ORGANIC CHEMISTRY

Dehydration: Alcohols undergo dehydration (removal of a molecule of water) to form alkenes on treating with a protic acid e.g., concentrated H$_2$SO$_4$ or H$_3$PO$_4$, or catalysts such as anhydrous zinc chloride or alumina. Ethanol undergoes dehydration by heating it with concentrated H$_2$SO$_4$ at 443 K.

\[
\text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{H}_2\text{SO}_4, 443 \text{ K}} \text{CH}_2 = \text{CH}_2 + \text{H}_2\text{O}
\]

The mechanism of dehydration of ethanol involves the following steps:

**Mechanism**

**Step 1:** Formation of protonated alcohol.

\[
\begin{array}{c}
\text{H} - \text{C} - \text{C} - \underset{\text{O} - \text{H}}{\text{O}} - \text{H} + \text{H}^+ \\
\text{Ethanol} \\
\end{array}
\xrightarrow{\text{Fast}}
\begin{array}{c}
\text{H} - \text{C} - \text{C} - \underset{\text{O}^+ - \text{H}}{\text{O}^+} - \text{H} \\
\text{Protonated alcohol} \\
\end{array}
\]

**Step 2:** Formation of carbocation: It is the slowest step and hence, the rate determining step of the reaction.

\[
\begin{array}{c}
\text{H} - \text{C} - \text{C} - \underset{\text{O} - \text{H}}{\text{O} - \text{H}} \\
\text{H} - \text{H} - \text{H} \\
\end{array}
\xrightarrow{\text{Slow}}
\begin{array}{c}
\text{H} - \text{C} - \text{C}^+ - \text{H}_2\text{O} \\
\text{H} - \text{H} \\
\end{array}
\]

**Step 3:** Formation of ethene by elimination of a proton.

\[
\begin{array}{c}
\text{H} - \text{C} - \text{C}^+ \\
\text{H} - \text{H} \\
\end{array}
\xleftrightarrow{\text{Ethene}}
\begin{array}{c}
\text{H} - \text{C} = \text{C} - \text{H} \\
\text{H} - \text{H} \\
\end{array} + \text{H}^+
\]

The acid used in step 1 is released in step 3. To drive the equilibrium to the right, ethene is removed as it is formed.

**Lucas Test distinction of primary, secondary and tertiary alcohols.** In this method, the alcohol is treated with Lucas reagent (a mixture of conc. HCl and anhydrous ZnCl$_2$). The alcohol is converted into alkyl halides. Alcohols are soluble in Lucas reagent while their halides are insoluble. The formation of alkyl halide is indicated by the appearance of turbidity in the reaction mixture. As the reactivity of alcohols with halogen acids is in the order tertiary > secondary > primary, the time required for the appearance of turbidity will be different for primary, secondary and tertiary alcohols which helps to distinguish them from one another.

In the case of tertiary alcohols, turbidity is produced immediately at room temperature. Secondary alcohols give turbidity in few minutes while primary alcohols do not produce appreciable turbidity at room temperature, but give turbidity only on heating.

Ethylene glycol reacts with hydrogen chloride gas as follows:

\[
\text{CH}_2\text{OH} \xrightarrow{\text{HCl / 433 K}} \text{CH}_2\text{Cl} \xrightarrow{\text{HCl / 473 K}} \text{CH}_2\text{Cl}
\]

Dilute nitric acid or alkaline KMnO$_4$ oxidizes ethylene glycol to the
following oxidation products.

**Glycerol: Action with oxalic acid:**
Depending upon the temperature, glycerol is converted to allyl alcohol or formic acid. At 383 K glycerol mono formate is formed.

\[
\begin{align*}
\text{CH}_2\text{OH} & \quad \text{HO} - \text{C} = \text{O} \\
\text{CHOH} + \text{CO} - \text{OH} & \xrightarrow{383\text{K}} \text{CH}_2\text{OH} - \text{C} = \text{O} \\
\text{CH}_2\text{OH} & \\
\end{align*}
\]

This on hydrolysis gives formic acid.

\[
\begin{align*}
\text{CH}_2\text{OCOH} & \quad \text{CH}_2\text{OH} \\
\text{CHOH} & \quad \text{CHOH} + \text{HCOOH} \\
\text{CH}_2\text{OH} & \quad \text{CH}_2\text{OH} \\
\end{align*}
\]

In this reaction glycerol acts as a catalyst.

