl}$. Such an electron displacement is the example of resonance only (not the mesomerism).

## 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 $\pi$ systems (multiple bonds) and the adjacent $\sigma$ bonds (single $H-C$ bonds) of the substituent groups in organic compounds is called **hyperconjugation**.* The concept of hyperconjugation was developed by Baker and Nathan and is also known as *Baker and Nathan effect*.

In fact hyperconjugation effect is similar to resonance effect. Since there is no bond between the $\alpha$-carbon atom and one of the hydrogen atoms, the hyperconjugation is also called *no-bond resonance*.

(2) **Structural requirements for hyperconjugation**

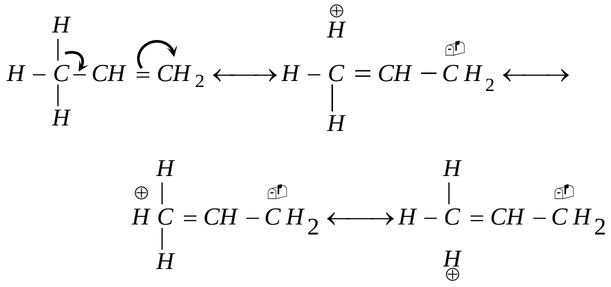
(i) Compound should have at least one $sp^2$-hybrid carbon of either alkene alkyl carbocation or alkyl free radical.

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

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

(iii) Hyperconjugation is of three types

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



$$H - \underset{H}{\overset{H}{C}} - CH = CH_2 \longleftrightarrow H - \underset{H}{\overset{\overset{\oplus}{H}}{C}} = CH - \overset{\ominus}{C}H_2 \longleftrightarrow$$

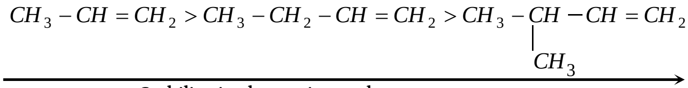
$$\overset{\oplus}{H}\underset{H}{\overset{H}{C}} = CH - \overset{\ominus}{C}H_2 \longleftrightarrow H - \underset{\underset{\oplus}{H}}{\overset{H}{C}} = CH - \overset{\ominus}{C}H_2$$

(v) Number of resonating structures due to the hyperconjugation = Number of $\alpha$-hydrogens + 1.

**Applications of hyperconjugation**

(1) **Stability of alkenes :** Hyperconjugation explains the stability of certain alkenes over other alkenes.

Stability of alkenes ∝ Number of alpha hydrogens ∝ Number of resonating structures



$$CH_3 - CH = CH_2 > CH_3 - CH_2 - CH = CH_2 > CH_3 - \underset{CH_3}{\underset{|}{CH}} - CH = CH_2$$

Stability in decreasing order

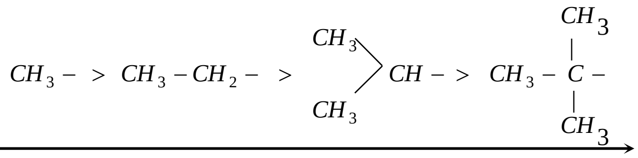
(2) **Carbon-carbon double bond length in alkenes :** As we know that the more is the number of resonating structures, the more will be single bond character in carbon-carbon double bond.

(3) **Stability of alkyl carbocations :** Stability of alkyl carbocations ∝ number of resonating structures ∝ number of alpha hydrogens.

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

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

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,



$$CH_3- > CH_3 - CH_2 - > \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!> CH - > CH_3 - \underset{CH_3}{\underset{|}{\overset{\overset{CH_3}{|}}{C}}} -$$

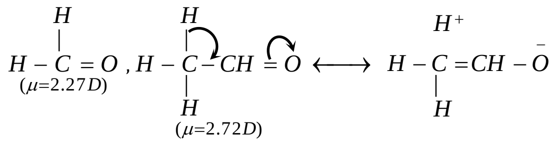
Increasing inductive effect

Electron donating power in decreasing order due to the hyperconjugation.

(6) **Heat of hydrogenation :** Hyperconjugation decreases the heat of hydrogenation.

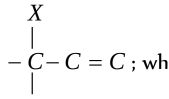
(7) **Dipole moment :** Since hyperconjugation causes the development of charges, it also affects the dipole moment in the molecule.

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 hyperconjugation, which leads to development of charges.



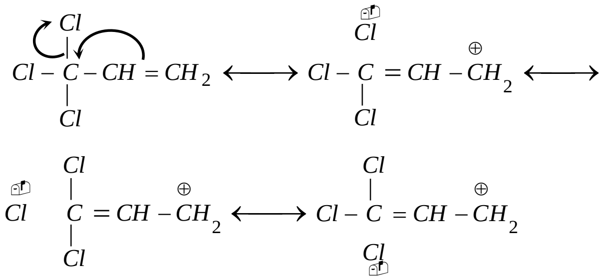
(8) **Orienting influence of alkyl group in $o, p$-positions and of $-CCl_3$ group in $m$-position :** Ortho-para directing property of methyl group in toluene is partly due to $+I$ effect and partly due to hyperconjugation.

**Reverse Hyperconjugation :** The phenomenon of hyperconjugation is also observed in the system given below,

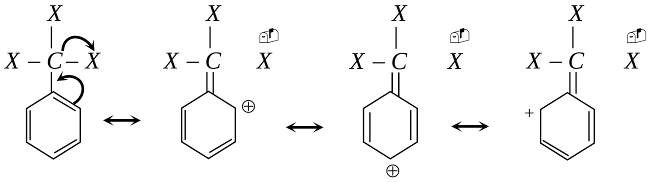


$-\overset{X}{C}-C=C$ ; where $X =$ halogen

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



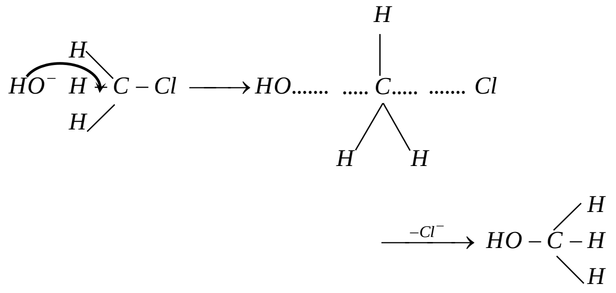
The *meta* directing influence and the deactivating effect of $CX_3$ group in electrophilic aromatic substitution reaction can be explained by this effect.



## Inductomeric effect

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

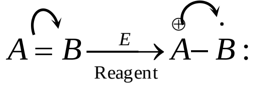
Example,



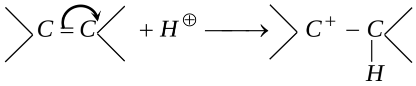
In methyl chloride the $-I$ effect of $Cl$ group is further increased temporarily by the approach of hydroxyl ion.

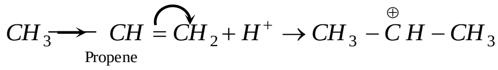
## Electromeric effect

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



(2) (i)When the transfer of electrons take place towards the attacking reagent, the effect is called $+E$ effect. The addition of acids to alkenes.

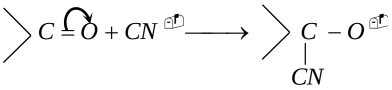




Since, $-CH_3$ group is electron donating, the electrons are transferred in the direction shown.

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

(ii) 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.



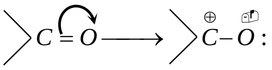
The attacking reagent is not attached to that atom on which electrons have been transferred.

(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 in either direction.

(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.

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



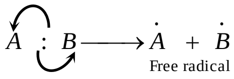
In cases where inductive effect and electromeric effect simultaneously operate, usually electrometric effect predominates.

## 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 favours homolysis is that the difference in electronegativity between $A$ and $B$ is less or zero.

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

$$A : B \longrightarrow \underset{\text{carbanion}}{\overset{\ominus}{A}:} + \underset{\text{carbocation}}{\overset{\oplus}{B}}$$

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 **carbanion**.

(ii) The factor which favours heterolysis is greater difference of electronegativities 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 forces of attraction between ions.

## Reaction Intermediates

Short lived fragments called reaction intermediates result from homolytic and heterolytic bond fission. The important reaction intermediates are free radicals, carbocations, carbanions, carbenes, benzyne and nitrenes.

