General Organic Chemistry Part 2

Types of organic reactions.

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

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

Substitution reactions

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

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

(Bromine atom is replaced by hydroxyl group)

$$\underset{\text{Methyl alcohol}}{CH_3OH}+H-Br \longrightarrow \underset{\text{Methyl bromide}}{CH_3-Br}+H_2O$$

(Hydroxyl group is replaced by bromine)

$$\underset{\text{Benzene}}{C_6H_6}+\underset{\text{(Conc.)}}{HNO_3} \xrightarrow{H_2SO_4\,(\text{conc.})} \underset{\text{Nitrobenzene}}{C_6H_5NO_2}+H_2O$$

(Hydrogen is replaced by NO_2 group)

$$\underset{\text{Propylene}}{CH_3-CH=CH_2}+Cl_2 \xrightarrow{500°C} \underset{\text{Allyl chloride}}{Cl-CH_2-CH=CH_2}+H-Cl$$

(Hydrogen is replaced by chlorine)

$$\underset{\text{Benzene}}{C_6H_6}+Cl_2 \xrightarrow{FeCl_3} \underset{\text{Chlorobenzene}}{C_6H_5-Cl}+H-Cl$$

(Hydrogen is replaced by chlorine)

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

(1) Nucleophilic substitution reactions, (2) Electrophilic substitution reactions,

(3) Free radical substitution reactions

(1) Nucleophilic substitution reactions

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

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

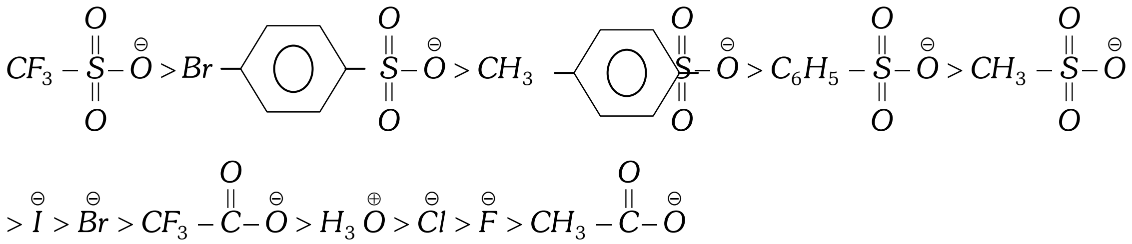
Such substitution reactions are called nucleophilic substitution reactions, *i.e.*, S_N reactions (*S* stands for substitution and *N* for nucleophile).

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

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

$$\text{Example}: \underset{\text{Decreasing acidity}}{\xrightarrow{HI>HBr>HCl>HF}} \quad \underset{\substack{\text{Increasing basicity}\\ \Downarrow \\ \text{Decreasing leaving ability}}}{\xrightarrow{\overset{\ominus}{I}\;\overset{\ominus}{Br}\;\;\overset{\ominus}{Cl}\,\overset{\ominus}{F}}}$$

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



$$> \overset{\ominus}{I} > \overset{\ominus}{Br} > CF_3-\overset{\overset{O}{||}}{C}-\overset{\ominus}{O} > H_3\overset{\oplus}{O} > \overset{\ominus}{Cl} > \overset{\ominus}{F} > CH_3-\overset{\overset{O}{||}}{C}-\overset{\ominus}{O}$$

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

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

(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.

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

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

$$R-OH \overset{\overset{\ominus}{Cl}}{\underset{(HCl)}{\not\longrightarrow}} R-Cl+\overset{\Theta}{OH}$$

Basicity of $\overset{\ominus}{Cl}$ is less than $\overset{\ominus}{OH}$ hence $\overset{\ominus}{Cl}$ will not replace OH as $\overset{\ominus}{OH}$.

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

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

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

Distinction between $S_N{}^2$ and $S_N{}^1$ reactions

Factors	$S_N{}^2$ Reactions	$S_N{}^1$ Reactions
Number of steps	**One:** $R:L+:\overset{\ominus}{Nu}\rightarrow R:Nu+:\overset{\ominus}{L}$	**Two: (i)** $R:L\xrightarrow{Slow}R^{+}+:L^{\ominus}$ **(ii)** $R^{+}+:Nu^{-}\xrightarrow{Fast}R:Nu$
Reaction rate and order	**Second order:** **Rate ∝ [Substrate] [Nucleophile] or Rate =** $K_2[RL][:Nu^{\ominus}]$	**First order:** **Rate ∝ [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 on the back and front sides although the back side attack predominates.**
Stereochemistry	**Complete inversion of configuration takes place.**	**Inversion and retention takes place.**

Reactivity order of alkyl halides	**Methyl>1°>2°>3°halides.** $(I > Br > Cl > F)$	**3°>2°>1° > methyl halides.** $(I > Br > Cl > F)$
Rearrangement	**No rearrange product is form (except for allylic).**	**Rearrange products can be formed.**
Nature of nucleophiles	**Favoured by strong and high concentration of nucleophiles.**	**Favoured by mild and low concentration of nucleosides.**
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 tarnsfer).**	**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).

$S_E{}^1$ Reaction mechanism : Electrophilic substitution in aliphatic compounds ($S_N{}^1$) 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:

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

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

$S_E{}^2$ Reaction mechanism : Electophilic substitution ($S_E{}^2$) 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 electorphilic aromatic substitution reactions, it involves:

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

In halogenation; $Cl - Cl + FeCl_3 \rightarrow \overset{\oplus}{Cl} + Fe\overset{\ominus}{C}l_4$

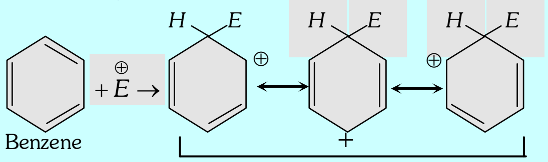
In nitration; $HNO_3 2H_2SO_4 \rightarrow \overset{\oplus}{N}O_2 + 2\,\overset{\ominus}{H}SO_4 + \overset{\oplus}{H_3}O$

In sulphonation; $2H_2SO_4 \rightarrow SO_3 + \overset{\ominus}{H}SO_4 + \overset{\oplus}{H_3}O$

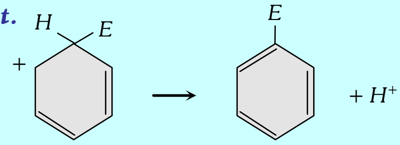
In Friedel-crafts reaction; $R - Cl + AlCl_3 \rightarrow \overset{\oplus}{R} + \overset{\ominus}{A}lCl_4$

$RCOCl + AlCl_3 \rightarrow \overset{\oplus}{R}CO + \overset{\ominus}{A}lCl_4$

Step 2. The electrophile attacks the aromatic ring to form carbonium ion (or arenium ion) which is stabilized by resonance.



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



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

Similarly, Nitration, sulphonation and Friedel-

Crafts reaction.....etc., in benzene nucleus are the other examples of electrophilic substitution.

(3) **Free radical substitution reactions :** Free radical substitution reactions involves the attack by an 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 (HOMOLYSIS).

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

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

$$CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl$$

$$CH_2Cl_2 + Cl_2 \rightarrow CHCl_3 + HCl$$

$$CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$$

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

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

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

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

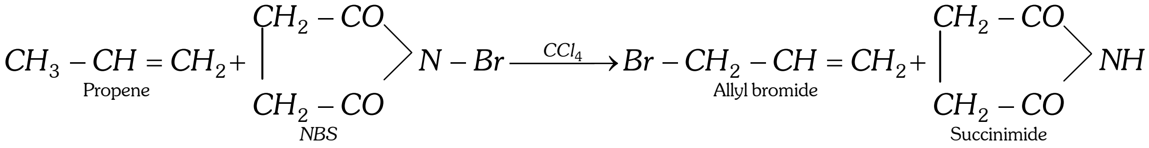
$$C_2H_5-Br + 2Na + Br-C_2H_5 \xrightarrow{\text{Ether}} C_2H_5-C_2H_5 + 2NaBr$$

$$C_2H_5-Br + Na \rightarrow \dot{C}_2H_5 + NaBr$$

$$\dot{C}_2H_5 + \dot{C}_2H_5 \rightarrow C_2H_5-C_2H_5 \text{ (Butane)}$$

$$2CH_3-\dot{C}H_2 \xrightarrow{\text{Disproportionation}} \underset{\text{Ethane}}{CH_3-CH_3} + \underset{\text{Ethylene}}{CH_2=CH_2}$$

(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:

(a) 

$$\underset{\text{Propene}}{CH_3-CH=CH_2} + \underset{NBS}{\left.\begin{array}{l}CH_2-CO\\ |\\ CH_2-CO\end{array}\right\rangle N-Br} \xrightarrow{CCl_4} \underset{\text{Allyl bromide}}{Br-CH_2-CH=CH_2} + \underset{\text{Succinimide}}{\left.\begin{array}{l}CH_2-CO\\ |\\ CH_2-CO\end{array}\right\rangle NH}$$

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

Addition reactions

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

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

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

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

(1) Electrophilic addition reactions

(i) This reaction is mainly given by alkenes and alkynes.

(ii) Electrophilic addition reactions of alkenes and alkynes are generally two step reactions.

(iii) Alkenes and alkynes give electrophilic addition with those reagents which on dissociation gives electrophile as well as nucleophile.