At 533 K, glyceryl dioxalate is formed which eliminates two molecules of carbondioxide forming **allyl alcohol**.
The elimination of two molecules of carbon dioxide takes place by the cyclic reorganization of bonds in the diester. Strong oxidizing agents like warm acidified permanganate convert glycerol to oxalic acid and carbondioxide.

Industrially phenol is prepared from cumene. Cumene is prepared from benzene and propylene in presence of Lewis acid like anhydrous aluminium chloride.

\[
\begin{align*}
\text{CH}_2\text{OH} & \quad \text{HO-CO} \\
\text{CHOH} & \quad \text{HO-CO} \\
\text{CH}_2\text{OH} & \quad \text{HO-CO}
\end{align*}
\]

\[
\text{CH}_2\text{O} \quad \text{CO} \quad \text{CH}_2
\]

\[
\text{unstable} \quad \text{CH}_2\text{OH} \quad \text{CH}_2\text{OH} \quad \text{allyl alcohol}
\]

This is oxidised to hydro peroxide by oxygen of the air.

\[
\begin{align*}
\text{CH(CH}_3\text{)}_2 & \\
\text{O}_2 & \quad \text{O}_2
\end{align*}
\]

This is cleaved to phenol and acetone by aqueous hydrochloric acid.
Coupling with diazonium chloride:

Phenol couples with benzene diazonium chloride in alkaline medium to form \( p \)-hydroxy azobenzene. Diazonium ion \( \text{C}_8\text{H}_5\text{N} = \text{N}^+ \) is the electrophile in this reaction.

\[
\begin{array}{c}
\text{C}_8\text{H}_5\text{N} = \text{N}^+ \text{Cl}^- + \text{H}_2\text{O} \rightarrow \text{C}_8\text{H}_5\text{N} = \text{N}^+ \text{C}_8\text{H}_5\text{OH} \quad \text{(Benzene diazonium chloride)} \\
\text{OH}^{-} \quad \text{273 K} \\
\end{array}
\]

\( \text{(p-hydroxy azobenzene - a red orange dye)} \)

This is also called dye test, which is characteristic of phenol.

**Kolbe Schmidt or Kolbe's reaction**

When sodium phenoxide is heated with carbon dioxide at 400 K under pressure, sodium salicylate is formed. This is decomposed by dilute hydrochloric acid, when salicylic acid is formed. \( \text{CO}_2 \) is the electrophile in this reaction.

\[
\begin{array}{c}
\text{C}_6\text{H}_4\text{ONa} \quad \text{CO}_2 \quad \text{HCl} \\
\text{400 K} \quad \text{atm} \quad \text{4 - 7 atm} \\
\text{OH} \quad \text{COONa} \quad + \text{NaCl} \\
\text{COOH} \\
\end{array}
\]
**Riemer-Tiemann reaction**

This reaction is an example of formylation reaction. When phenol is refluxed with chloroform and sodium hydroxide, a formyl group –CHO is introduced at the ortho or para position to –OH group.

\[
\begin{align*}
\text{OH} & \quad \text{CHCl}_3 \quad \text{NaOH} \\
\text{OH} & \quad \text{CHO} + \quad \text{OH} \\
\text{Ortho} & \quad \text{Para} \\
\text{(Hydroxy benzaldehyde)} & \\
\end{align*}
\]

Similarly with CCl₄ and NaOH, hydroxy benzoic acid is formed.

\[
\begin{align*}
\text{OH} & \quad \text{CCl}_4 \quad \text{NaOH} \\
\text{OH} & \quad \text{COOH} + \quad \text{HOOC} \\
\text{Ortho} & \quad \text{Para} \\
\text{(Hydroxy benzoic acid)} & \\
\end{align*}
\]

**Tests for Phenols**

i) They dissolve in strong alkali like NaOH. A compound which is insoluble in water but soluble in aqueous NaOH may be a phenol.

ii) Decolourisation of bromine water with the formation of a dull yellow precipitate indicates a phenol.

iii) Phenols give typical colours like purple, violet, green etc. with neutral FeCl₃ solution.

iv) **Libermann’s nitroso reaction.**

On warming with concentrated sulphuric acid and sodium nitrite, phenol gives a brown or red colour which soon changes into blue green. The colour changes to red when diluted with water and deep blue, when treated with sodium hydroxide.

