



**BSCCH- 202**

# **B. Sc. II YEAR ORGANIC CHEMISTRY-II**



**SCHOOL OF SCIENCES  
DEPARTMENT OF CHEMISTRY  
UTTARAKHAND OPEN UNIVERSITY**

**BSCCH-202**

**ORGANIC CHEMISTRY-II**



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**UNIT - 1 ALCOHOL**

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## 1.1 OBJECTIVES

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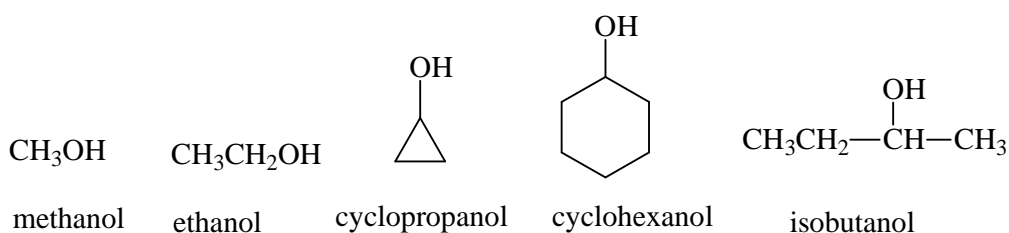
Objectives of this unit are to study the alcohols, their structures, nomenclature, and classification on the basis of number of –OH groups present like monohydric alcohol, dihydric and polyhydric alcohols. Classification on the basis of nature of carbon attached with –OH group like primary, secondary and tertiary alcohols. This unit also aims on methods of preparation of alcohols with their physical and chemical properties, acidic and basic characters. Chemical reactions of alcohols like Acid-catalyseddehydration etc, Study on chemical properties of dihydric and polyhydric alcohols have also been aimed in this unit

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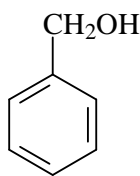
## 1.2 INTRODUCTION

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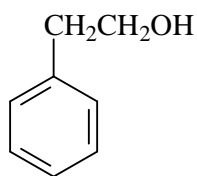
Alcohols are organic compounds in which one or more hydrogen atoms from hydrocarbon have been replaced by hydroxyl (-OH) group. They are some of the most common and useful compounds in nature, in industry, and around the house. The general formula for a simple acyclic alcohol is  $C_nH_{2n+1}OH$ , where  $n=1, 2, 3$ , etc. The saturated carbon chain is often designated by the symbol R, so that ROH can represent any alcohol in the homologous series. Alcohols can be viewed as organic analogues of water in which one hydrogen atom is replaced by an alkyl group. The simplest and most commonly used alcohols are methanol and ethanol. They occur widely in nature and have many industrial and pharmaceutical applications.



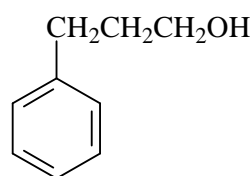
Aromatic compounds, which contain a hydroxy group on a side chain, behave like alcohols are called aromatic alcohol. In these alcohols, the —OH group is attached to a  $sp^3$  hybridised carbon atom next to an aromatic ring.



benzyl alcohol

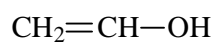


2- phenyl ethanol

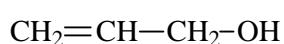


3- phenyl propanol

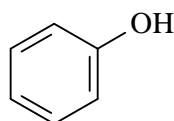
In some alcohols, the —OH group is attached to a  $\text{sp}^3$  hybridised carbon next to the carbon-carbon double bond that is to an allylic carbon are known as allylic alcohols. In some alcohols —OH group bonded to a carbon-carbon double bond i.e., to a vinylic carbon or to an aryl carbon. These alcohols are also known as vinylic alcohols. Allylic and benzylic alcohols may be primary, secondary or tertiary in nature.



vinylic alcohol



allylic alcohol



phenol

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### 1.3 CLASSIFICATION OF ALCOHOLS

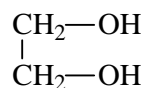
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Alcohols are classified into following types on the basis of number of —OH groups present in the molecule and nature of carbon attached with —OH group as follow:

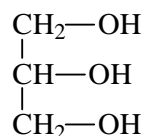
(a) **Monohydric Alcohols:** These compounds contain only one —OH group.