(iv) If the reagent is a weak acid then electrophilic additon 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 reagent adds on that doubly bonded carbon of the alkene which has least number of hydrogen (*s*).

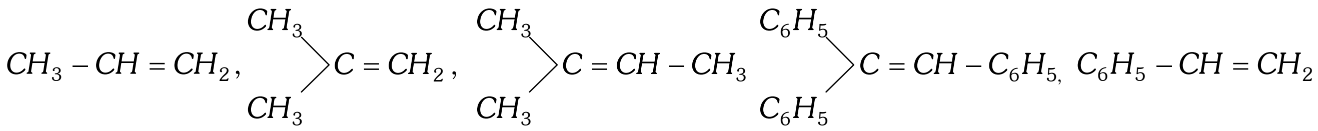
This rule can be used only in those alkenes which fulfil the following conditions:

(a) Alkene should be unsymmetrical.

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

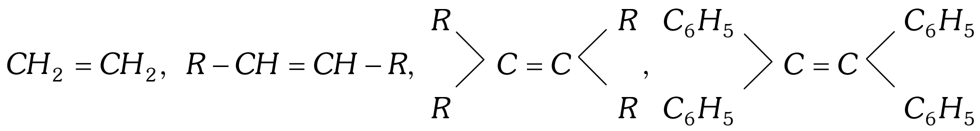
(c) If phenyl group is present on doublly bonded carbon, then both doublly bonded carbons should be substituted by phenyl groups.

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



$$CH_3-CH=CH_2,\quad \begin{matrix}CH_3\\ \\ CH_3\end{matrix}\!\!>C=CH_2,\quad \begin{matrix}CH_3\\ \\ CH_3\end{matrix}\!\!>C=CH-CH_3\quad \begin{matrix}C_6H_5\\ \\ C_6H_5\end{matrix}\!\!>C=CH-C_6H_5,\ C_6H_5-CH=CH_2$$

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

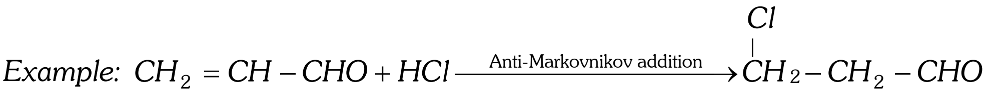


$$CH_2=CH_2,\ R-CH=CH-R,\ \begin{matrix}R\\ \\ R\end{matrix}\!\!>C=C<\!\!\begin{matrix}R\\ \\ R\end{matrix},\ \begin{matrix}C_6H_5\\ \\ C_6H_5\end{matrix}\!\!>C=C<\!\!\begin{matrix}C_6H_5\\ \\ C_6H_5\end{matrix}$$

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

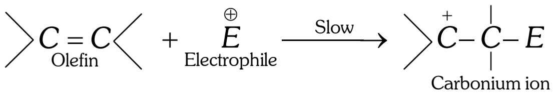
$CH_2=CH-G$

where G is a strong $-I$ group such as $-CX_3, -NO_2, -CN, -CHO, -COR, -COOH, -\overset{O}{\overset{||}{C}}-Z\ (Z=Cl, OH, OR, NH_2)$

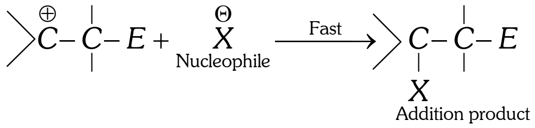


Example: $CH_2=CH-CHO+HCl\xrightarrow{\text{Anti-Markovnikov addition}}\overset{\overset{Cl}{|}}{C}H_2-CH_2-CHO$

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

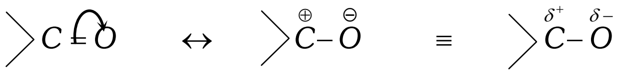


$$\underset{\text{Olefin}}{>C=C<}+\underset{\text{Electrophile}}{\overset{\oplus}{E}}\xrightarrow{\text{Slow}}\underset{\text{Carbonium ion}}{>\overset{+}{C}-\overset{|}{\underset{|}{C}}-E}$$



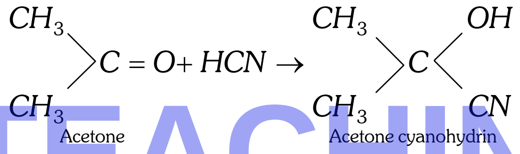
$$>\overset{\oplus}{C}-\overset{|}{\underset{|}{C}}-E+\underset{\text{Nucleophile}}{\overset{\ominus}{X}}\xrightarrow{\text{Fast}}\underset{\text{Addition product}}{>\underset{X}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-E}$$

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



$$>C=O\ \leftrightarrow\ >\overset{\oplus}{C}-\overset{\ominus}{O}\ \equiv\ >\overset{\delta^+}{C}-\overset{\delta-}{O}$$

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



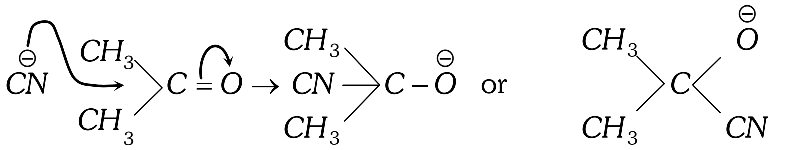
$$\underset{\text{Acetone}}{(CH_3)_2C=O}+HCN\rightarrow\underset{\text{Acetone cyanohydrin}}{(CH_3)_2C(OH)(CN)}$$

The mechanism of the reaction involves the following steps:

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

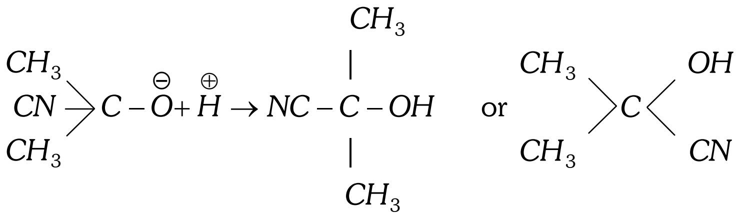
$$HCN\rightarrow H^{\oplus}+CN^{\ominus}$$

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



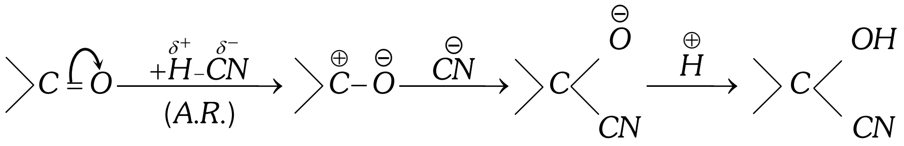
$$\overset{\ominus}{CN}+(CH_3)_2C=O\rightarrow (CH_3)_2(CN)C-\overset{\ominus}{O}\ \text{or}\ (CH_3)_2C(\overset{\ominus}{O})(CN)$$

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



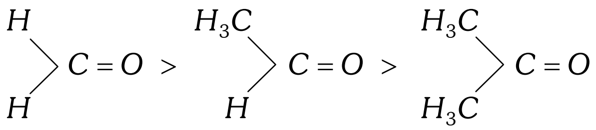
$$(CH_3)_2(CN)C-\overset{\ominus}{O}+\overset{\oplus}{H}\rightarrow NC-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH\ \text{or}\ (CH_3)_2C(OH)(CN)$$

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



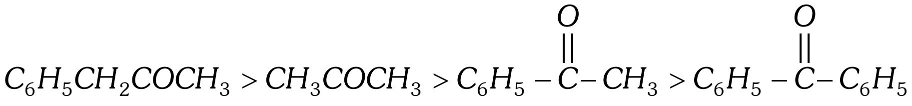
$$>C\overset{\frown}{=}O \xrightarrow[(A.R.)]{+\overset{\delta+}{H}-\overset{\delta-}{CN}} >\overset{\oplus}{C}-\overset{\ominus}{O} \xrightarrow{\overset{\ominus}{CN}} >C<^{\overset{\ominus}{O}}_{CN} \xrightarrow{\overset{\oplus}{H}} >C<^{OH}_{CN}$$

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



$$\begin{matrix}H\\H\end{matrix}>C=O > \begin{matrix}H_3C\\H\end{matrix}>C=O > \begin{matrix}H_3C\\H_3C\end{matrix}>C=O$$

Note : ✸ Decreasing order of nucleophilic addition in some species.



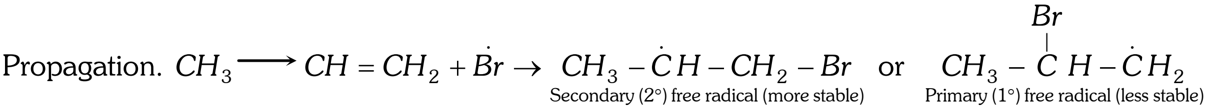
$$C_6H_5CH_2COCH_3 > CH_3COCH_3 > C_6H_5-\overset{\overset{O}{||}}{C}-CH_3 > C_6H_5-\overset{\overset{O}{||}}{C}-C_6H_5$$

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

(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. The essential steps of the reactions are as follows.