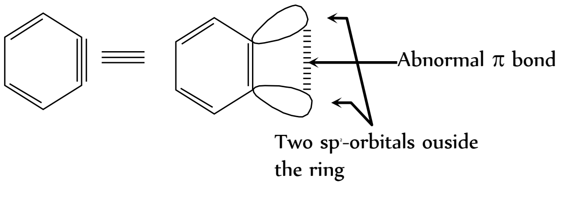
**Table : 23.4**

| **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 |
| Hybridisation | $sp^2$ | $sp^2$ | $sp^3$ (non-conjugated)<br>$sp^2$ (Conjugated) | (i) $sp^2$ (singlet)<br>(ii) $sp$ (triplet) |
| Structure | Planar | Planar | Pyramidal/Planar | (i) Planar (singlet)<br>(ii) Linear (triplet) |
| Magnetism | Paramagnetic | Diamagnetic | Diamagnetic | (i) Diamagnetic<br>(ii) Paramagnetic |
| Stability order | $Ph_3\dot{C} > Ph_2\dot{C}H > Ph\dot{C}H_2 >$<br>$CH_2 = CH - \dot{C}H_2 > 3^o > 2^o >$<br>$1^o > \dot{C}H_2 > CH_2 = \dot{C}H$ | $Ph_3\overset{+}{C} > Ph_2\overset{+}{C}H > \overset{+}{P}hCH_2 >$<br>$CH_2 = CH - \overset{+}{C}H_2 >$<br>$3^o > 2^o > 1^o > \overset{+}{C}H_3$ | $\overset{\ominus}{Ph_3C} > \overset{\ominus}{Ph_2CH} >$<br>$\overset{\ominus}{PhCH_2} > \text{Allyl}$<br>$\overset{\ominus}{CH_2} > 1^o > 2^o > 3^o$ | Triplet > singlet |

## Benzyne

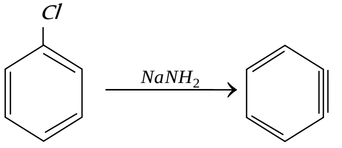
(1) 1, 2-Didehydrobenzene, $C_6H_4$ and its derivatives are called benzyne or arynes and the simplest member is benzyne.

(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 from of nucleophile leaving behind two electrons to be distributed between two orbitals.



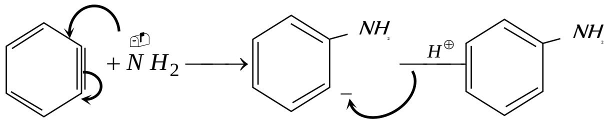
(3) Benzyne intermediate is aromatic in character.

(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.

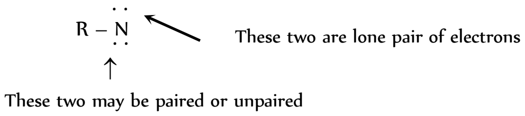
(ii) It reacts with strong nucleophile like $\overset{\ominus}{NH_2}$



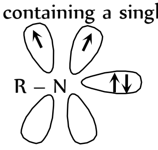
## Nitrenes (R – $\ddot{\text{N}}$ : )

(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.



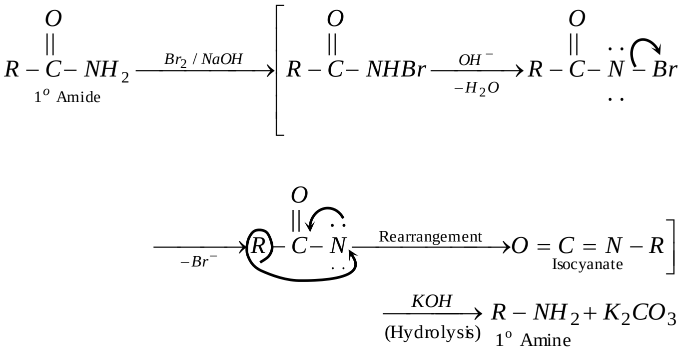
(3) In general nitrenes obey Hunds rule and the ground state triplet with two degenerate $sp$ -orbitals containing a single electron each.



*sp*-Triplet nitrene

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

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



$$R-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow{Br_2\,/\,NaOH} \left[ R-\overset{\overset{O}{\|}}{C}-NHBr \xrightarrow[-H_2O]{OH^-} R-\overset{\overset{O}{\|}}{C}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}-Br \right.$$

1° Amide

$$\xrightarrow[-Br^-]{} R-\overset{\overset{O}{\|}}{C}-\underset{\cdot\cdot}{\overset{\cdot\cdot}{N}} \xrightarrow{\text{Rearrangement}} \left. O=C=N-R \right]$$

Isocyanate

$$\xrightarrow[\text{(Hydrolysis)}]{KOH} R-NH_2+K_2CO_3$$

1° Amine

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

$$R-\overset{\cdot\cdot}{N}=\overset{+}{N}=\overset{\cdot\cdot}{N}:^- \xrightarrow{\Delta\, or\, h\nu} R-\overset{\cdot\cdot}{N}: + N\equiv N$$

Alkyl azide          Alkyl nitrene

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

## Attacking reagents

The fission of the substrate molecule to create centres of high or low electron density is influenced by attacking reagents. Most of the attacking reagents can be classified into two main groups.

Electrophiles or electrophilic reagents and Nucleophiles or nucleophilic reagents.

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

It can be classified into two categories :

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

$$H^{\oplus}, X^{\oplus}, R^{\oplus}, \overset{\oplus}{N}\genfrac{}{}{0pt}{}{\nearrow\!\!\!\!= O}{\searrow O}, \overset{\oplus}{N}=O, \overset{\oplus}{S}O_3H$$

All cations are charged electrophiles except cations of IA, IIA group elements, $Al^{+++}$ and $\overset{\oplus}{N}H_4$

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

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

$$BeCl_2, BH_3, ZnCl_2, AlX_3, FeX_3, \dot{C}H_3, \ddot{C}H_2, \ddot{C}X_2$$

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

$$SnCl_4, SiCl_4, PCl_5, SF_6, IF_7$$

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

$$BeCl_2, BX_3, AlX_3, FeX_3, SnCl_4, PCl_3\,;$$

$$PCl_5,\ NF_3,\ \ddot{C}X_2,\ CO_2, SO_3,\ CS_2,$$

$Cl_2, Br_2$ and $I_2$ also behave as neutral electrophiles.

Electrophiles are Lewis acids.

(2) **Nucleophiles :** Electron rich species or electron donors are called nucleophiles. Nucleophiles can be classified into three categories :

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

$$\overset{\ominus}{H}, \overset{\ominus}{O}H, R-\overset{\ominus}{O}, \overset{\ominus}{C}H_3, \overset{\ominus}{X}, \overset{\ominus}{S}H, R-\overset{\ominus}{S}$$

(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.

$\overset{\cdot\cdot}{N}H_3, R-\overset{\cdot\cdot}{N}H_2, R_2\overset{\cdot\cdot}{N}H, R_3\overset{\cdot\cdot}{N}, \overset{\cdot\cdot}{N}H_2-\overset{\cdot\cdot}{N}H_2$ (Nitrogen nucleophile)

$H-\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}-H, R-\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}-H, R-\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}-R$ (Oxygen nucleophiles)

$H-\underset{\cdot\cdot}{\overset{\cdot\cdot}{S}}-H, R-\underset{\cdot\cdot}{\overset{\cdot\cdot}{S}}-H, R-\underset{\cdot\cdot}{\overset{\cdot\cdot}{S}}-R$ (Sulphur nucleophiles)

$\overset{\cdot\cdot}{P}H_3, R\overset{\cdot\cdot}{P}H_2, R_2\overset{\cdot\cdot}{P}H, R_3\overset{\cdot\cdot}{P}$ (Phosphorus nucleophiles)

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

Alkenes, Alkynes, Benzene,

$$CH_2=CH-CH=CH_2, CH_2=CH-C\equiv CH$$

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

$$\overset{\ominus}{C}\equiv \overset{\cdot\cdot}{N}, \overset{\ominus}{O}-\overset{\cdot\cdot}{N}=O, \overset{\ominus}{O}-\underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{S}}-OH$$

❑ Organometallic compounds are nucleophiles.

❑ Nucleophiles are Lewis bases.

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

$$R-\overset{\overset{O}{\|}}{C}-H, R-\overset{\overset{O}{\|}}{C}-R, R-\overset{\overset{O}{\|}}{C}-OH, R-\overset{\overset{O}{\|}}{C}-Cl\,,$$

$$R-\overset{\overset{O}{\|}}{C}-OR, R-\overset{\overset{O}{\|}}{C}-NH_2, R-C\equiv N, R-\overset{\oplus}{N}\equiv\overset{\ominus}{C}$$

❑ During the course of chemical reaction electrophile reacts with nucleophile.