Identify the product A and B.
Reaction of ether oxygen : Formation of peroxide :

Ether oxygen is capable of forming a coordinate covalent bond with electron deficient species. Thus it forms peroxide by the action of air or oxygen.

\[
\begin{align*}
R - O - R + O &\rightarrow R - O - R \quad \text{or} \quad R - O - R \\
\downarrow &\quad \downarrow \\
&\quad O
\end{align*}
\]

Ether forms Diethyl peroxide

\[
C_2H_5 - O - C_2H_5 \xrightarrow{(O)} (C_2H_5)_2O_2 \\
\quad \text{diethyl peroxide}
\]

These peroxides are unstable and decomposes violently with explosion on heating. Hence ether should not be evaporated to dryness.

Industrial Preparation of Ethanol

Ethanol is prepared commercially by hydration of ethene (see preparation of alcohols). Mainly it is produced by fermentation of carbohydrates. E.g: starch. Fermentation is the gradual decomposition of complex organic compounds into simple compounds in the presence of biological catalysts called enzymes.

Fermentation of carbohydrate gives ethanol.

For example a dilute solution of cane sugar when mixed with yeast and the temperature maintained at 30-35°C, fermentation occurs in a few days. The enzyme invertase from yeast, catalyses the hydrolysis of
sugar (sucrose) into glucose and fructose. Glucose and fructose are decomposed into alcohol in presence of the enzyme zymase, present in yeast. A dilute solution of alcohol (8 to 10%) called ‘wash’ is obtained.

**Use of acid chloride:**

1. **Rosenmund Reduction.** Acid chlorides are reduced to aldehydes by hydrogen in presence of palladium suspended in barium sulphate as catalyst.

   \[ R - C = O + \text{H-H} \xrightarrow{\text{Pd, BaSO}_4} R - C = O + \text{HCl} \]

   \[ \text{CH}_3 - C = O + \text{H}_2 \xrightarrow{\text{Pd, BaSO}_4} \text{CH}_3 - C = O + \text{HCl} \]

   acetyl chloride

   As formyl chloride is unstable at room temperature, formaldehyde cannot be prepared by this method. This is called **Rosenmund’s reduction.** BaSO₄ is used as a catalytic poison, to stop the reduction at the stage of aldehyde. Otherwise, the aldehyde formed will be further reduced to primary alcohol.

2. **Using Dialkyl cadmium.** Ketones can be prepared by the action of organometallic reagent on acid chlorides. (e.g.,) **Dialkyl cadmium** is the reagent of choice.

   \[ R - C = O \xrightarrow{\text{Cd, Cl, R'}} 2R - C = O + \text{CdCl}_2 \]

   Cannizzaro reaction: Aldehydes which do not have an alpha-hydrogen atom, undergo self oxidation and reduction (disproportionation) reaction on treatment with concentrated alkali. In this reaction, one molecule of the aldehyde is reduced to alcohol while another is oxidised to carboxylic acid salt.

   \[ \text{HCHO} + \text{HCHO} + \text{KOH} \rightarrow \text{HCOOH} + \text{HCOOK} \]

   Formaldehyde

   Methanol

   Potassium formate

   \[ 2 \text{CHO} + \text{NaOH} \rightarrow \text{CH}_3\text{OH} + \text{COONa} \]

   Benzaldehyde

   Benzyl alcohol

   Sodium benzoate

**Aldol condensation:** Aldehydes and ketones having at least one alpha-hydrogen undergo a reaction in the presence of dilute alkali as catalyst to form β-hydroxy aldehydes (aldol) or β-hydroxyketones (ketol), respectively. This is known as **Aldol reaction.**
The name aldol is derived from the names of the two functional groups, aldehyde and alcohol, present in the products. The aldol and ketol readily lose water to give \( \text{\textit{\textdegree}} \)-unsaturated carbonyl compounds which are aldol condensation products and the reaction is called \textit{Aldol condensation}. Though ketones give ketols (compounds containing a keto and alcohol groups), the general name aldol condensation still applies to the reactions of ketones due to their similarity with aldehydes.