Initiation (Formation of free radical)

(a) $\underset{\text{Peroxide}}{RO-OR} \rightarrow \underset{\text{Free radicals}}{2R\dot{O}}$ (b) $HBr + R\dot{O} \rightarrow ROH + \dot{B}r$



Propagation. $CH_3 \longrightarrow CH=CH_2 + \dot{B}r \rightarrow \underset{\text{Secondary (2°) free radical (more stable)}}{CH_3-\dot{C}H-CH_2-Br}$ or $\underset{\text{Primary (1°) free radical (less stable)}}{CH_3-\overset{\overset{Br}{|}}{C}H-\dot{C}H_2}$

$CH_3-\dot{C}H-CH_2-Br + HBr \rightarrow CH_3-CH_2-CH_2-Br + \dot{B}r$ and so on

Termination : $\dot{B}r + \dot{B}r \rightarrow Br-Br$

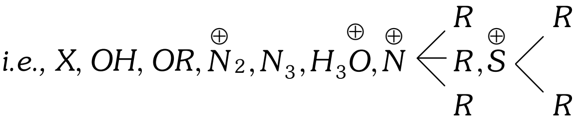
Polymerisation of ethylene to polyethylene and vinyl monomers to polyvinyl polymers are free radical addition reactions.

$$\underset{\text{Ethylene}}{nCH_2=CH_2} \xrightarrow{\text{Catalyst}} \underset{\text{Polyethylene}}{(-CH_2-CH_2-)_n}$$

Elimination reactions

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

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



i.e., $X, OH, OR, \overset{\oplus}{N}_2, N_3, H_3\overset{\oplus}{O}, \overset{\oplus}{N}<^{R}_{R}R, \overset{\oplus}{S}<^{R}_{R}$

Elimination reactions are generally endothermic and take place on heating.

Elimination reactions are classified into two general types,

(I) α- elimination reactions or 1, 1-elimination reactions.

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

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

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

$$CH_2X_2 \xrightarrow{\text{Alc, KOH}/\Delta} \ddot{C}HX + \overset{\ominus}{X} + \overset{\oplus}{H}$$

$$CH_3CHI_2 + Zn \rightarrow CH_3\ddot{C}H + ZnI_2$$

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

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

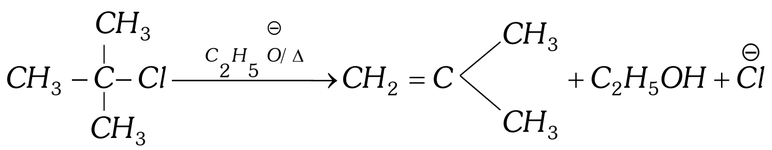
$$CH_3-\underset{\beta}{CH_2}-\underset{\alpha}{CH_2}-L \rightarrow CH_3-CH=CH_2+\overset{\oplus}{H}+\overset{\ominus}{L}$$

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

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

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

(i) $\boldsymbol{E_1}$ (Elimination unimolecular) **reaction :** Consider the following reaction,



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-Cl \xrightarrow{C_2H_5\overset{\ominus}{O}/\Delta} CH_2=C\begin{matrix}\diagup CH_3\\ \diagdown CH_3\end{matrix} + C_2H_5OH + \overset{\ominus}{Cl}$$

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

Rate $\propto$ [Substrate]

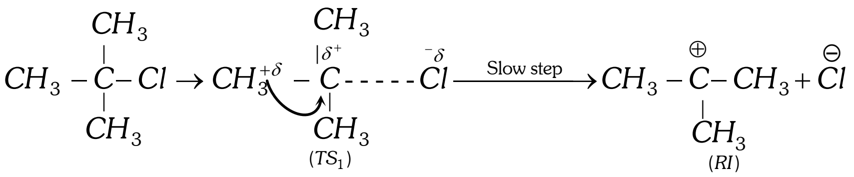
(b) Product formation takes place by formation of carbocation as reaction intermediate (*RI*).

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

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

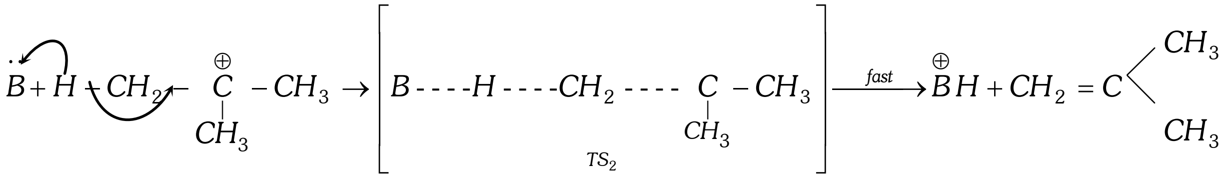
(e) The E_1 reaction occurs in two steps,

Step 1.



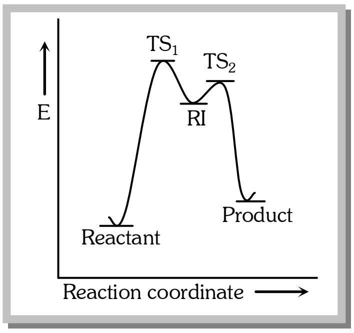
$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Cl \rightarrow \underset{(TS_1)}{CH_3^{+\delta}-\underset{CH_3}{\overset{CH_3}{\overset{|\delta^+}{C}}}{-}{-}{-}{-}{-}\overset{-\delta}{Cl}} \xrightarrow{\text{Slow step}} \underset{(RI)}{CH_3-\underset{CH_3}{\overset{\oplus}{C}}-CH_3}+\overset{\ominus}{Cl}$$

Step 2.



$$\overset{\cdot\cdot}{B}+H-CH_2-\underset{CH_3}{\overset{\oplus}{C}}-CH_3 \rightarrow \underset{TS_2}{\left[B{-}{-}{-}{-}H{-}{-}{-}{-}CH_2{-}{-}{-}{-}\underset{CH_3}{C}-CH_3\right]} \xrightarrow{fast} \overset{\oplus}{B}H+CH_2=C\begin{matrix}CH_3\\ CH_3\end{matrix}$$

(f) Energy profile diagram for E_1 reaction is,



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

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

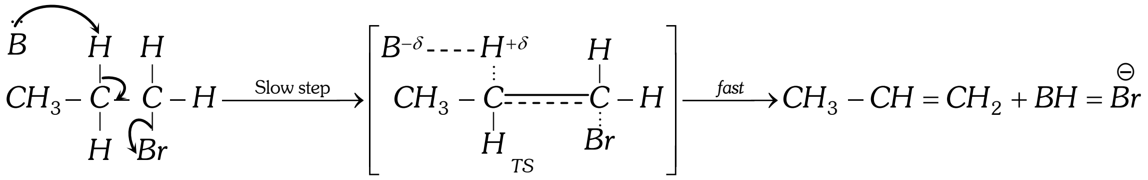
(a) Reaction velocity depends only on the concentration of the substrate and the base used; thus reaction is bimolecular reaction. Rate $\propto$[Substrate] [Base]

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

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

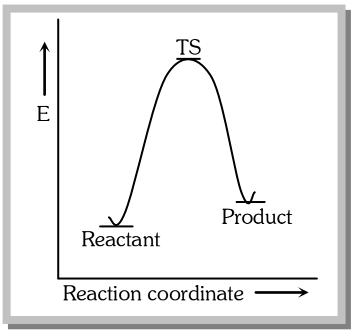
(d) Reaction is carried out in the presence of polar aprotic solvent.

(e) The E_1 reaction occurs in one step,



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

(f) Energy profile diagram for E_2 reaction is,



(iii) ***E*₁cb** (Elimination unimolecular conjugate base) **reaction**

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

Thus β- carbon should contain strong –*I* group, *e.g.*, $-\overset{O}{\overset{||}{C}}-, -NO_2, -C\equiv N$ or other carbanion stabilising group.

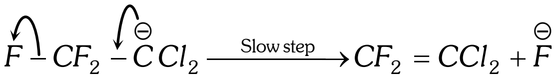
(b) This reaction is given by those compounds, which have poor leaving group, otherwise carbanion will not be formed.

(c) β- hydrogen should be highly acidic so that it can easily be removed as proton to give carbanion.

$$CF_3-CHCl_2 \xrightarrow{C_2H_5\overset{\ominus}{O}} CF_2=CCl_2; \quad C_6H_5-CH_2-CH_2-F \xrightarrow{C_2H_5\overset{\ominus}{O}} C_6H_5-CH=CH_2$$

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

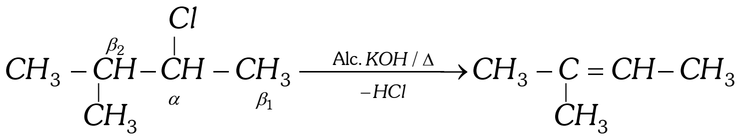
Step 1. $CF_3-CHCl_2 \xrightarrow[\text{Fast step}]{C_2H_5\overset{\ominus}{O}} \underset{\text{Conjugate base of sustrate which is stabilised by } CF_3 \text{ and } Cl}{CF_3-\overset{\ominus}{C}Cl_2}$

Step 2. 