❑ Strong Lewis acid is stronger electrophile $CO_2 < \overset{\oplus}{N}O_2 < \overset{\oplus}{S}O_3H$ . Stronger is an acid, weaker is its conjugated base or weaker is the nucleophile.

*Examples* : $HF > H_2O > NH_3 > CH_4$

$$\underrightarrow{F^- < OH^- < NH_2^- < CH_3^-}$$

Increasing order of nucleophilicity.

## 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,
- Rearrangement reactions,

## Substitution reactions

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

*Examples :*

$$\underset{Ethyl\,bromide}{CH_3-CH_2-\overset{\overset{\text{Leaving group}}{\downarrow}}{Br}}+NaOH\longrightarrow \underset{Ethyl\,alcohol}{CH_3-CH_2\overset{\overset{\text{Substituting or attacking group}}{\downarrow}}{OH}}+NaBr$$

(Bromine atom is replaced by hydroxyl group)

**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.

$$\underset{Substrate}{R-X}+\underset{Nucleophile}{OH^{\ominus}}\longrightarrow R-OH+\underset{Leaving\ group}{X^{\ominus}}$$

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

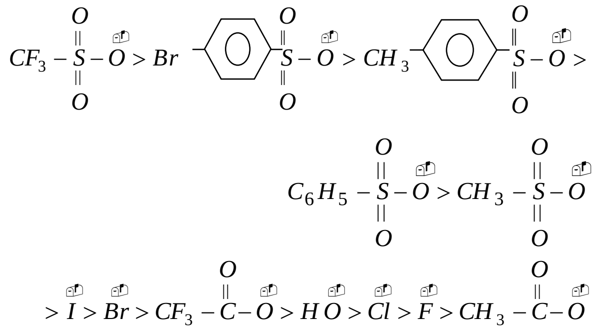
(ii) The weaker the basicity of a group of the substrate, the better is its leaving ability.

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

*Example :* $\underset{\text{Decreasing acidity}}{\xrightarrow{HI > HBr > HCl > HF}}$

$$\underset{\substack{\text{Increasing basicity}\\ \Downarrow \\ \text{Decreasing leaving ability}}}{\xrightarrow{\overset{\ominus}{I}\quad \overset{\ominus}{Br}\quad \overset{\ominus}{Cl}\quad \overset{\ominus}{F}}}$$

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



$$CF_3-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-\overset{\ominus}{O} > Br$$

$$C_6H_5-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-\overset{\ominus}{O} > CH_3-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-\overset{\ominus}{O}$$

$$> \overset{\ominus}{I} > \overset{\ominus}{Br} > CF_3-\overset{\overset{O}{\|}}{C}-\overset{\ominus}{O} > H\overset{\ominus}{O} > \overset{\ominus}{Cl} > \overset{\ominus}{F} > CH_3-\overset{\overset{O}{\|}}{C}-\overset{\ominus}{O}$$

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

$$R-L\xrightarrow{\overset{+\delta\ \ -\delta}{E-Nu}}R-Nu+\overset{\ominus}{L}\,;\quad R-L+\overset{\ominus}{Nu}\longrightarrow R-Nu+\overset{\ominus}{L}$$

(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.

*Example :* $R-Cl\xrightarrow[(NaOH)]{OH^{\ominus}}R-OH+\overset{\ominus}{Cl}$ .....(A)

Basicity of $OH^{\ominus}$is more than $\overset{\ominus}{Cl}$ hence $\overset{\ominus}{OH}$ replaces *Cl* as $\overset{\ominus}{Cl}$ .

$$R-OH\xrightarrow[(HCl)]{\overset{\Theta}{Cl}}R-Cl+\overset{\Theta}{OH}\ \text{......(B)}$$

Basicity of $\overset{\ominus}{Cl}$ is less than $\overset{\ominus}{OH}$ , hence $\overset{\ominus}{Cl}$ will not replace *OH* as $\overset{\ominus}{OH}$ hence reaction (B) will not occur.

(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 of electron or $\pi$ bond on the 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.

**Table : 23.5** ***Distinction between $S_N2$ and $S_N1$ reactions***

| **Factors** | **$S_N2$ Reactions** | **$S_N1$ Reactions** |
|---|---|---|
| Number of steps | **One:** $R:L+:\overset{\Theta}{Nu}\to R:Nu+:\overset{\Theta}{L}$ | **Two:** (i) $R:L\xrightarrow{Slow}R^{+}+:L^{\ominus}$<br>(ii) $R^{+}+:Nu^{-}\xrightarrow{Fast}R:Nu$ |
| Reaction rate and order | **Second order:**<br>Rate $\propto$ [Substrate] [Nucleophile] or Rate $=K_2[RL][:Nu^{\ominus}]$ | **First order:**<br>Rate $\propto$ [Substrate] or Rate $=K_1[RL]$ |
| Molecularity | Bimolecular | Unimolecular |
| TS of slow step | $:\overset{\delta^-}{Nu}---C---:\overset{\delta^-}{L}$ | $:Nu---\overset{\delta^+}{C}---\overset{\delta^-}{L}---Nu:$ |
| 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 from 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. $(I > Br > Cl > F)$ |
| Rearrangement | No rearranged product is formed (except for allylic). | Rearranged products can be formed. |
| Nature of nucleophiles | Favoured by strong and high concentration of nucleophiles. | Favoured by mild and low concentration of nucleophiles. |
| Polarity | Favoured by solvents of low polarity. | Favoured by solvents of high polarity. |
| Reaction rate determining factor | By steric hindrance. | By electronic factor (stability of $\overset{\oplus}{R}$ ). |
| Catalysis | Not catalysed by any catalyst (phase transfer). | Catalysed by Lewis and Bronsted acids, *e.g.*, $\overset{\oplus}{Ag}, AlCl_3, ZnCl_2$ and strong *HA*. |

(2) **Electrophilic substitutions reactions :** Electrophilic substitution involves the attack by an electrophile. It is represented as $S_E$ (*S* stands for substitution and *E* stands for elctrophile). If the order of reaction is 1, it is written as $S_{E^1}$ (unimolecular)and if the order is 2, it is $S_{E^2}$ (Bimolecular).

**$S_{E1}$ Reaction mechanism :** Electrophilic substitution in aliphatic compounds are very rare; some of the important examples are:

(i) Replacement of the metal atom in an organometallic compound by hydrogen :

$$R-M+\overset{\oplus}{H}\rightarrow R-H+\overset{\oplus}{M}$$

*e.g.*, $CH_3-CH_2-MgBr\xrightarrow{-MgBr}CH_3-\overset{\ominus}{C}H_2\xrightarrow{\overset{\oplus}{H}}CH_3-CH_3$

$$CH_3-CH_2-MgBr+H-Br\rightarrow CH_3-\overset{\ominus}{C}H_2\xrightarrow{\overset{\oplus}{H}}CH_3-CH_3+MgBr_2$$

$$CH_3-CH_2Na+C_6H_6\rightarrow CH_3-CH_3+C_6H_5Na$$

(ii) Decarboxylation of silver salt of carboxylic acid by means of bromine:

$$R_3C-\underset{\underset{O}{\|}}{C}-OAg+Br-Br\rightarrow R_3C-\underset{\underset{O}{\|}}{C}-\overset{\ominus}{O}+\overset{\delta^+}{Br}-\overset{\delta^-}{Br}+\overset{\oplus}{Ag}$$

$$\rightarrow R_3C-Br+CO_2+AgBr$$

(iii) Isotopic exchange of hydrogen for deuterium or tritium:

$$R-H+\overset{\oplus}{D}\leftrightharpoons R-D+\overset{\oplus}{H}$$

$$R-H+\overset{\oplus}{T}\leftrightharpoons R-T+\overset{\oplus}{H}$$

**$S_{E2}$ Reaction mechanism :** Electrophilic substitution is very common in benzene nucleus (aromatic compounds) in which π-electrons are highly delocalized and an electrophile can attack this region of high electron density.