**Cross aldol condensation:** When aldol condensation is carried out between two different aldehydes and / or ketones, it is called cross aldol condensation. If both of them contain \( \text{\textalpha}- \)hydrogen atoms, it gives a mixture of four products. This is illustrated below by aldol reaction of a mixture of ethanal and propanal.

Ketones can also be used as one component in the cross aldol reactions.
Clemmenson Reduction:
Aldehydes and ketones can be reduced to hydrocarbons by zinc amalgam and con.HCl.

\[
\begin{align*}
\text{CH}_3\text{C} = \text{O} + 4 \text{ (H)} & \xrightarrow{\text{Zn/Hg, HCl}} \text{CH}_3\text{CH}_2 + \text{H}_2\text{O} \\
\text{H}_3\text{C} & \quad \text{(Propane)}
\end{align*}
\]

This reaction proceeds by electron addition to carbonyl carbon followed by protonation. **Zinc metal** is the electron source. In the absence of mercury, hydrogen gas will be evolved and the reduction is incomplete. This reduction is called **Clemmenson reduction**.

Wolff-Kishner Reduction
Aldehydes and ketones are reduced to hydrocarbons by heating with hydrazine and sodium ethoxide.

\[
\begin{align*}
\text{CH}_3\text{C} = \text{O} & \xrightarrow{\text{N}_2\text{H}_4, \text{C}_2\text{H}_4\text{ONa}} \text{CH}_3\text{CH}_2 + \text{N}_2 + \text{H}_2\text{O} \\
\text{H} & \quad \text{Hydrazone}
\end{align*}
\]

Hydrazones are formed as intermediates. The base removes the –NH₂ hydrogen atoms as protons generating carbanion. Proton addition to carbanion gives alkanes.

\[
\begin{align*}
\text{CH}_3\text{C} = \text{NNH}_2 \\
\text{H} & \quad \text{Hydrazone}
\end{align*}
\]

This is called **Wolff-Kishner reduction**.

Haloform reaction
The compounds having CH₃CHOH– or CH₃CO– group undergoes haloform reaction. It undergoes halogenation at α-carbon atom.

\[
\text{CH}_3\text{CO–CH}_3 + 3 \text{Cl}_2 \quad \xrightarrow{} \quad \text{CCl}_3 – \text{CO–CH}_3 + 3 \text{HCl}
\]

In the presence of NaOH, chloroform is formed.
### Comparison of Aldehyde and Ketone.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>( \text{CH}_3\text{CHO} )</th>
<th>( \text{CH}_2\text{COCH}_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. With Fehling’s solution.</td>
<td>gives a red precipitate</td>
<td>does not react.</td>
</tr>
<tr>
<td>2. With Tollens reagent.</td>
<td>gives silver mirror.</td>
<td>no silver mirror.</td>
</tr>
<tr>
<td>3. Oxidation</td>
<td>gives acetic acid</td>
<td>gives acetic acid with loss of one carbon atom.</td>
</tr>
<tr>
<td>4. Reduction with NaBH(_4)</td>
<td>ethanol (primary alcohol)</td>
<td>isopropyl alcohol (secondary alcohol)</td>
</tr>
<tr>
<td>5. With NH(_3)</td>
<td>simple addition product is formed.</td>
<td>forms complex ketonic amine.</td>
</tr>
<tr>
<td>6. Iodoform reaction</td>
<td>forms iodoform and formic acid.</td>
<td>forms iodoform and acetic acid.</td>
</tr>
<tr>
<td>7. Polymerisation</td>
<td>forms paraldehyde</td>
<td>forms condensation products.</td>
</tr>
<tr>
<td>8. With Schiff’s reagent.</td>
<td>pink colour appears in cold.</td>
<td>no pink colour in cold.</td>
</tr>
<tr>
<td>9. Warming with NaOH</td>
<td>a brown resinous mass.</td>
<td>no resinous mass.</td>
</tr>
</tbody>
</table>

How will you distinguish between 2-pentanone and 3-pentanone?