$F-CF_2-\overset{\ominus}{C}Cl_2 \xrightarrow{\text{Slow step}} CF_2=CCl_2+\overset{\ominus}{F}$

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

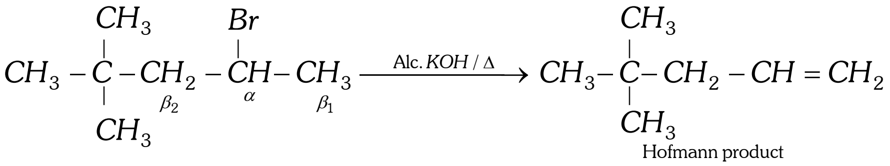
(i) ***Saytzeff rule* :** According to this rule, major product is the most substituted alkene *i.e.*, major product is obtained by elimination of $\overset{\oplus}{H}$ from that β- carbon which has the least number of hydrogen. Product of the reaction in this case is known as Saytzeff product.



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

Saytzeff product

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



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

Hofmann product

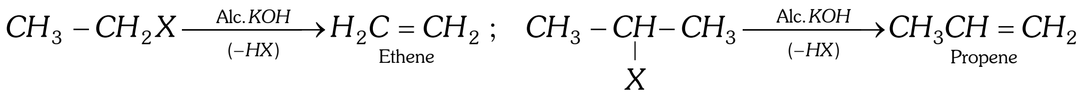
Note : ✹ In E_1 reactions, product formation always takes place by Saytzeff rule.

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

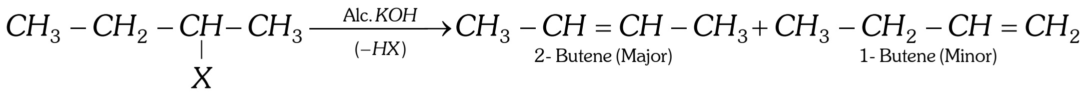
✹ In E_2 reactions, product formation takes place by Saytzeff as well as Hofmann rule. In almost all E_2 reactions product formation take place by Saytzeff rule.

(3) Examples of β - elimination reactions

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



$$CH_3-CH_2X\xrightarrow[(-HX)]{\text{Alc.}KOH}\underset{\text{Ethene}}{H_2C=CH_2}\ ;\quad CH_3-\underset{X}{CH}-CH_3\xrightarrow[(-HX)]{\text{Alc.}KOH}\underset{\text{Propene}}{CH_3CH=CH_2}$$



$$CH_3-CH_2-\underset{X}{CH}-CH_3\xrightarrow[(-HX)]{\text{Alc.}KOH}\underset{\text{2- Butene (Major)}}{CH_3-CH=CH-CH_3}+\underset{\text{1- Butene (Minor)}}{CH_3-CH_2-CH=CH_2}$$

(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,

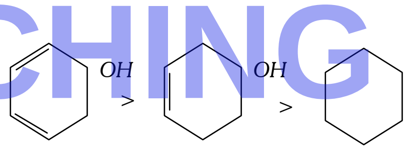
e.g.,

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

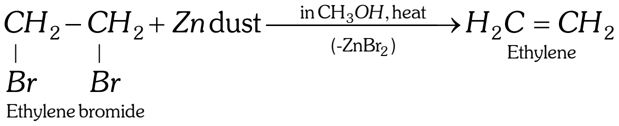
$$CH_3-CH_2-CH_2-OH\xrightarrow[(-H_2O)]{\text{Conc. }H_2SO_4,170°C}CH_3-CH=CH_2$$

Note :✹ 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

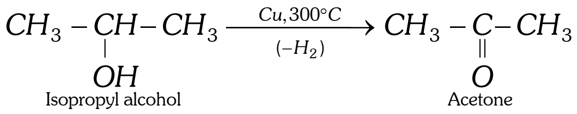


(iii) **Dehalogenation :** It is removal of halogens, *e.g.,*



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

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



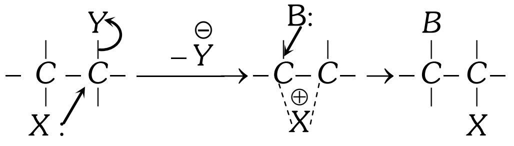
$$\underset{\text{Isopropyl alcohol}}{CH_3-\underset{OH}{CH}-CH_3}\xrightarrow[(-H_2)]{Cu,300°C}\underset{\text{Acetone}}{CH_3-\underset{\parallel \atop O}{C}-CH_3}$$

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.

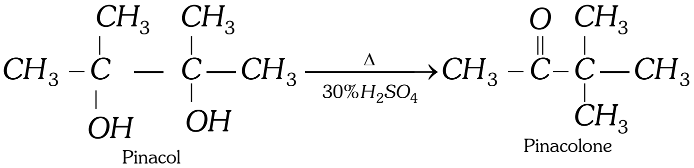


Bridged or
non-classical carbocation

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

Examples:

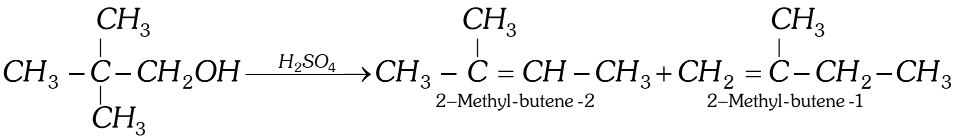
(i) ***Pinacol – pinacolone rearrangement***



$$CH_3-\underset{OH}{\overset{CH_3}{C}}-\underset{OH}{\overset{CH_3}{C}}-CH_3 \xrightarrow[30\%H_2SO_4]{\Delta} CH_3-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$$

Pinacol Pinacolone

(ii) ***Wagner – Meerwein rearrangement***



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2OH \xrightarrow{H_2SO_4} CH_3-\overset{CH_3}{C}=CH-CH_3+CH_2=\overset{CH_3}{C}-CH_2-CH_3$$

2–Methyl-butene -2 2–Methyl-butene -1

Neopentyl alcohol

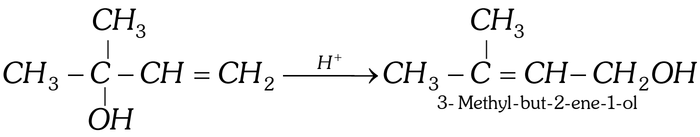
(iii) ***Benzilic acid rearrangement***

Bezilic acid anion

(iv) ***Wolf rearrangement*** **:** $CH_3-COOH+CH_2N_2 \rightarrow CH_3-CH_2-COOH$

Acetic acid diazo methan Propinoic acid

(v) ***Allylic rearrangement***

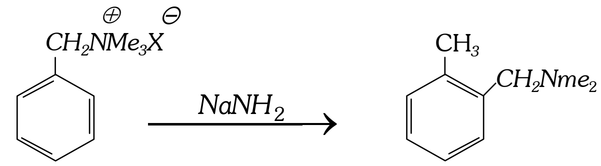


$$CH_3-\underset{OH}{\overset{CH_3}{C}}-CH=CH_2 \xrightarrow{H^+} CH_3-\overset{CH_3}{C}=CH-CH_2OH$$

3- Methyl-but-2-ene-1-ol

3- Methyl-but-1-ene-3-ol

(vi) ***Sommelet – Hauser rearrangement***



Benzyl quaternary ammonium salt O-Substituted benzyl tertiary amine

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

(viii) ***Curtius rearrangement*** **:** $\underset{\text{Acid azide}}{RCON_3} \xrightarrow{\Delta} \underset{\text{Isocyanate}}{RNCO}+N_2$

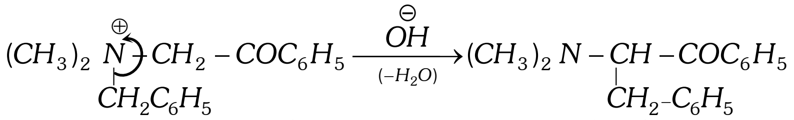
(ix) ***Schimdt rearrangement*** **:** $RCOOH+HN_3 \xrightarrow{H_2SO_4} R-NH_2+CO_2+N_2$

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

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

Examples :

(i) ***Stevens rearrangement* :**

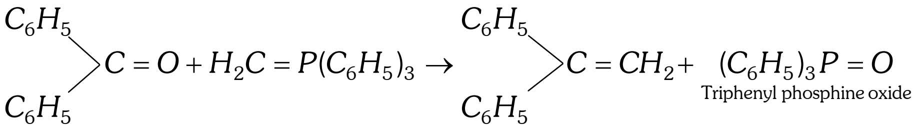


$$(CH_3)_2\overset{\oplus}{N}(CH_2C_6H_5)-CH_2-COC_6H_5\xrightarrow[(-H_2O)]{\overset{\ominus}{O}H}(CH_3)_2N-CH(CH_2-C_6H_5)-COC_6H_5$$

Keto-quaternary ammonium salt

Amino keto

(ii) ***Witting rearrangement* :**

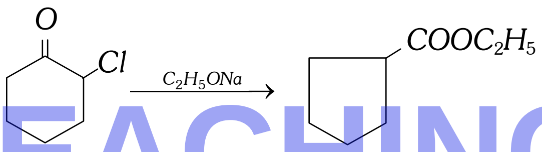


$$(C_6H_5)_2C=O+H_2C=P(C_6H_5)_3\to(C_6H_5)_2C=CH_2+(C_6H_5)_3P=O$$

1,1–Diphenyl ethylene

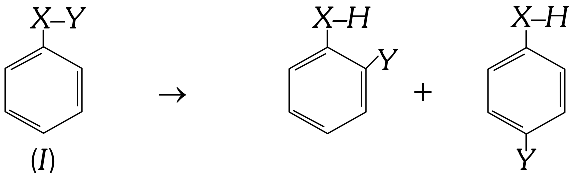
Triphenyl phosphine oxide

(iii) ***Favorskii rearrangement* :** $CH_3-CO-CH_2-Cl+\overset{\ominus}{O}C_2H_5\to CH_3-CH_2-COO-C_2H_5+\overset{\ominus}{Cl}$



(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.