In all electrophilic aromatic substitution reactions, it involves:

***Step 1.*** The formation of an electrophile, $\overset{\oplus}{E}$, *i.e.,*

In halogenation; $Cl-Cl+FeCl_3\rightarrow\overset{\oplus}{Cl}+Fe\overset{\ominus}{Cl_4}$

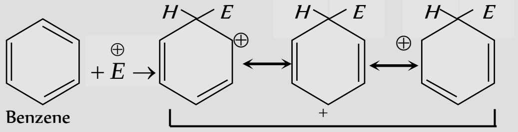
In nitration; $HNO_3+2H_2SO_4\rightarrow\overset{\oplus}{NO_2}+2\overset{\ominus}{HSO_4}+\overset{\oplus}{H_3O}$

In sulphonation; $2H_2SO_4\rightarrow SO_3+\overset{\ominus}{HSO_4}+\overset{\oplus}{H_3O}$

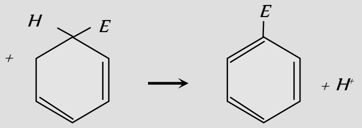
In Friedel-crafts reaction; $R-Cl+AlCl_3\rightarrow\overset{\oplus}{R}+\overset{\ominus}{AlCl_4}$

$$RCOCl+AlCl_3\rightarrow\overset{\oplus}{RCO}+\overset{\ominus}{AlCl_4}$$

***Step 2.*** The electrophile attacks the aromatic ring to form carbonium ion (or arenium ion) whi[illegible] ed [illegible] e.



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



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

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

(3) **Free radical substitution reactions :** Free radical substitution reactions involves the attack by a free radical. These reactions occurs 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 examples of free radical substitution.

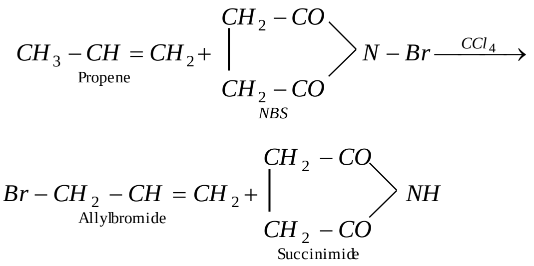
$$\underset{Methane}{CH_4}+Cl_2\xrightarrow[light]{UV}\underset{\text{Methylchloride}}{CH_3Cl}+HCl$$

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

$$C_6H_5-H+\underset{\text{Benzenediazoniumhalide}}{C_6H_5N_2X}\xrightarrow{\text{Alkali}}\underset{\text{Diphenyl}}{C_6H_5-C_6H_5}+N_2+HX$$

(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:



## Addition reactions

These reactions are given by those compounds which have at least one $\pi$ bond,

*i.e.,* $(>C=C<, -C\equiv C-, -\overset{O}{\overset{\|}{C}}-, C\equiv N)$. In such reaction there is loss of one $\pi$ bond and gain of two $\sigma$ 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

(3) Free radical additions

(1) **Electrophilic addition reactions**

(i) Such reactions are 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 catalysed 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 addendum adds on that doubly bonded carbon of the alkene which has least number of hydrogen atom.

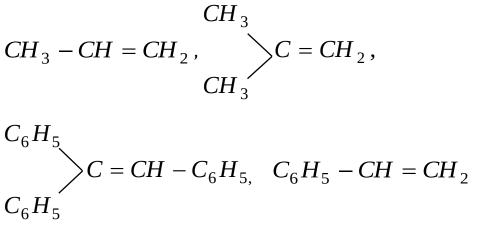
This rule can be used only in those alkenes which fulfil the following conditions:

(a) Alkene should be unsymmetrical.

(b) Substituent/substituents present on doubly bonded carbon/(*s*) should only be $+I$ group.

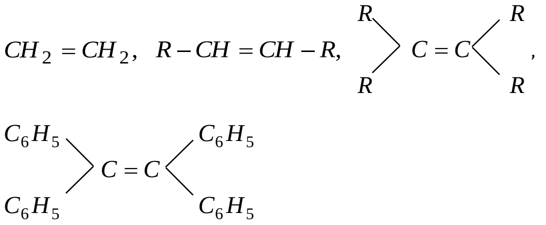
(c) If phenyl group is present on doubly bonded carbon, then both doubly bonded carbons should be substituted by phenyl groups.

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



$CH_3-CH=CH_2$, $C_6H_5-CH=CH_2$

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



$CH_2=CH_2$, $R-CH=CH-R$,

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

$CH_2=CH-G$, where $G$ is a strong $-I$ group such as

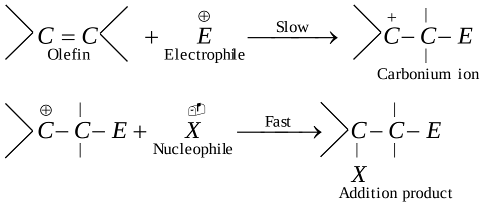
$$-CX_3, -NO_2, -CN, -CHO, -COR, -COOH, -\overset{O}{\overset{\|}{C}}-Z$$

$$(Z=Cl, OH, OR, NH_2)$$

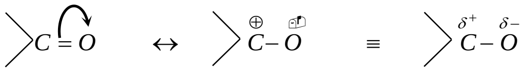
*Example:*

$$CH_2=CH-CHO+HCl\xrightarrow{\text{Anti-Markownikoff's addition}}\overset{Cl}{\overset{|}{C}}H_2-CH_2-CHO$$

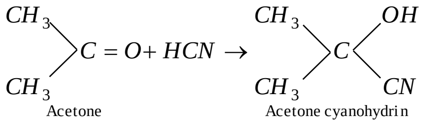
(vii) Mechanism of electrophilic addition reactions is as follows,



(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 $\pi$-electrons of the carbon-oxygen double bond in carbonyl group ( $C=O$ ) get shifted towards the oxygen atom and thereby such bond is highly polarised. This makes carbon atom of the carbonyl group electron deficient.



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

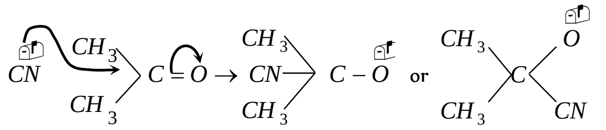


The mechanism of the reaction involves the following steps:

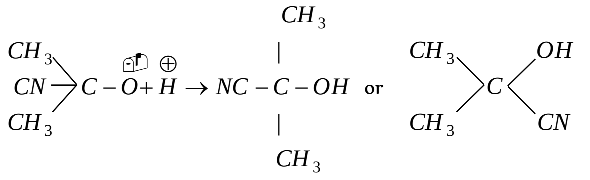
***Step 1.*** *HCN* gives a proton $(\overset{\oplus}{H})$ and a nucleophile, cyanide ion $(\overset{\ominus}{CN})$.

$$HCN \to H^{\oplus} + CN^{\ominus}$$

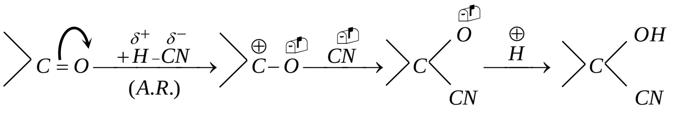
***Step 2.*** The nucleophile $(CN^{\ominus})$ attacks the positively charged carbon so as to form an anion [ $H^{\oplus}$ does not initiate the negatively charged oxygen as anion is more stable than cation].



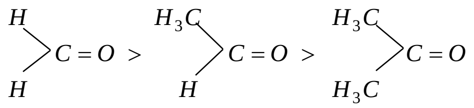
***Step 3.*** The proton $(H^{+})$ combines with anion to form the addition product.



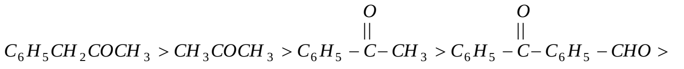
In >C = O compounds, the addition of liquid *HCN* gives cyanohydrin and the addendum is $CN^{-}$ ion and not *HCN* directly (addition is catalysed by bases or salts of weak acids and retarded by acids or unaffected by neutral compounds).



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



Decreasing order of nucleophilic addition in some species.



$$C_6H_5CH_2COCH_3 > CH_3COCH_3 > C_6H_5-\overset{O}{\overset{||}{C}}-CH_3 > C_6H_5-\overset{O}{\overset{||}{C}}-C_6H_5 - CHO >$$

$$-COCH_3 > -COCl > -COOCH_3 > -CONH_2 > -COOH$$

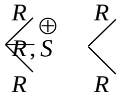
(3) **Free radical addition reactions :** Those reactions which involve the initial attack by a free radical are known as free radical reactions. Addition of hydrogen bromide to alkenes (say, propylene) in the presence of peroxide (radical initiator) follows free radical mechanism. Free radical reactions 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.

## Elimination reactions

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

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

*i.e.,* X, OH, OR, $\overset{\oplus}{N_2}$, $N_3$, $H_3\overset{\oplus}{O}$, $\overset{\oplus}{N}$



Elimination reactions are generally endothermic and take place on heating.