(b) **Dihydric Alcohols:** These contain two —OH groups.



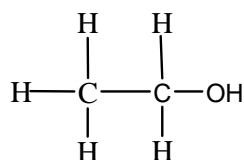
(c) **Trihydric Alcohols:** These contain three —OH groups.



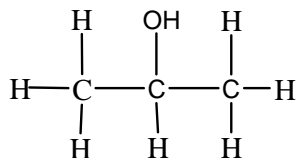


On the basis of nature of carbon atom attached with -OH group the monohydric Alcohols can be further classified as primary ( $1^\circ$ ), secondary ( $2^\circ$ ), or tertiary ( $3^\circ$ ) depending on the number of carbon atoms bound to the hydroxyl-bearing carbon.

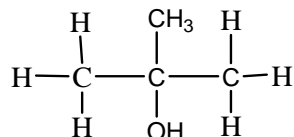
**(a) Primary alcohol ( $1^\circ$  alcohol):** A primary alcohol has one alkyl group attached to the carbon bound to the -OH, *i.e.*, a compound in which the hydroxyl group is bounded to a primary carbon. Primary alcohols have the group  $-\text{CH}_2\text{OH}$ , where the carbon atom with the alcoholic hydroxyl group has at least two additional hydrogen attached to that carbon. Primary alcohol has -OH group bonded to a carbon which is bonded to one other carbon:



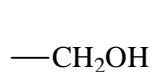
**(b) Secondary alcohol ( $2^\circ$  alcohol):** A secondary alcohol has two alkyl group attached to the carbon bound to the -OH, *i.e.*, the hydroxyl group is bounded to a secondary carbon. Secondary alcohols have the group  $-\text{CHOH}$ , where the carbon atom with the alcoholic hydroxyl group has only **one** additional H atom attached to it. There are two R groups (R stands for any other organic chain or group), and the alcoholic hydroxyl group is attached to a secondary carbon. Secondary alcohol has -OH group bonded to a carbon which is bonded to two other carbon:



**(c) Tertiary alcohol ( $3^\circ$  alcohol):** A tertiary alcohol has three alkyl group attached to the carbon bound to the -OH, *i.e.*, the hydroxyl group is bounded to a tertiary carbon. Tertiary alcohols have the group  $-\text{COH}$ , where the carbon atom with the alcoholic hydroxyl group has no additional H atoms attached to it.



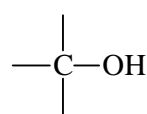
If we replace hydrogen with a  $-\text{OH}$  group we get the following groups for three alcohols:



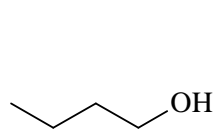
primary alcohol



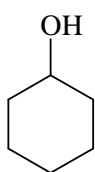
secondary alcohol



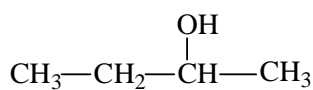
tertiary alcohol



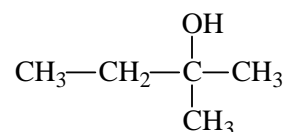
primary alcohol



secondary alcohol



secondary alcohol



tertiary alcohol

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## 1.4 NOMENCLATURE OF ALCOHOLS

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According to the IUPAC system of nomenclature, alcohols are called alkanols. They are named as the derivatives of the corresponding alkane in which the  $-e$  of the alkane is replaced by  $-ol$ . The IUPAC have come up with a set of rules that are used to name any alcohol regardless of its complexity. These rules are summarized as follows:

**Step 1.** Name the longest continuous chain to which the hydroxyl ( $-\text{OH}$ ) group is attached. Count the number of carbon atoms and identify the corresponding alkane. The name for this chain is obtained by dropping the final  $-e$  from the name of the hydrocarbon parent name and adding the ending  $-ol$ .