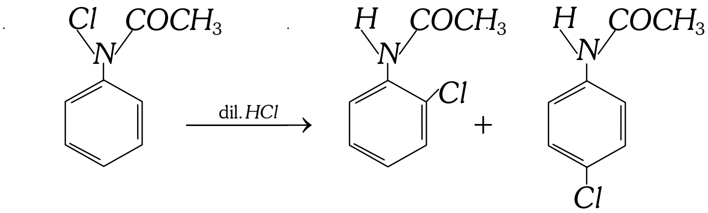
(4) **Aromatic rearrangement :** Those rearrangement reactions in which the migrating group moves to aromatic nucleus. Aromatic compounds of the type (*I*) undergo rearrangements in the manner mentioned below,



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

Examples :

(i) ***Orton rearrangement***

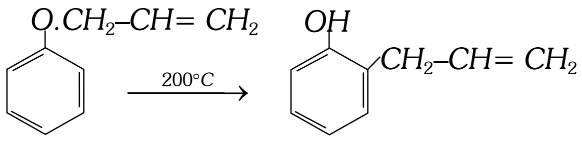


N- Chloroacetanilide

o- Chloroacetanilide

p- Chloroacetanilide

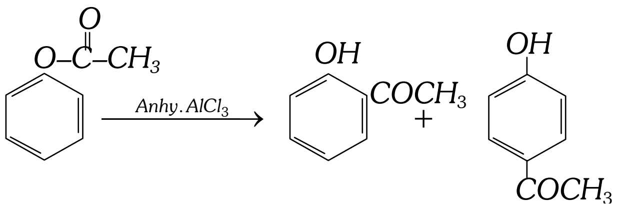
(ii) ***Claisen rearrangement***



Phenyl allyl ether

o- Allyl phenol

(iii) ***Fries rearrangement***



Phenylacetate (Ester) *o*- and *p*- hydoxy acetophenone

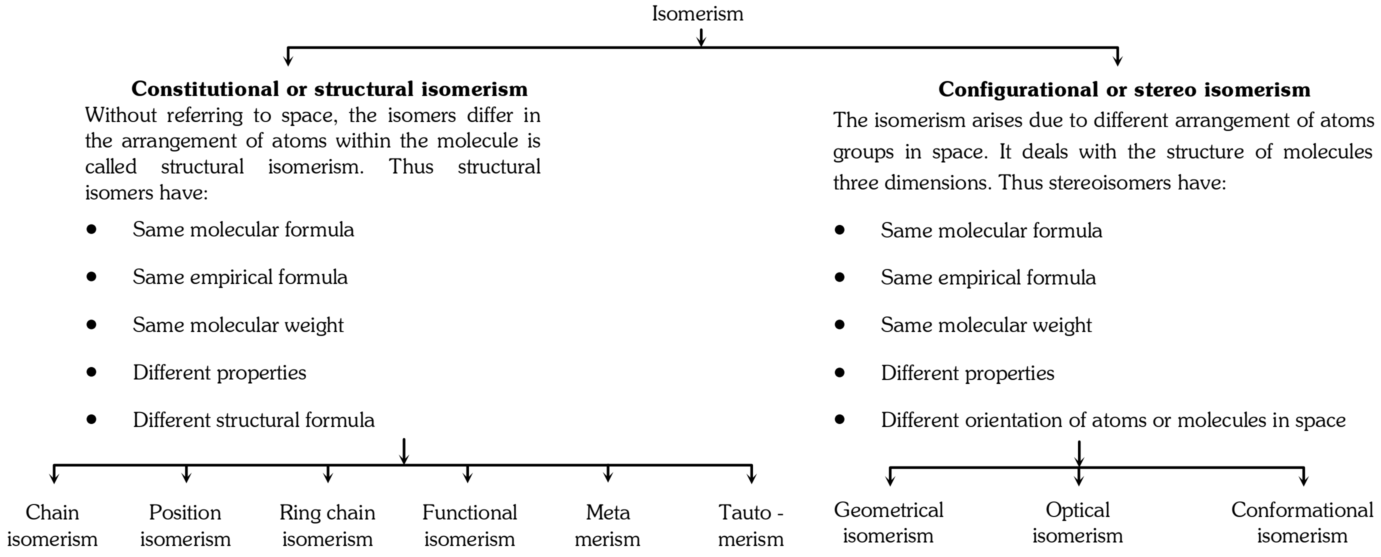
Isomerism.

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

For example,

Ethyl alcohol (C_2H_6O)	***Dimethyl ether (C_2H_6O)***
$CH_3 - CH_2 - OH$ $\Downarrow$	$CH_3 - O - CH_3$ $\Downarrow$
It is liquid.	**It is a gas.**
Its boiling point is 78°C	**Its boiling point is - 24°C.**
It reacts vigorously with sodium and evolves hydrogen.	**It does not react with sodium.**
It reacts with HI and forms ethyl iodide, C_2H_5I .	**It reacts with HI and forms methyl iodide,** CH_3I .

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



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:

- Same molecular formula
- Same empirical formula
- Same molecular weight
- Different properties
- Different structural formula

Chain isomerism, Position isomerism, Ring chain isomerism, Functional isomerism, Meta merism, Tauto - merism

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:

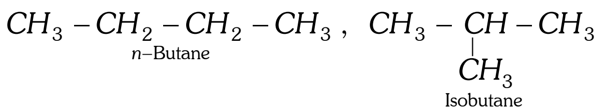
- Same molecular formula
- Same empirical formula
- Same molecular weight
- Different properties
- Different orientation of atoms or molecules in space

Geometrical isomerism, Optical isomerism, Conformational isomerism

Constitutional or structural isomerism.

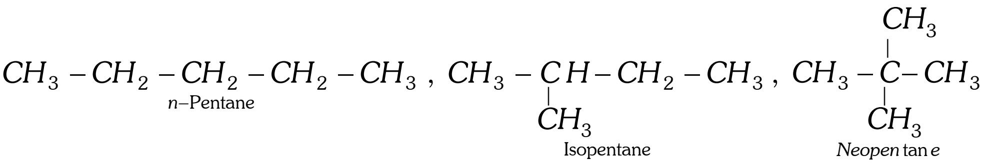
(1) **Chain, nuclear or skeleton isomerism :** This type of isomerism is arises due to the difference in the nature of the carbon chain (*i.e.*, straight or branched) which forms the nucleus of the molecule.

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



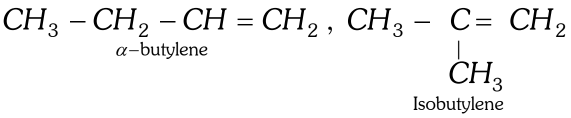
$CH_3-CH_2-CH_2-CH_3$ (*n*–Butane), $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$ (Isobutane)

(ii) **C_5H_{12} :** (Three)



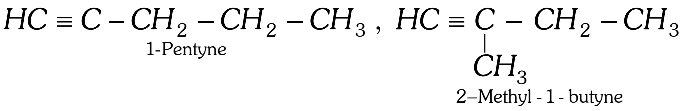
$CH_3-CH_2-CH_2-CH_2-CH_3$ (*n*–Pentane), $CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}H-CH_2-CH_3$ (Isopentane), $CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_3$ (*Neopentane*)

(iii) **C_4H_8 :**



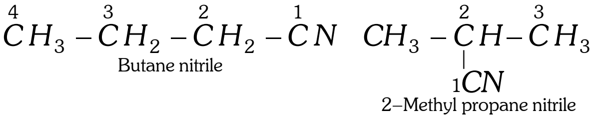
$CH_3-CH_2-CH=CH_2$ (α–butylene), $CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2$ (Isobutylene)

(iv) **C_5H_8 :**



$HC\equiv C-CH_2-CH_2-CH_3$ (1-Pentyne), $HC\equiv\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_2-CH_3$ (2–Methyl - 1 - butyne)

(v) **C_4H_7N :**



$\overset{4}{C}H_3-\overset{3}{C}H_2-\overset{2}{C}H_2-\overset{1}{C}N$ (Butane nitrile), $CH_3-\underset{\displaystyle {}_1CN}{\underset{|}{\overset{2}{C}}}H-\overset{3}{C}H_3$ (2–Methyl propane nitrile)

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

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

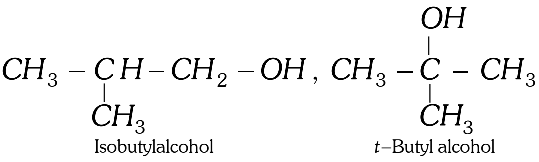
✸ The isomers showing chain isomerism belong to the same homologous series, *i.e.*, functional group, class of the compound (Cyclic or open) remains unchanged.