Elimination reactions are classified into two general types,

(I) $\alpha$- elimination reactions or 1, 1-elimination reactions.

(II) $\beta$- elimination reaction or 1, 2-elimination reactions.

(I) ***$\alpha$-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 $\alpha$- elimination reaction. This reaction is mainly given by gem dihalides and gem trihalides having at least one $\alpha$- hydrogen.

$$CHX_3 \xrightarrow{\text{Alc. } KOH/\Delta} \ddot{C}X_2 + \overset{\ominus}{X} + \overset{\oplus}{H}$$

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

(II) ***$\beta$-elimination reactions or 1, 2-elimination reactions:*** Consider the following reactions,

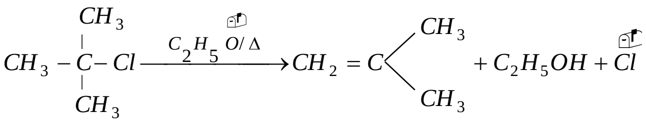
$$\underset{\beta}{CH_3 - CH_2} - \underset{\alpha}{CH_2} - L \to CH_3 - CH = CH_2 + \overset{\oplus}{H} + \overset{\ominus}{L}$$

A reaction in which functional group (*i.e.,* leaving group) is removed from $\alpha$- carbon and other group (Generally hydrogen atom) from the $\beta$- carbon is called $\beta$- elimination reaction. In this reaction there is loss of two $\sigma$ bonds and gain of one $\pi$ bond. Product of the reaction is generally less stable than the reactant.

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

(i) $E_1$ (Elimination unimolecular) reaction, (ii) $E_2$ (Elimination bimolecular) reaction and (iii) $E_{1cb}$ (Elimination unimolecular conjugate base) reaction

(i) $E_1$ (Elimination unimolecular) **reaction :** Consider the following reaction,



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

Rate ∝ [Substrate]

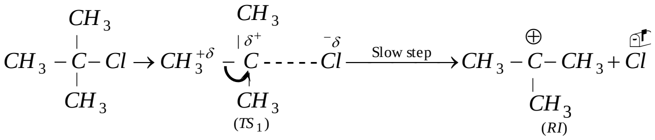
(b) Product formation takes place by the formation of carbocation as reaction intermediate (*RI*).

(c) Since reaction intermediate is carbocation, rearrangement is possible in $E_1$ reaction.

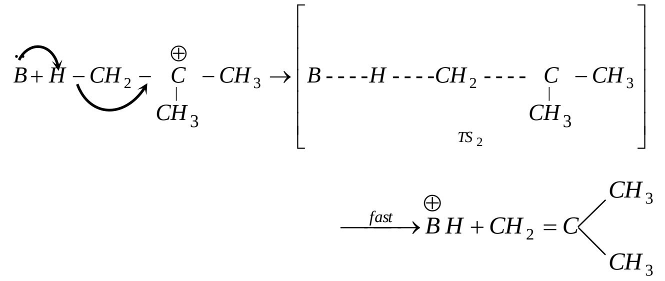
(d) Reaction is carried out in the presence of polar protic solvent.

(e) The $E_1$ reaction occurs in two steps,

***Step 1.***



***Step 2.***



$$\ddot{B} + H - CH_2 - \overset{\oplus}{\underset{CH_3}{C}} - CH_3 \rightarrow \left[ B{-}{-}{-}{-}H{-}{-}{-}{-}CH_2{-}{-}{-}{-}\underset{CH_3}{C} - CH_3 \right]_{TS_2} \xrightarrow{fast} \overset{\oplus}{B}H + CH_2 = C(CH_3)_2$$

(ii) ***E*₂** (Elimination bimolecular) ***reaction*** : Consider the following reaction,

$$CH_3 - CH_2 - CH_2 - Br \xrightarrow[\Delta]{Base\,(B)} CH_3 - CH = CH_2 + \overset{\oplus}{H} + \overset{\ominus}{Br}$$

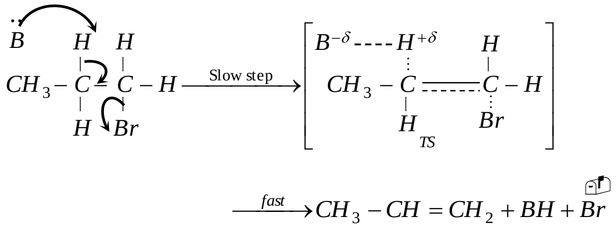
(a) Reaction velocity depends only on the concentration of the substrate and the base used; thus reaction is bimolecular reaction. Rate ∝[Substrate] [Base]

(b) Since the reaction is a bimolecular reaction, the product formation will take place by formation of transition state (TS).

(c) Rearrangement does not take place in $E_2$ reaction but in case of allylic compound rearrangement is possible.

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

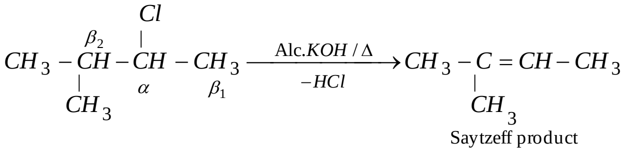
(e) The $E_2$ reaction occurs in one step,



$$\ddot{B} \quad CH_3 - \underset{H}{\overset{H}{C}} - \underset{Br}{\overset{H}{C}} - H \xrightarrow{\text{Slow step}} \left[ \begin{matrix} B^{-\delta}{-}{-}{-}{-}H^{+\delta} & & H \\ CH_3 - \underset{H}{C} & \overset{}{=\!=\!=} & \underset{Br}{C} - H \end{matrix} \right]_{TS} \xrightarrow{fast} CH_3 - CH = CH_2 + BH + \overset{\ominus}{Br}$$

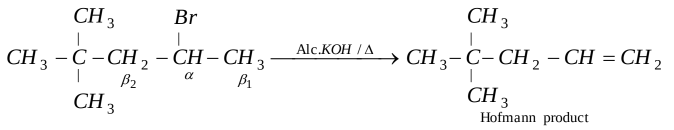
(2) **Orientation in $\beta$ - elimination reactions :** If substrate is unsymmetrical, then this will give more than one product. Major product of the reaction can be known by two emperical rules.

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



$$CH_3 - \underset{CH_3}{\overset{\beta_2}{CH}} - \underset{\alpha}{\overset{Cl}{CH}} - \underset{\beta_1}{CH_3} \xrightarrow[-HCl]{\text{Alc.}KOH/\Delta} \underset{\text{Saytzeff product}}{CH_3 - \underset{CH_3}{C} = CH - CH_3}$$

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



$$CH_3 - \underset{CH_3}{\overset{CH_3}{C}} - \underset{\beta_2}{CH_2} - \underset{\alpha}{\overset{Br}{CH}} - \underset{\beta_1}{CH_3} \xrightarrow{\text{Alc.}KOH\,/\,\Delta} \underset{\text{Hofmann product}}{CH_3 - \underset{CH_3}{\overset{CH_3}{C}} - CH_2 - CH = CH_2}$$

❑ In $E_1$ reactions, product formation always takes place by Saytzeff rule.

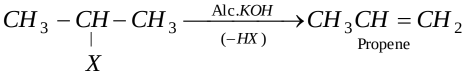
❑ In $E_{1cb}$ reactions, product formation always takes place by Hofmann rule.

❑ 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.

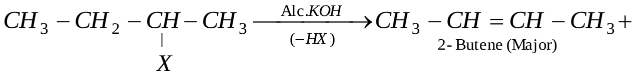
(3) **Examples of $\beta$ - elimination reactions**

(i) ***Dehydrohalogenation*** is removal of *HX* from alkyl halides with alcoholic *KOH* or $KNH_2$ or ter- BuO*K* (Potassium tertiary butoxide) and an example of $\alpha$-$\beta$ elimination,

*e.g.,* $$CH_3 - CH_2X \xrightarrow[(-HX)]{\text{Alc.}KOH} \underset{\text{Ethene}}{H_2C = CH_2}\ ;$$



$$CH_3 - \underset{X}{CH} - CH_3 \xrightarrow[(-HX)]{\text{Alc.}KOH} \underset{\text{Propene}}{CH_3CH = CH_2}$$



$$CH_3 - CH_2 - \underset{X}{CH} - CH_3 \xrightarrow[(-HX)]{\text{Alc.}KOH} \underset{\text{2- Butene (Major)}}{CH_3 - CH = CH - CH_3} +$$

$$\underset{\text{1- Butene (Minor)}}{CH_3 - CH_2 - CH = CH_2}$$

(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 $E_1$. The proton given by acid is taken up by alcohol.