**Answers:** Since 2-pentanone contains methyl ketone \((\text{CH}_3 - \text{C} -)\), it undergoes iodoform test with an alkaline solution of iodine and forms yellow precipitate of iodoform. But 3-pentanone does not give this test.

\[
\begin{align*}
\text{CH}_3 - \text{CH} - \text{CH}_2 - \text{C} - \text{CH}_2 + 4 \text{NaOH} + 3 \text{I}_2 & \rightarrow \text{CH}_3 \text{CH}_2 - \text{CH}_2 - \text{C} - \text{ONa} + \text{CH}_3 \text{I} + 3\text{H}_2\text{O} + 3\text{NaI} \\
\text{2-pentanone} & \quad \text{Iodoform (yellow precipitate)}
\end{align*}
\]

How will you synthesise acetone from acetaldehyde?

**Answers:**

\[
\begin{align*}
\text{CH}_3 - \text{C} - \text{H} & \quad \text{CH}_3\text{MgI} \\
\text{acetaldehyde} & \quad \xrightarrow{\text{CH}_3\text{MgI}} \text{CH}_3 - \text{CH} - \text{CH}_3 \\
& \quad \text{K}_2\text{Cr}_2\text{O}_7 \quad \text{H}_2\text{SO}_4 \\
& \quad \xrightarrow{\text{K}_2\text{Cr}_2\text{O}_7 \quad \text{H}_2\text{SO}_4} \text{CH}_3 - \text{C} - \text{CH}_3
\end{align*}
\]

An organic compound, \(\text{C}_2\text{H}_4\text{O}\) gives a red precipitate when warmed with Fehling’s solution. It also undergoes aldol condensation in presence of alkali.
(i) Write IUPAC name of the compound.  
(ii) What is the hybridization of carbon atoms in the compound?  
(iii) Write equation for the reaction.

**Answers:**  
(i) Ethanal  
(ii) $sp^2$ and  
(iii) $\text{CH}_3\text{CHO} + 2\text{Cu}^{2+} + 3\text{OH}^- \rightarrow \text{CH}_3\text{COO}^- + 2\text{Cu}^+ + 2\text{H}_2\text{O}$

**Benzoin Condensation:**  
This is another reaction, which is characteristic of aromatic aldehydes. When benzaldehyde is refluxed with aqueous alcoholic potassium cyanide - $\alpha$-hydroxy ketone called benzoin is formed. Cyanide ion (CN$^-$) is the specific catalyst in this reaction. Benzoin can be considered as dimer of benzaldehyde.

In presence of cyanide ion, one molecule of benzaldehyde behaves as a carbanion. That brings forth nucleophilic attack on the carbonyl group of another molecule of benzaldehyde. This results to Benzoin.

**THE TRIIODOMETHANE (IDOFORM) REACTION WITH ALCOHOLS**

The triiodomethane (iodoform) reaction can be used to identify the presence of a CH$_3$CH(OH) group in alcohols. Iodine solution is added to a small amount of an alcohol, followed by just enough sodium hydroxide solution to remove the colour of the iodine. If nothing happens in the cold, it may be necessary to warm the mixture very gently. A positive result is the appearance of a very pale yellow precipitate of triiodomethane (previously known as iodoform) - CH$_3$I. Apart from its colour, this can be recognised by its faintly "medical" smell. It is used as an antiseptic on the sort of sticky plasters you put on minor cuts, for example.

**Carbylamine reaction:**

Primary amines on heating with chloroform and alcoholic potash forms a foul smelling substance called carbylamine or alkyl isocyanide.

$$\text{CH}_3\text{NH}_2 + \text{CHCl}_3 + 3\text{KOH} \xrightarrow{\text{Chloroform}} \text{CH}_3\text{NC} + 3\text{KCl} + 3\text{H}_2\text{O}$$

This reaction is characteristic of primary amines. Secondary and tertiary amines do not undergo this reaction.

**Hoffmann reaction: Using benzamide.**

When an amide is treated with bromine and alkali, the amide is converted into primary amine containing one carbon less than that of amide.

$$\text{C}_6\text{H}_5\text{CONH}_2 \xrightarrow{\text{Br}_2/\text{KOH}} \text{C}_6\text{H}_5\text{NH}_2 + \text{CO}_2$$
Distinction between primary, secondary and tertiary amines: Hinsberg Test for Amine

**Distinction between primary, secondary and tertiary amine Using Hinsberg reagent**

Three classes of amines are distinguished by **Hinsberg reagent test**. The **Hinsberg reagent** is benzene sulphonyl chloride (C₆H₅SO₂Cl).