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

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

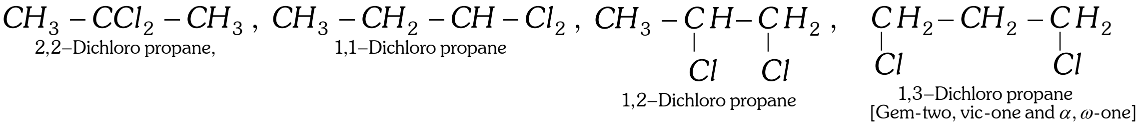
Examples :

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



$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}H-CH_2-OH$ (Isobutylalcohol), $CH_3-\overset{\displaystyle OH}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_3$ (*t*–Butyl alcohol)

(ii) **$C_3H_6Cl_2$:**

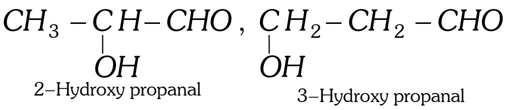


$CH_3-CCl_2-CH_3$ (2,2–Dichloro propane,), $CH_3-CH_2-CH-Cl_2$ (1,1–Dichloro propane), $CH_3-\underset{\displaystyle Cl}{\underset{|}{C}}H-\underset{\displaystyle Cl}{\underset{|}{C}}H_2$ (1,2–Dichloro propane), $\underset{\displaystyle Cl}{\underset{|}{C}}H_2-CH_2-\underset{\displaystyle Cl}{\underset{|}{C}}H_2$ (1,3–Dichloro propane [Gem-two, vic-one and α,ω-one])

(iii) **C_4H_8 :** $CH_3-CH_2-CH=CH_2$ (1–Butene), $CH_3-CH=CH-CH_3$ (2–Butene)

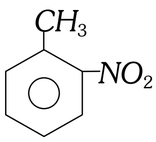
(iv) **C_4H_6 :** $CH_3-CH_2-C\equiv CH$ (1–Butyne), $CH_3-C\equiv C-CH_3$ (2–Butyne), $CH_2=C=CH-CH_3$ (1,2–Butadiene), $CH_2=CH-CH=CH_2$ (1,3–Butadiene)

(v) **$C_3H_6O_2$:**

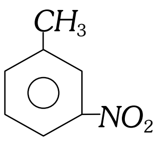


$CH_3-\underset{\displaystyle OH}{\underset{|}{C}}H-CHO$ (2–Hydroxy propanal), $\underset{\displaystyle OH}{\underset{|}{C}}H_2-CH_2-CHO$ (3–Hydroxy propanal)

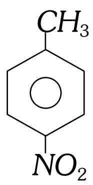
(vi) **$C_7H_7NO_2$ *(Three aromatic)* :**



o - Nitrotoluene

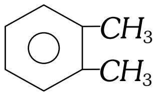


m - Nitrotoluene

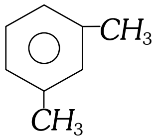


p - Nitrotoluene

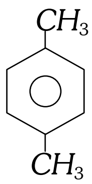
(vii) **C_8H_{10} *(Three aromatic)* :**



o - Xylene

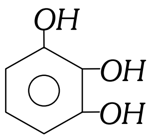


m - Xylene

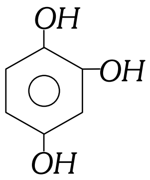


p - Xylene

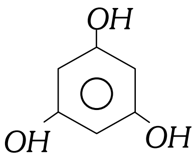
(viii) **$C_6H_3(OH)_3$ *(Three aromatic)* :**



Paragallol

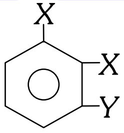


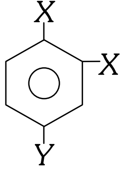
1,2,4 - Trihydroxybenzene

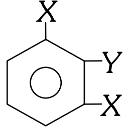


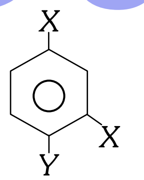
Phloroglucinol

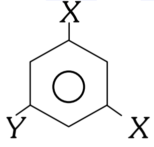
(ix) **$C_6H_3X_2Y$ *(Six aromatic)* :**

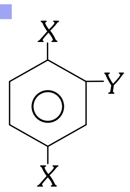




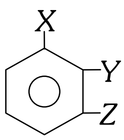


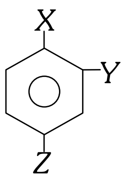


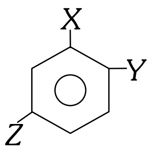


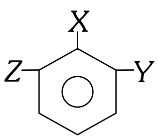


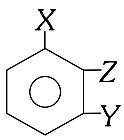
(x) **C_6H_3XYZ *(Ten aromatic)* :**

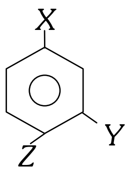


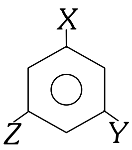


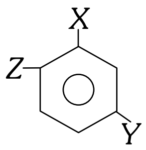


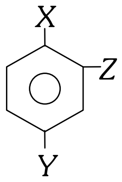


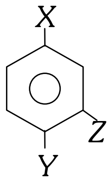




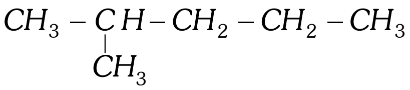






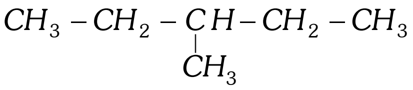


(xi) **C_6H_{14} :**



$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}H-CH_2-CH_2-CH_3$

2–Methylpentane

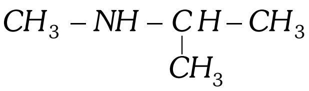


$CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}H-CH_2-CH_3$

3–Methylpentane

(xii) **$C_4H_{11}N$:** $CH_3-NH-CH_2-CH_2-CH_3$

N–Methyl-1-propaneamine

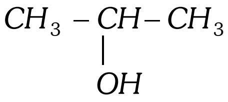


$CH_3-NH-\underset{\displaystyle CH_3}{\underset{|}{C}}H-CH_3$

N–Methyl-2-propaneamine

Note : ✹ 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 :

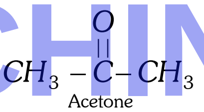
(i) ***Alcohols and ethers ($C_n H_{2n+2}O$)***

C_2H_6O : $\underset{\text{Ethyle alcohol}}{CH_3-CH_2-OH}$; $\underset{\text{Dimethyl ether}}{H_3C-O-CH_3}$

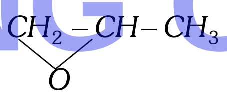
C_3H_8O : $\underset{n-\text{propyl alcohol}}{CH_3-CH_2-CH_2-OH}$; $\underset{\text{Ethyl methyl ether}}{C_2H_5-O-CH_3}$

$C_4H_{10}O$: $\underset{n-\text{Butyl alcohol}}{CH_3-CH_2-CH_2-CH_2-OH}$; $\underset{\text{Diethyl ether}}{C_2H_5-O-C_2H_5}$

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

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

Acetone

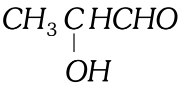
; 

1,2–Epoxy propane

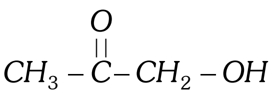
; $\underset{\text{Allyl alcohol}}{CH_2=CH-CH_2OH}$

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

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

$C_3H_6O_2$: $\underset{\text{Propionic acid}}{CH_3-CH_2-COOH}$; $\underset{\text{Methyl acetate}}{CH_3COOCH_3}$;  $CH_3\underset{|\atop OH}{C}HCHO$

2–Hydroxy propanal

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

1–Hydroxy propan-2-one

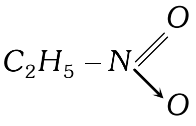
(iv) ***Alkynes and alkadienes ($C_n H_{2n-2}$)***

C_4H_6 : $\underset{1-\text{Butyne}}{CH_3-CH_2-C\equiv CH}$; $\underset{1,3-\text{Butadiene}}{H_2C=CH-CH=CH_2}$; $\underset{2-\text{Butyne}}{CH_3-C\equiv C-CH_3}$; $\underset{1,2-\text{Butadiene}}{H_2C=C=CH-CH_3}$

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

C_2H_3N : $\underset{\text{Methyl cyanide}}{CH_3CN}$; $\underset{\text{Methyle isocyanide}}{CH_3NC}$

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

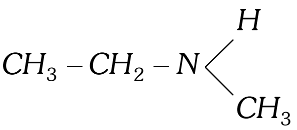
$C_2H_5NO_2$: 

Nitro ethane

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

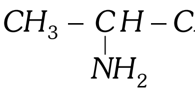
(vii) ***Amines*** (Primary, secondary and tertiary)

C_3H_9N : $CH_3-CH_2-CH_2-NH_2$;
Propan-1-amine



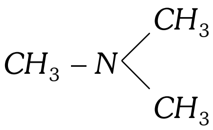
$CH_3-CH_2-N(H)(CH_3)$

N–Methyl ethanamine



$CH_3-\underset{\displaystyle NH_2}{\underset{|}{CH}}-CH_3$;

Propan-2-amine

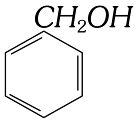


$CH_3-N(CH_3)(CH_3)$

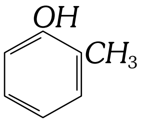
N,N–*D*imethyl methanamine

(viii) ***Alcohols and phenols***

C_7H_8O ;



Benzyl alcohol

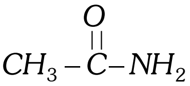


o-Cresol

(ix) ***Oximes and amides***

C_2H_5NO : $CH_3-CH=NOH$
Acetaldoxime

;



$CH_3-\overset{\displaystyle O}{\overset{||}{C}}-NH_2$

Acetamide

(x) ***Thio alcohols and thio ethers***

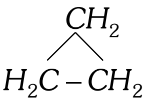
C_2H_6S : C_2H_5SH ; CH_3-S-CH_3

Ethyl thioalcohol ; Dimethyl thioether

(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.