Dehydration is removal of $H_2O$ from alcohols,

*e.g.,*

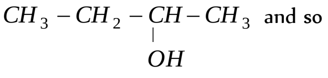
$$CH_3 - CH_2 - OH \xrightarrow[(-H_2O)]{\text{Conc. } H_2SO_4, 170°C} H_2C = CH_2$$

$$\underset{\text{Propan -1-ol}}{CH_3 - CH_2 - CH_2 - OH} \xrightarrow[(-H_2O)]{\text{Conc. } H_2SO_4, 170°C} \underset{\text{Propene}}{CH_3 - CH = CH_2}$$

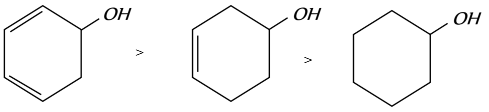
❑ Dehydration of alcohols is in the order:

$$\underset{(3°)}{\text{Tertiary}} > \underset{(2°)}{\text{Secondary}} > \underset{(1°)}{\text{Primary}}$$

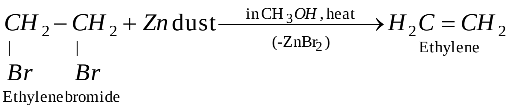
❑ 2° and 3° alcohol by $E_1$ process and 1° alcohol by $E_2$ process. Alcohols leading to conjugated alkenes are more easily dehydrated than the alcohols leading to non-conjugated alkenes. $CH_2 = CH - \underset{OH}{CH} - CH_3$ is easily dehydrated than



$CH_3 - CH_2 - \underset{OH}{CH} - CH_3$ and so

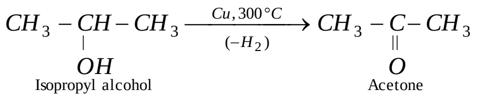


(iii) ***Dehalogenation*** : It is removal of halogens, *e.g.,*



$$\underset{\text{Ethylenebromide}}{\underset{Br}{CH_2} - \underset{Br}{CH_2}} + Zn\,\text{dust} \xrightarrow[(\text{-ZnBr}_2)]{\text{in}\,CH_3OH,\,\text{heat}} \underset{\text{Ethylene}}{H_2C = CH_2}$$

(iv) ***Dehydrogenation*** **:** It is removal of hydrogen, *e.g.,*



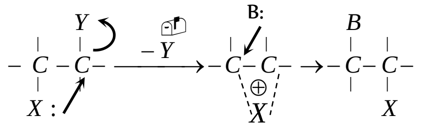
$$\underset{\text{Isopropyl alcohol}}{CH_3-\underset{OH}{\underset{|}{CH}}-CH_3} \xrightarrow[(-H_2)]{Cu,\,300°C} \underset{\text{Acetone}}{CH_3-\underset{O}{\underset{||}{C}}-CH_3}$$

## 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 centre which may be carbon, nitrogen and oxygen.



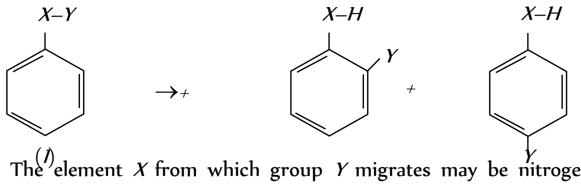
Bridged or
non-classical carbocation

*X*= Nucleophilic species, *Y* = Electronegative group, *B* = Another nucleophile.

(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 centre.

(3) **Rearrangement or migration to free radical species** (Free radical rearrangement) **:** Those rearrangement reactions in which the migrating group moves to a free radical centre. 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,

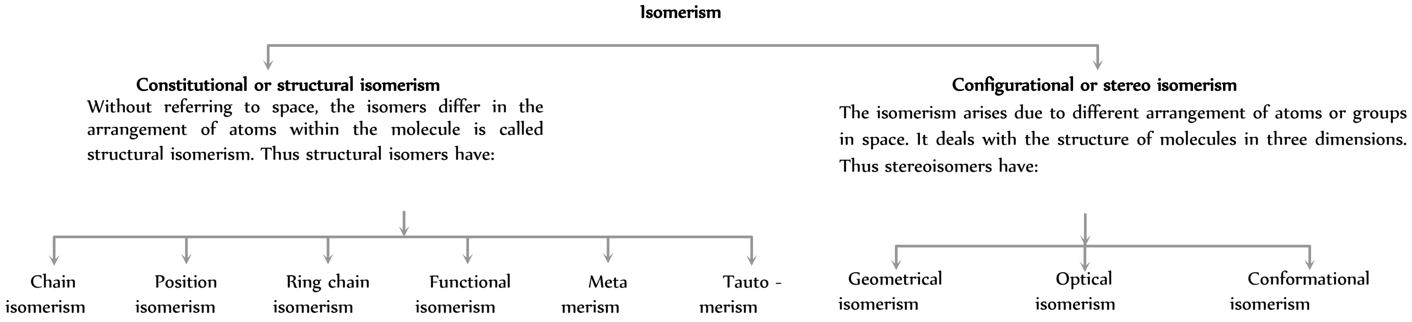


The element *X* from which group *Y* migrates may be nitrogen or oxygen.

## Isomerism

Organic 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.

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:



**Isomerism**

**Constitutional or structural isomerism**
Without referring to space, the isomers differ in the arrangement of atoms within the molecule is called structural isomerism. Thus structural isomers have:

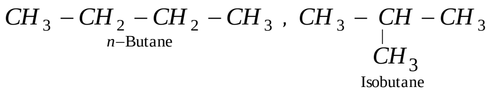
**Configurational or stereo isomerism**
The isomerism arises due to different arrangement of atoms or groups in space. It deals with the structure of molecules in three dimensions. Thus stereoisomers have:

## 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.

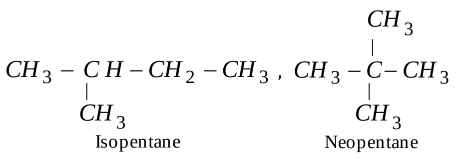
*Examples :*

(i) **$C_4H_{10}$ :**



$$\underset{n-\text{Butane}}{CH_3-CH_2-CH_2-CH_3}\ ,\ \underset{\text{Isobutane}}{CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_3}$$

(ii) **$C_5H_{12}$:** (Three) $CH_3-CH_2-CH_2-CH_2-CH_3$ ,
*n*–Pentane



$$\underset{\text{Isopentane}}{CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_3}\ ,\ \underset{\text{Neopentane}}{CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_3}$$

❒ Except alkynes chain isomerism is observed when the number of carbon atoms is four or more than four.

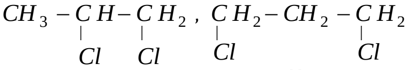
❒ Chain isomers differ in the nature of carbon chain, *i.e.,* in the length of carbon chain.

❒ 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 substiuent atom or group or an unsaturated linkage in the same carbon chain.

(ii) $C_3H_6Cl_2$ : $\underset{\text{2,2–Dichloro propane, (gemdihalide)}}{CH_3-CCl_2-CH_3}$ , $\underset{\text{1,1–Dichloro propane (gemdihalide)}}{CH_3-CH_2-CH-Cl_2}$ ,



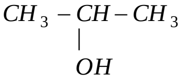
$CH_3-\underset{|\atop Cl}{C}H-\underset{|\atop Cl}{C}H_2$ , $\underset{|\atop Cl}{C}H_2-CH_2-\underset{|\atop Cl}{C}H_2$

1,2–Dichloro propane (Vicdihalide) 1,3–Dichloro propane ($\alpha,\gamma$-dihalide)

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

❒ Monosubstituted alicylic 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) $CH_3-CH_2-CH_2-OH$



(ii) $CH_3-\underset{|\atop OH}{CH}-CH_3$

(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 ($C_nH_{2n+2}O$)***

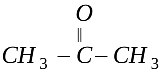
$C_2H_6O$ : $\underset{\text{Ethyl alcohol}}{CH_3-CH_2-OH}$ ; $\underset{\text{Dimethylether}}{H_3C-O-CH_3}$

$C_3H_8O$ : $\underset{n\text{–propyl alcohol}}{CH_3-CH_2-CH_2-OH}$ ; $\underset{\text{Ethyl methylether}}{C_2H_5-O-CH_3}$