1. **Reaction of Hinsberg reagent with Primary amine**
   A primary amine forms a precipitate of N-alkyl benzene sulphonamide with Hinsberg reagent. This precipitate is soluble in alkali.
   
   \[
   \text{R}_1\text{NH}_2 \text{ (primary amine) } + \text{C}_6\text{H}_5\text{SO}_2\text{Cl (Hinsberg reagent)} \rightarrow \text{R}-\text{NH-SO}_2\text{-C}_6\text{H}_5 \text{ (soluble)}
   \]
   
   \[
   \text{R}-\text{NH-SO}_2\text{-C}_6\text{H}_5 \rightarrow \text{R}-\text{NH}^- \text{Na}^+ \text{-SO}_2\text{C}_6\text{H}_5 \text{ (soluble)}
   \]

2. **Reaction of Hinsberg reagent with secondary amine**
   Secondary amine reacts with Hinsberg reagent to form a precipitate N,N-dialkyl benzene sulphonamide. But this precipitate is insoluble in alkali.
   
   \[
   \text{R}_2\text{NH} \text{ (secondary amine) } + \text{C}_6\text{H}_5\text{SO}_2\text{Cl (Hinsberg reagent)} \rightarrow \text{R}_2\text{NSO}_2\text{C}_6\text{H}_5 \text{ (precipitate)} \rightarrow \text{R}_2\text{NSO}_2\text{C}_6\text{H}_5 \text{ (precipitate) (NaOH) } \rightarrow \text{no reaction}
   \]

3. **Reaction of Hinsberg reagent with Tertiary amine**
   Tertiary amines do not react with Hinsberg reagent,
   
   \[
   \text{R}_3\text{N} \text{ (Tertiary amine) } + \text{C}_6\text{H}_5\text{SO}_2\text{Cl (Hinsberg reagent)} \rightarrow \text{No reaction}
   \]

Hinsberg reagent can also be used for the separation of primary, secondary and tertiary amine from a mixture.

**Uses of aniline**
1. For preparing dyes and dye intermediates.
2. For the manufacture of anti oxidants in Rubber industry.
3. For preparing drugs (e.g.,) sulpha drugs.
4. For making isocyanates required for polyurethane plastics

Acylation of amines: Both aliphatic and aromatic primary and secondary amines undergo N-acetylation. This acetylation can be effected using acid halides or anhydrides in presence of a base (pyridine) and the product obtained is an amide. Base remove HCl and prevent protonation of amine.

\[
\text{CH}_3-\text{NH}_2 + \text{CH}_3\text{COCl} \quad \text{Pyridine} \quad \text{Methylamine} \quad \text{acetyl chloride}
\]

\[
\text{O}
\]

\[
\text{CH}_3-\text{NH}^- \text{C}^- \text{-CH}_3 + \text{HCl}
\]

N- methylacetyl amide

Acylation of primary amine

\[
\text{R}_2\text{NH} + \text{CH}_3\text{COCl} \quad \text{Pyridine} \quad \text{Secondary amine} \quad \text{acetyl chloride}
\]

\[
\text{O}
\]

\[
\text{R}_2\text{N}^- \text{C}^- \text{-CH}_3 + \text{HCl}
\]

Tertiary amide

Acylation of Secondary amine
Since amides formed are not basic, they do not undergo further acylation. Acid chlorides are stronger acetylating agent than acetic anhydride. In tertiary amines there is no replaceable hydrogen and they do not undergo acylation.

**Hell-Volhard-Zelinsky Reaction** is an organic reaction that involves the halogenation of carboxylic acid at the \(\alpha\)-carbon atom of the carboxylic group. This reaction is named after three chemists, German chemists Carl Magnus von Hell, Jacob Volhard and Russian chemist Nikolay Dmitrievich Zelinsky.

In this reaction, when bromine is treated with catalytic amount of phosphorus leads to selective \(\alpha\)-bromination of carboxylic acid. This reaction is carried out in the absence of halogen carrier. This is because, Hell-Volhard-Zelinsky Reaction is carried forward by catalytic amount of \(\text{PBr}_3\).

\[
\text{R-COOH} + \text{Br}_2 \xrightarrow{\underset{\text{P (cat)}}{-\text{H}_3\text{PO}_3}} \text{R-Br-COOH} + \text{HBr}
\]

**Optical Isomerism** Optical isomerism arises due to chirality or asymmetry of the molecule. Optical isomers resemble one another in chemical properties and most of their physical properties but differ in their behavior towards polarized light. The isomer, which rotate the plane of polarized light clockwise is called dextro rotatory isomer (d - isomer) and the one which rotate the plane of polarized light anticlockwise is called laevo rotatory isomer (l - Isomer).