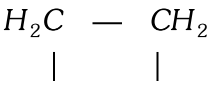
Examples :

(i) **C_3H_6 :** $CH_3-CH=CH_2$;
Propene



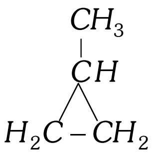
Cyclopropane

(ii) **C_4H_8 :** $CH_3-CH_2-CH=CH_2$;
1–Butene



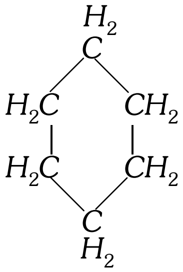
Cyclobutane

;



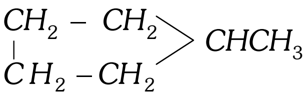
Methyl cyclopropane

(iii) **C_6H_{12} :**



Cyclohexane

;



Methyle cyclopentane

; $CH_3CH_2CH_2CH_2CH=CH_2$
1–Hexene

Note : ✹ Ring – chain isomers are always functional isomers.

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

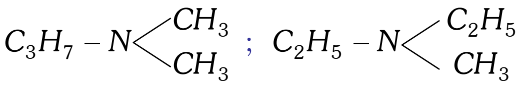
Examples :

(i) **$C_4H_{10}O$:** $\underset{\text{Diethyl ether}}{C_2H_5-O-CH_3}$; $\underset{\text{Methyl propyl ethers}}{C_3H_7-O-CH_3}$

(ii) **$C_5H_{10}O$:** $\underset{\text{Diethyl ketone}}{C_2H_5-CO-C_2H_5}$; $\underset{\text{Methyl propyl ketone}}{C_3H_7-CO-CH_3}$

(iii) **$C_4H_{11}N$:** $\underset{\text{Diethyl amine}}{C_2H_5-NH-C_2H_5}$; $\underset{\text{Methyl propyl amine}}{C_3H_7-NH-CH_3}$

(iv) **$C_5H_{13}N$:**



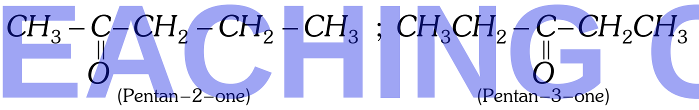
$C_3H_7-N\begin{matrix}\diagup CH_3\\ \diagdown CH_3\end{matrix}$; $C_2H_5-N\begin{matrix}\diagup C_2H_5\\ \diagdown CH_3\end{matrix}$

Dimethyl propyl amine Diethyl methyl amine

(v) **$C_6H_{15}N$:** $\underset{\text{Dipropyl amine}}{C_3H_7-NH-C_3H_7}$; $\underset{\text{Ethyl butyl amine}}{C_2H_5-NH-C_4H_9}$

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

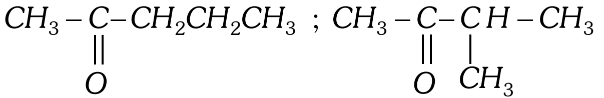
(a)



$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-CH_3$; $CH_3CH_2-\underset{\underset{O}{\|}}{C}-CH_2CH_3$ are metamers and not position isomers.

(Pentan–2–one) (Pentan–3–one)

(b)



$CH_3-\underset{\underset{O}{\|}}{C}-CH_2CH_2CH_3$; $CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-CH_3$ are metamers and not chain isomers.

(Pentan–2–one) (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.

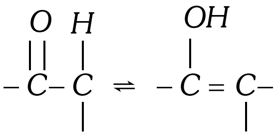
(ii) It is caused by the wandering of hydrogen atom between two polyvalent atoms. It is also known as **Desmotropism** (Desmos = bond and tropos = turn). If the hydrogen atom oscillates between two polyvalent atoms linked together, the system is a **dyad** and if the hydrogen atom travels from first to third 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. $H-C\equiv N \rightleftharpoons C\overset{\leftarrow}{=}N-H$

(b) *Triad system*

Keto-enol system : Polyvalent atoms are oxygen and two carbon atoms.

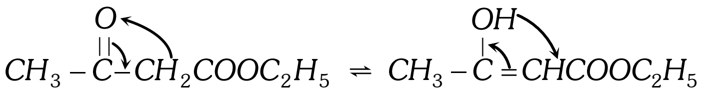
Examples :



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

(Keto) (Enol)

Acetoacetic ester (Ethyl acetoacetate) :

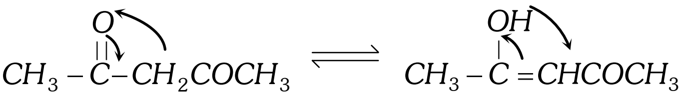


$$CH_3-\overset{\overset{O}{||}}{C}-CH_2COOC_2H_5 \rightleftharpoons CH_3-\overset{\overset{OH}{|}}{C}=CHCOOC_2H_5$$

Keto form Enol form

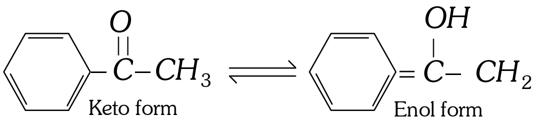
Acetoacetic ester gives certain reactions showing the presence of keto group (Reactions with HCN, H_2NOH, $H_2NNHC_6H_5$, *etc.*) and certain reactions showing the presence of enolic group (Reactions with $Na, CH_3COCl, NH_3, PCl_5, Br_2$ water and colour with neutral $FeCl_3$, *etc.*).

Acetyl acetone :

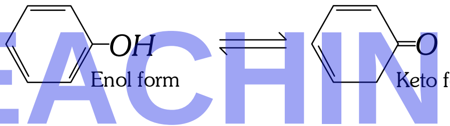


$$CH_3-\overset{\overset{O}{||}}{C}-CH_2COCH_3 \rightleftharpoons CH_3-\overset{\overset{OH}{|}}{C}=CHCOCH_3$$

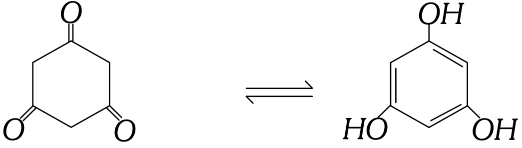
Keto form Enol form



Keto form Enol form



Enol form Keto form

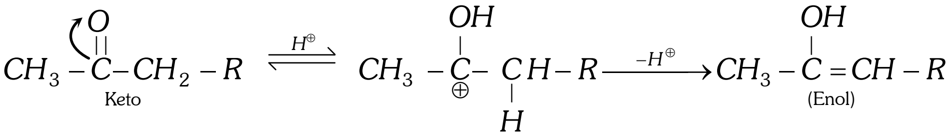


Keto form Enol form

Enolisation is in order

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

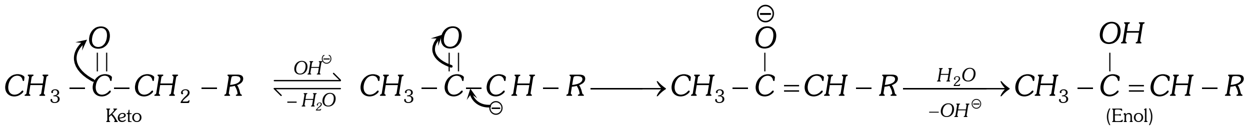
Acid catalysed conversion



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

Keto (Enol)

Base catalysed conversion



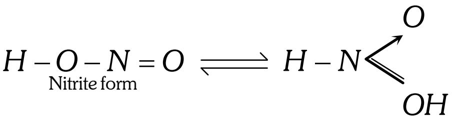
$$CH_3-\overset{\overset{O}{||}}{C}-CH_2-R \underset{-H_2O}{\overset{OH^{\ominus}}{\rightleftharpoons}} CH_3-\overset{\overset{O}{||}}{C}-\underset{\ominus}{C}H-R \longrightarrow CH_3-\overset{\overset{\overset{\ominus}{O}}{|}}{C}=CH-R \underset{-OH^{\ominus}}{\xrightarrow{H_2O}} CH_3-\overset{\overset{OH}{|}}{C}=CH-R$$

Keto (Enol)

Triad system containing nitrogen

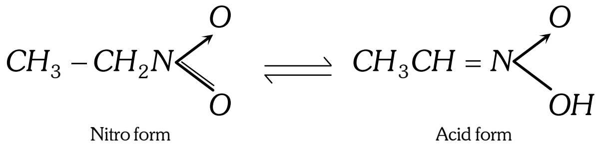
Examples :

Nitrous acid :



$$H-O-N=O \rightleftharpoons H-N\begin{array}{l}\nearrow O\\ \searrow OH\end{array}$$

Nitrite form Nitro form

Nitroethane : 
$$CH_3-CH_2N\begin{matrix}O\\O\end{matrix} \rightleftharpoons CH_3CH=N\begin{matrix}O\\OH\end{matrix}$$

(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.