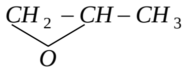
$C_4H_{10}O$ : $\underset{n\text{–Butyl alcohol}}{CH_3-CH_2-CH_2-CH_2-OH}$ ;

$\underset{\text{Diethyl ether}}{C_2H_5-O-C_2H_5}$

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



$C_3H_6O$ : $\underset{\text{Propionaldehyde}}{CH_3-CH_2-CHO}$ ; $\underset{\text{Acetone}}{CH_3-\overset{O\atop\|}{C}-CH_3}$ ;



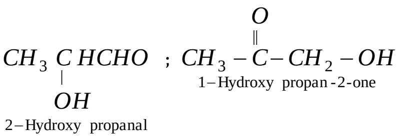
1,2–Epoxy propane

; $\underset{\text{Allylalcohol}}{CH_2=CH-CH_2OH}$

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

$C_2H_4O_2$ : $\underset{\text{Aceticacid}}{CH_3COOH}$ ; $\underset{\text{Methyl formate}}{HCOOCH_3}$

$C_3H_6O_2$ : $\underset{\text{Propionic acid}}{CH_3-CH_2-COOH}$ ; $\underset{\text{Methyl acetate}}{CH_3COOCH_3}$ ;



$CH_3\underset{|\atop OH}{C}HCHO$ ; $CH_3-\overset{O\atop\|}{C}-CH_2-OH$

2–Hydroxy propanal 1–Hydroxy propan-2-one

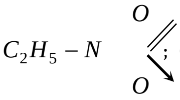
(iv) ***Alkynes and alkadienes ($C_nH_{2n-2}$)***

$C_4H_6$ : $\underset{\text{1–Butyne}}{CH_3-CH_2-C\equiv CH}$ ; $\underset{\text{1,3–Butadiene}}{H_2C=CH-CH=CH_2}$ ;

$\underset{\text{2–Butyne}}{CH_3-C\equiv C-CH_3}$ ; $\underset{\text{1,2–Butadiene}}{H_2C=C=CH-CH_3}$

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

$C_2H_5NO_2$ :

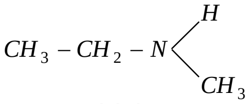


Nitro ethane

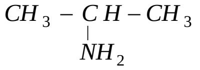
; $\underset{\text{Ethyl nitrite}}{C_2H_5-O-N=O}$

(vi) ***Amines*** (Primary, secondary and tertiary)

$C_3H_9N$ : $\underset{\text{Propan -1- amine}}{CH_3-CH_2-CH_2-NH_2}$ ;



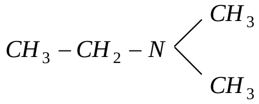
$N$–Methyl ethanamine



$CH_3-\underset{|\atop NH_2}{C}H-CH_3$

Propan -2- amine

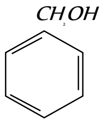
;



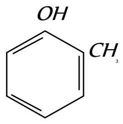
$N,N$–Dimethyl methanamine

(vii) ***Alcohols and phenols***

$C_7H_8O$ ;

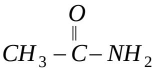


Benzyl alcohol



*o*-Cresol

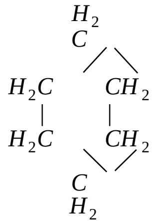
(viii) ***Oximes and amides***



$C_2H_5NO$ : $\underset{\text{Acetaldoxime}}{CH_3-CH=NOH}$ ; $\underset{\text{Acetamide}}{CH_3-\overset{O\atop\|}{C}-NH_2}$

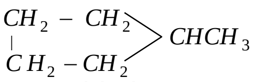
(4) **Ring-chain isomerism :** This type of isomerism is due to different modes of linking of carbon atoms, *i.e.,* the isomers possess either open chain or closed chain sturctures.

$C_6H_{12}$ :



Cyclohexane

;



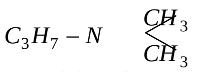
Methyl cyclopentane

; $\underset{\text{1–Hexene}}{CH_3CH_2CH_2CH_2CH=CH_2}$

❒ Ring – chain isomers are always functional isomers.

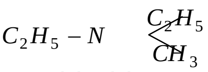
(5) **Metamerism :** This type of isomerism is due to the difference in the nature of alkyl groups attached to the polyvalent atoms or functional group. Metamers always belong to the same homologous series. Compounds like ethers, thio-ethers ketones, secondary amines, *etc.* show metamerism.

(i) $C_5H_{13}N$ :



Dimethyl propyl amine

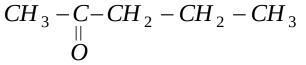
;



Diethyl methyl amine

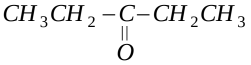
(ii) $C_6H_{15}N$ : $\underset{\text{Dipropyl amine}}{C_3H_7-NH-C_3H_7}$ ; $\underset{\text{Butyl ethyl amine}}{C_2H_5-NH-C_4H_9}$

❒ If same polyvalent functional group is there in two or more organic compounds, then chain or position isomerism is not possible, there will be metamerism *e.g.,*



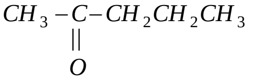
(a) $CH_3-\underset{\|\atop O}{C}-CH_2-CH_2-CH_3$ ;

(Pentan –2–one)



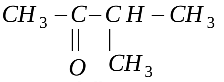
$CH_3CH_2-\underset{\underset{O}{\parallel}}{C}-CH_2CH_3$ are metamers and not position isomers.

(Pentan –3–one)

(b) 

$CH_3-\underset{\underset{O}{\parallel}}{C}-CH_2CH_2CH_3$ ;

(Pentan –2–one)



$CH_3-\underset{\underset{O}{\parallel}}{C}-\underset{\underset{CH_3}{|}}{C}H-CH_3$ are metamers and not chain isomers.

(3-Methylbutan-2-one)

❐ 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.

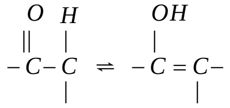
(ii) It is caused by the wandering of hydrogen atom between two polyvalent atoms. It is also known as **Desmotropism** (Desmos = bond and tropos = turn). If the hydrogen atom oscillates between two polyvalent atoms linked together, the system is a **dyad** and if the hydrogen atom travels from first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

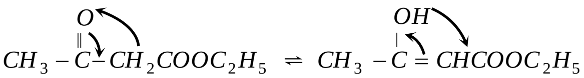
*Examples :*



$-\overset{O}{\overset{\parallel}{C}}-\underset{|}{\overset{H}{\overset{|}{C}}} \rightleftharpoons -\overset{OH}{\overset{|}{C}}=\underset{|}{C}-$

(Keto) (Enol)

*Acetoacetic ester (Ethyl acetoacetate) :*



$CH_3-\overset{O}{\overset{\parallel}{C}}-CH_2COOC_2H_5 \rightleftharpoons CH_3-\overset{OH}{\overset{|}{C}}=CHCOOC_2H_5$

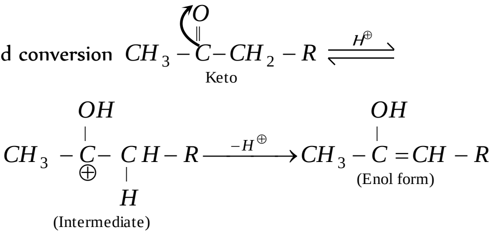
Keto form (92.1%) Enol form (7.9%)

Acetoacetic ester gives certain reactions showing the presence of keto group (Reactions with $HCN$, $H_2NOH$, $H_2NNHC_6H_5$, *etc.*) and certain reactions showing the presence of enolic group (Reactions with $Na, CH_3COCl, NH_3, PCl_5, Br_2$ water and colour with neutral $FeCl_3$, *etc.*).