The necessary condition for a molecule to be optically active is asymmetry or chirality of the molecule. Chirality is not just the presence of the asymmetric carbon atom but asymmetry of the molecule as a whole. Most of the chiral molecule contains at least one asymmetric carbon atom (Chiral Carbon atom). Still, there are some organic molecules which exhibit optical isomerism with out having chiral carbon (example: Substituted biphenyls). Some of the organic molecules are optically inactive even though they contain chiral carbon. This is due to internal compensation.

Examples of Optical Isomerism

**Optical Isomers of Tartaric acid (HOOC-CHOH-CHOH-COOH)**

Two chiral carbon atoms are present in tartaric acid. The difference in spatial arrangements of various groups in tartaric acid results in d-tartaric acid, l-tartaric acid and an active form known as meso form. In addition to these, racemic modification, another inactive form also exist.

Dextro tartaric acid rotates the plane of polarization of light to right. The rotation due to upper half is strengthened by the rotation of lower half. Laevo tartaric acid is a mirror image of d-form, which rotate the plane of polarization to left.

Racemic tartaric acid is an equimolar mixture of d and l -isomers. It is optically inactive due to external compensation, it can be resolved into d and l forms.

Meso tartaric acid is an inactive variety and the rotation of upper half is compensated by the rotation due to lower half. It cannot be resolved into active constituents. It is therefore inactive due to internal compensation. Mesotartaric acid possess a plane of symmetry.

**Optical Isomers Example: lactic acid**

In lactic acid \(\text{CH}_3 - \text{CHOH} - \text{COOH}\), second carbon is chiral.

There are two optically active isomers of Lactic acid: d-lactic acid and l-lactic acid. In addition to these
optically active varieties there is an optically inactive form which results when dextro and laevo (levo) varieties are present in equal quantities. It is called racemic mixture or (+-) lactic acid.

The **racemic mixture** is 50:50 mixture of d and l -isomers and hence have zero optical rotation as the rotation due to one enantiomer cancels the rotation due to the other. That is **racemic mixture** is optically inactive due to external compensation. The process of conversion of an enantiomer in to a racemic mixture is known as **racemisation**. **Racemisation** can be brought about by the action of heat, light and chemical reagent.

**Dextro rotatory lactic acid** may be obtained from meat extract and is known as **sarcolactic acid**. With muscular activity glycogen present in muscles break down to sarcolactic acid. During rest sarcolactic acid is converted back to glycogen.

Leavo rotatory lactic acid may be obtained by the fermentation of sucroseby Bacillus Acidi laevolactiti. Ordinary lactic acid in sour milk or manufactured by fermentation or by synthetic method is racemic mixture.  

**Geometrical Isomerism:**  
Isomerism that arises out of difference in the spatial arrangement of atoms or groups about the doubly bonded carbon atoms is called **Geometrical isomerism**. These isomers are not mirror images of each other. Rotation about C=C is not possible at normal conditions and hence the isomers are isolable. If different atoms or groups are bonded to the ‘C=C’ bond in a molecule, more than one spatial arrangement is possible. For example, 2-butene exists in two isomeric forms.

The isomer in which **similar groups** lie on the same side is called ‘**cis isomer**’ (I). The other in which similar groups lie in **opposite direction** is called ‘**Trans isomer**’ (II). This isomerism is called ‘Cis-Trans’ isomerism. The two groups attached to the carbon atoms need not be same, it may be different also. e.g.,
2-pentene

\[
\begin{align*}
\text{H} & \quad \text{C} & & \text{CH}_2\text{CH}_3 \\
\text{H} & \quad \text{C} & \quad \text{CH}_3
\end{align*}
\]

\textit{Cis}

\[
\begin{align*}
\text{H} & \quad \text{C} & & \text{CH}_2\text{CH}_3 \\
\text{H}_3 & \quad \text{C} & & \text{H}
\end{align*}
\]

\textit{Trans}

This isomerism arises out of the hindrance to rotation about the C=C bond in such molecules.