Note : ✹ Keto=enol tautomerism is exhibited only by such aldehydes and ketones which contain at least one α -hydrogen. For example $CH_3CHO, CH_3CH_2CHO, CH_3COCH_2COCH_3$.

✹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 carry $\alpha-H$.

Number of structural isomers

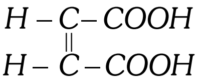
Molecular formula	***Number of isomers***
Alkanes	
C_4H_{10}	**Two**
C_5H_{12}	**Three**
C_6H_{14}	**Five**
C_7H_{16}	**Nine**
C_8H_{18}	**Eighteen**
C_9H_{20}	**Thirty five**
$C_{10}H_{22}$	**Seventy five**
Alkenes and cycloalkanes	
C_3H_6	**Two (One alkene + one cycloalkane)**
C_4H_8	**Six (Four alkene + 2 - cycloalkane)**
C_5H_{10}	**Nine (Five alkenes + 4 – cycloalkanes)**
Alkynes	
C_3H_4	**Two**

C_4H_6	**Six**
Monohalides	
C_3H_7X	**Two**
C_4H_9X	**Four**
$C_5H_{11}X$	**Eight**
Dihalides	
$C_2H_4X_2$	**Two**
$C_3H_6X_2$	**Four**
$C_4H_8X_2$	**Nine**
$C_5H_{10}X_2$	**Twenty one**
Alcohols and ethers	
C_2H_6O	**Two (One alcohol and one ether)**
C_3H_8O	**Three (Tow alcohols and one ether)**
$C_4H_{10}O$	**Seven (Four alcohols and three ethers)**
$C_5H_{12}O$	**Fourteen (Eight alcohols and six ethers)**
Aldehydes and ketones	
C_3H_6O	**Two (One aldehyde and one ketone)**
C_4H_8O	**Three (Two aldehydes and one ketone)**
$C_5H_{10}O$	**Three (Four aldehydes and three ketone)**
Monocarboxylic acids and esters	
$C_2H_4O_2$	**Two (One acid and one ester)**
$C_3H_6O_2$	**Three (One acid and two esters)**
$C_4H_8O_2$	**Six (Two acids and four esters)**
$C_5H_{10}O_2$	**Thirteen (Four acids and nine esters)**
Aliphatic amines	
C_2H_7N	**Two (One 1°-amine and one 2°-amine)**
C_3H_9N	**Four (Two 1°-amines, one 2°-amine and one 3°-amine)**
$C_4H_{11}N$	**Eight (Four 1°-amines, three 2°-amines and one 3°-amines)**
Aromatic compounds	
C_8H_{10}	**Four**
C_9H_{12}	**Nine**
C_7H_8O	**Five**

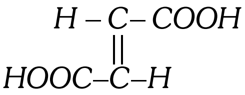
Geometrical or cis-trans isomerism.

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

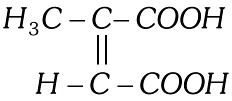
Examples :


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

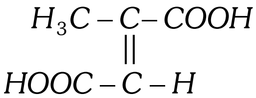
Maleic acid *(cis)*


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

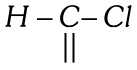
Fumaric acid *(trans)*


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

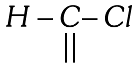
Citraconic acid (*cis*-isomer)


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

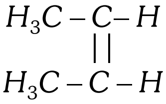
Mesaconic acid (*trnas*–isomer)


$\begin{array}{c} H-C-Cl \\ \| \\ H-C-Cl \end{array}$

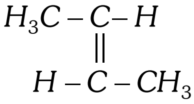
cis-1,2-Dichloroethylene


$\begin{array}{c} H-C-Cl \\ \| \\ Cl-C-H \end{array}$

trans-1,2-Dichloroethylene


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

cis-Butene-2

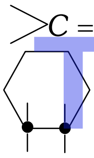

$\begin{array}{c} H_3C-C-H \\ \| \\ H-C-CH_3 \end{array}$

trans-Butene-2

(1) **Conditions for geometrical isomerism :** Compound will show geometrical iosomerism 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.

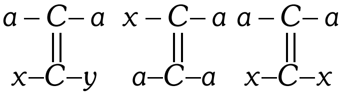
(b)  frozen rotation about carbon, carbon single bond in cycloalkanes.

(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.

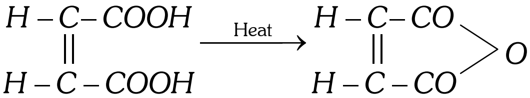
Note : ✸ The compounds of the following type will not show geometrical isomerism.


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

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

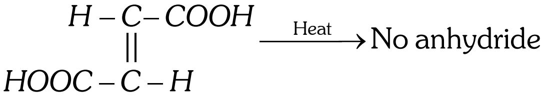
(2) **Distinction between *cis*- and *trans*- isomers**

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


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

Maleic acid(*cis*) Maleic anhydride

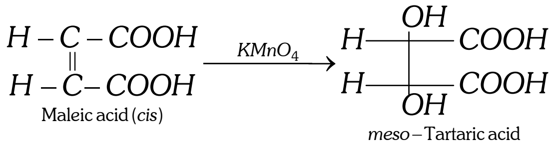
Note : ✸ Note that the two reacting groups (-*COOH)* are near to each other.


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

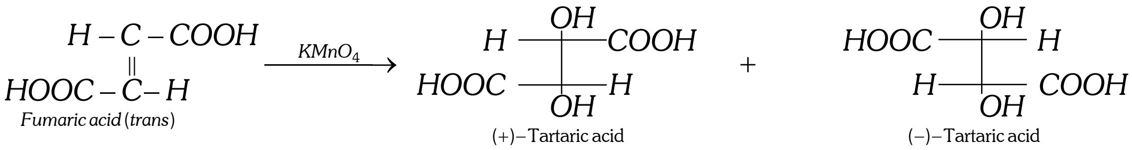
Fumaric acid (trans)

Note : ✹ 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,

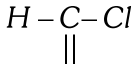


Maleic acid (*cis*) meso – Tartaric acid



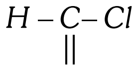
Fumaric acid (*trans*) (+)–Tartaric acid (–)–Tartaric acid

(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.



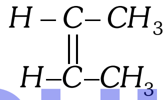
$$\begin{array}{c} H-C-Cl \\ \| \\ H-C-Cl \end{array}$$

cis–Dichloroethylene (μ=1.9*D*)



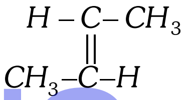
$$\begin{array}{c} H-C-Cl \\ \| \\ Cl-C-H \end{array}$$

trans–Dichloroethylene (μ=0.0*D*)



$$\begin{array}{c} H-C-CH_3 \\ \| \\ H-C-CH_3 \end{array}$$

cis–Butane–2



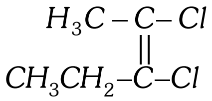
$$\begin{array}{c} H-C-CH_3 \\ \| \\ CH_3-C-H \end{array}$$

trans–Butane–2

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

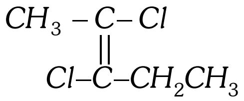
In case of unsymmetrical alkenes, the *cis*-isomer has higher dipole moment than the corresponding *trans*-isomer.

For Example,



$$\begin{array}{c} H_3C-C-Cl \\ \| \\ CH_3CH_2-C-Cl \end{array}$$

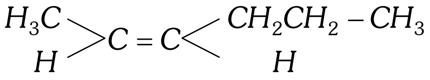
cis–2,3–Dichloropentene–2(High dipole moment)



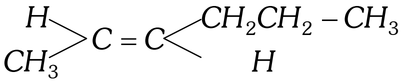
$$\begin{array}{c} CH_3-C-Cl \\ \| \\ Cl-C-CH_2CH_3 \end{array}$$

trans–2,3–Dichloropentene–2(*Less dipole moment*)

Similar is the case with hexene-2.



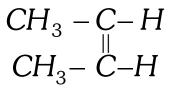
cis–Hexene–2(more polar)



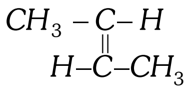
trans–Hexene–2(Less polar)

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

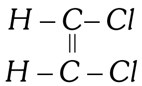
(iv) ***By studying other physical properties*****:** (*a*) The *cis*-isomer of a compound has higher boiling point due to higher polarity, higher density and higher refractive index than the corresponding *trans*-isomer (*Auwers-skita rule*).



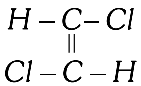
$$\begin{array}{c} CH_3-C-H \\ \| \\ CH_3-C-H \end{array}$$



$$\begin{array}{c} CH_3-C-H \\ \| \\ H-C-CH_3 \end{array}$$



$$\begin{array}{c} H-C-Cl \\ \| \\ H-C-Cl \end{array}$$



$$\begin{array}{c} H-C-Cl \\ \| \\ Cl-C-H \end{array}$$

	cis–2–Butene	trans–2Butene	cis–1,2–Dichloroethene	trans–1,2–Dichloroethene
b.p	4°C	1°C	60°C	48°C
m.p	–139°C	–106°C	–80°C	–50°C

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

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

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

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

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