Enolisation is in order

$$CH_3COCH_3 < CH_3COCH_2COOC_2H_5 < C_6H_5COCH_2COOC_2H_5 < CH_3COCH_2COCH_3 < CH_3COCH_2CHO$$

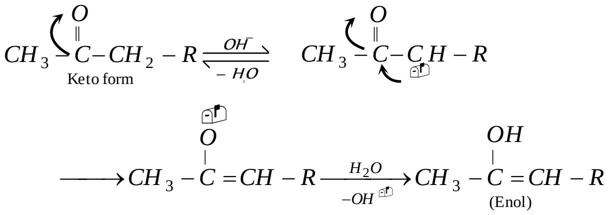
Acid catalysed conversion



$CH_3-\overset{O}{\overset{\parallel}{C}}-CH_2-R \overset{H^{\oplus}}{\rightleftharpoons}$ (Keto) $CH_3-\underset{\oplus}{\overset{OH}{\overset{|}{C}}}-\underset{\underset{H}{|}}{C}H-R \xrightarrow{-H^{\oplus}} CH_3-\overset{OH}{\overset{|}{C}}=CH-R$

(Intermediate) (Enol form)

Base catalysed conversion



$CH_3-\overset{O}{\overset{\parallel}{C}}-CH_2-R \underset{-\ HO}{\overset{OH^-}{\rightleftharpoons}} CH_3-\overset{O}{\overset{\parallel}{C}}-\overset{\ominus}{C}H-R$

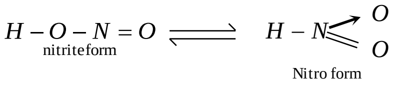
Keto form

$\longrightarrow CH_3-\overset{O^{\ominus}}{\overset{|}{C}}=CH-R \xrightarrow[-OH^{\ominus}]{H_2O} CH_3-\overset{OH}{\overset{|}{C}}=CH-R$

(Enol)

(c) Triad system containing nitrogen : Examples

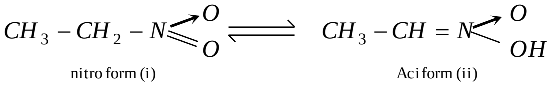
Nitrous acid exists in 2 forms



$H-O-N=O \rightleftharpoons H-N\overset{\nearrow O}{\underset{\searrow O}{}}$

nitriteform Nitro form

Nitro acinitro system



$CH_3-CH_2-N\overset{\nearrow O}{\underset{\searrow O}{}} \rightleftharpoons CH_3-CH=N\overset{\nearrow O}{\underset{\searrow OH}{}}$

nitro form (i) Aci form (ii)

(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 catalysed 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 stabilising the molecule and does not lower its energy.

(i) Tautomerism may occur in planar or nonplanar molecules.

❐ Keto=enol tautomerism is exhibited only by such aldehydes and ketones which contain at least one $\alpha$ -hydrogen.

For example

$CH_3CHO, CH_3CH_2CHO, CH_3COCH_2COCH_3$ etc,.

❐ Tautomerism is not possible in benzaldehyde $(C_6H_5CHO)$, benzophenone $(C_6H_5COC_6H_5)$, tri methyl acetaldehyde, $(CH_3)_3C-CHO$ and chloral $CCl_3-CHO$ as they do not have $\alpha-H$.

**Number of structural isomers**

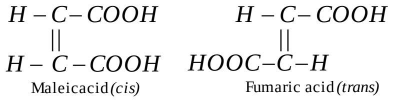
| **Molecular formula** | **Number of isomers** |
|---|---|
| **Alkanes** | |
| $C_4H_{10}$ | Two |
| $C_5H_{12}$ | Three |
| $C_6H_{14}$ | Five |
| $C_7H_{16}$ | Nine |
| $C_8H_{18}$ | Eighteen |
| $C_9H_{20}$ | Thirty five |

| | |
|---|---|
| $C_{10}H_{22}$ | 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 (Two 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) |
| $C_4H_8O$ | Three (Two aldehydes and one ketone) |
| $C_5H_{10}O$ | Seven (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 |

## Geometrical or cis-trans isomerism

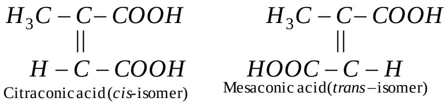
The compounds which have same molecular formula but differ in the relative spatial arrangement of atoms or groups in space are known as geometrical isomers and the phenomenon is known as geometrical isomerism. The isomer in which same groups or atoms are on the same side of the double bond is known as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

*Examples :*



$$\begin{array}{c} H-C-COOH \\ \| \\ H-C-COOH \end{array} \qquad \begin{array}{c} H-C-COOH \\ \| \\ HOOC-C-H \end{array}$$

Maleic acid (*cis*) Fumaric acid (*trans*)



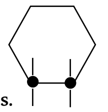
$$\begin{array}{c} H_3C-C-COOH \\ \| \\ H-C-COOH \end{array} \qquad \begin{array}{c} H_3C-C-COOH \\ \| \\ HOOC-C-H \end{array}$$

Citraconic acid (*cis*-isomer) Mesaconic acid (*trans*–isomer)

(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) $>C=C<$ frozen rotation about carbon, carbon double bond in alkenes.

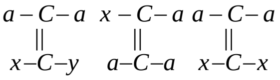
(b)  frozen rotation about carbon, carbon single bond in cycloalkanes.

(c) $>C=N-$ 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.

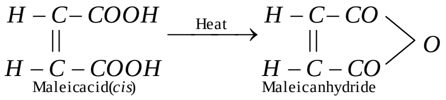
❒ The compounds of the following type will not show geometrical isomerism.



$$\begin{array}{c} a-C-a \\ \| \\ x-C-y \end{array} \quad \begin{array}{c} x-C-a \\ \| \\ a-C-a \end{array} \quad \begin{array}{c} a-C-a \\ \| \\ x-C-x \end{array}$$

(2) **Distinction between *cis*- and *trans*- isomers**

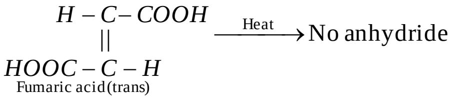
(i) ***By cyclization method*** **:** Generally, the *cis*-isomer (*e.g.* maleic acid) cyclises on heating to form the corresponding anhydride while the *trans*-isomer does not form its anhydride.



$$\begin{array}{c} H-C-COOH \\ \| \\ H-C-COOH \end{array} \xrightarrow{\text{Heat}} \begin{array}{c} H-C-CO \\ \| \\ H-C-CO \end{array}\!\!>O$$

Maleic acid (*cis*) Maleic anhydride

❒ Note that the two reacting groups (*–COOH)* are near to each other.

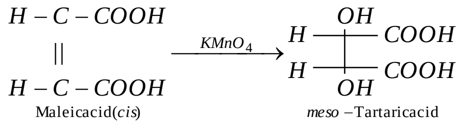


$$\begin{array}{c} H-C-COOH \\ \| \\ HOOC-C-H \end{array} \xrightarrow{\text{Heat}} \text{No anhydride}$$

Fumaric acid (trans)

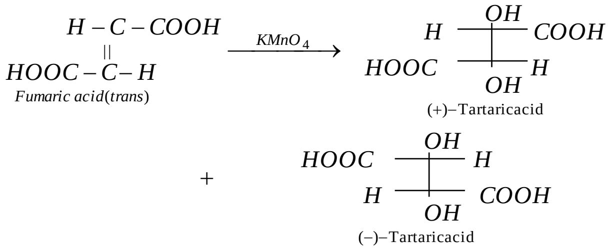
❒ Note that the two reacting groups (*–COOH)* are quite apart from each other, hence cyclisation is not possible.

(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,



$$\begin{matrix} H-C-COOH \\ \| \\ H-C-COOH \end{matrix} \xrightarrow{KMnO_4} \begin{matrix} & OH & \\ H & - & COOH \\ H & - & COOH \\ & OH & \end{matrix}$$

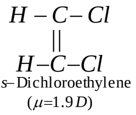
Maleicacid(*cis*) $\quad$ *meso* –Tartaricacid



$$\begin{matrix} H-C-COOH \\ \| \\ HOOC-C-H \end{matrix} \xrightarrow{KMnO_4} \begin{matrix} & OH & \\ H & - & COOH \\ HOOC & - & H \\ & OH & \end{matrix} + \begin{matrix} & OH & \\ HOOC & - & H \\ H & - & COOH \\ & OH & \end{matrix}$$

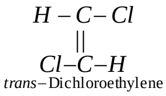
*Fumaric acid*(*trans*) $\quad$ (+)–Tartaricacid $\quad$ (–)–Tartaricacid

(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.



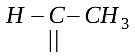
$$\begin{matrix} H-C-Cl \\ \| \\ H-C-Cl \end{matrix}$$

*cis*–Dichloroethylene
($\mu$=1.9*D*)



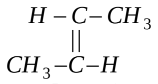
$$\begin{matrix} H-C-Cl \\ \| \\ Cl-C-H \end{matrix}$$

*trans*–Dichloroethylene
($\mu$=0.0*D*)



$$\begin{matrix} H-C-CH_3 \\ \| \\ H-C-CH_3 \end{matrix}$$

*cis*–Butene–2



$$\begin{matrix} H-C-CH_3 \\ \| \\ CH_3-C-H \end{matrix}$$

*trans*–Butene–2
($\mu$=0.0*D*)

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.