**Optical Activity**

*Optical activity* is the ability of a chiral molecule to rotate the plane of plane-polarized light, measured using a polarimeter. A simple polarimeter consists of a light source, polarizing lens, sample tube and analyzing lens.

![Polarimeter diagram](image)

When light passes through a sample that can rotate plane polarized light, the light appears to dim because it no longer passes straight through the polarizing filters. The amount of rotation is quantified as the number of degrees that the analyzing lens must be rotated by so that it appears as if no dimming of the light has occurred.

**Measuring Optical Activity** When rotation is quantified using a polarimeter it is known as an *observed rotation*, because rotation is affected by path length (l, the time the light travels through a sample) and concentration (c, how much of the sample is present that will rotate the light). When these effects are eliminated a standard for comparison of all molecules is obtained, the *specific rotation*, [\(\alpha\)].

\([\alpha] = 100a / c\) when concentration is expressed as g sample /100ml solution

Specific rotation is a physical property like the boiling point of a sample and can be looked up in reference texts. Enantiomers will rotate the plane of polarisation in exactly equal amounts (same magnitude) but in opposite directions.

- **Dextrorotary** designated as d or (+), clockwise rotation (to the right)
- **Levorotary** designated as l or (-), anti-clockwise rotation (to the left)

If only one enantiomer is present a sample is considered to be **optically pure**. When a sample consists of a mixture of enantiomers, the effect of each enantiomer cancels out, molecule for molecule. For example, a 50:50 mixture of two enantiomers or a racemic mixture will not rotate plane polarised light and is **optically inactive**. A mixture that contains one enantiomer excess, however, will display a net plane of polarisation in the direction characteristic of the enantiomer that is in excess.

**EXTERNAL AND INTERNAL COMPENSATION**

If equimolecular amounts of d- and l-isomers are mixed in a solvent, the solution is inactive. The rotation of each isomer is balanced or compensated by the equal but opposite rotation of the other. Optical inactivity having this origin is described as due to External compensation. Such mixtures of d- and l-isomers are called racemic mixtures.

In meso tartaric acid the inactivity is due to effects within the molecule and not external. The force of rotation due to one half of the molecule is balanced by the opposite and equal force due to the other half. The optical inactivity so produced is said to be due to **internal compensation**. It occurs whenever a compound containing two or more asymmetric carbon atoms has a plane or point of symmetry.
Meso tartaric acid.

**Zwitterions**

Since in amino acids both carboxylic group (-COOH) and amino group (-NH$_3$) exists, in aqueous solution the H$^+$ ion is transformed from one end of the molecule to the other end to form zwitterions. It is considered as both electrically charged and electrically neutral also. Since it is having both the charges (positive and negative) the net charge of zwitterion is zero.

\[
\begin{align*}
\text{NH}_2 & \quad \text{NH}_2^+ \\
R - C - COOH & \quad R - C - COO^- \\
\text{Zwitter ion} & \quad \text{Zwitter ion}
\end{align*}
\]

Amino acid in zwitter ion form reacts with both acids and bases and it shows the amphoteric behavior. The point at which the zwitter ion has no net charge is called **Iso-electric point**. At this point the amino acid is considered as electrically neutral.

**Isoelectric Point:** An important pH value relative to the various forms an amino acid can have in solution is the pH at which it exists primarily in its zwitterion form, that is, its neutral form (no net charge). This pH value is known as the isoelectric point for the amino acids. An isoelectric point is the pH at which an amino acid exists primarily in its zwitter form. At the isoelectric point, almost all amino acid molecules in a solution (more than 99%) are present in their zwitterion form.

**Thermoplastic polymers:**

These are the linear or slightly branched long chain molecules capable of repeatedly softening on heating and hardening on cooling. These polymers possess intermolecular forces of attraction intermediate between elastomers and fibres. Some common thermoplastics are polythene, polystyrene, polyvinyls, etc.

**Thermosetting polymers**

These polymers are cross linked or heavily branched molecules, which on heating undergo extensive cross linking in moulds and again become infusible. These cannot be reused. Some common examples are bakelite, urea-formaldehyde resins, etc.