**Step 2.** Number the longest chain to give the lowest possible number to the carbon bearing the hydroxyl group.

**Step 3.** Locate the position of the hydroxyl group by the number of the carbon to which it is attached.

**Step 4.** Number the any other substituents according to their position on the chain.

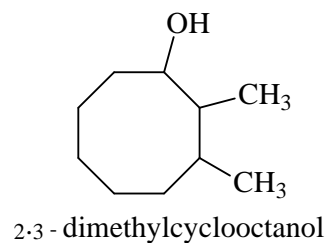
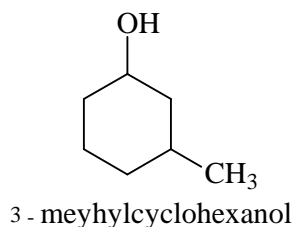
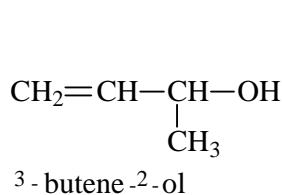
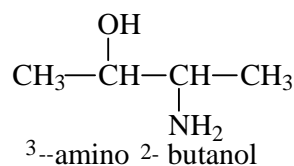
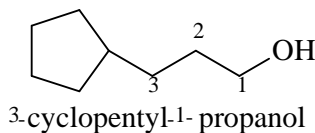
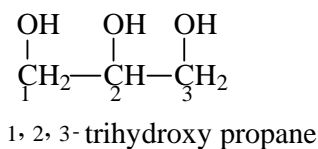
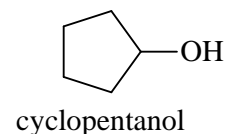
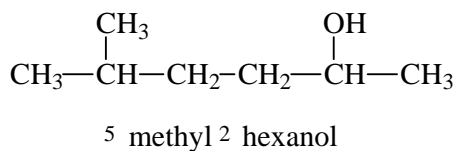
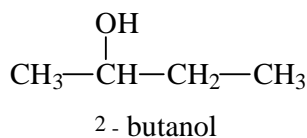
**Step 5.** Combine the name and location for other groups, the hydroxyl group location, and the longest chain into the final name.

**Step 6.** If there are more than one –OH group do not remove the –e from the suffix, but add a di- or tri- prefix to the –ol suffix.

**Step 7.** Identify and locate the other branches on the chain so that they are named alphabetically and their carbon number is hyphenated onto the front of the name.

viz;	Alcohols	Common name	IUPAC name
	CH <sub>3</sub> OH	Methyl alcohol	Methanol
	CH <sub>3</sub> CH <sub>2</sub> OH	Ethyl alcohol	Ethanol
	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH	n-Propyl alcohol	1-Propanol
	CH <sub>3</sub> CHOHCH <sub>3</sub>	Isopropyl alcohol	2-Propanol
	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> OH	n-Butyl alcohol	1-Butanol
	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>2</sub> OH	n-Pentyl alcohol	1-Pentanol

Other examples:



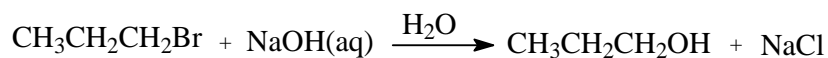
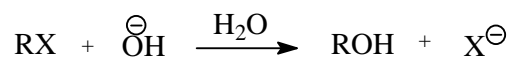
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*1.5 METHOD OF PREPARATION OF ALCOHOLS*

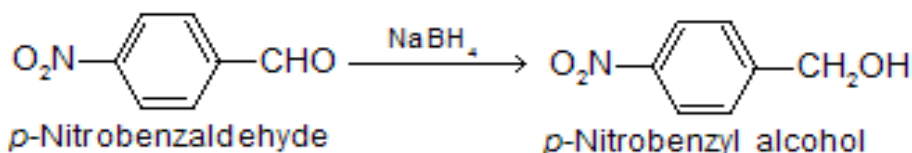
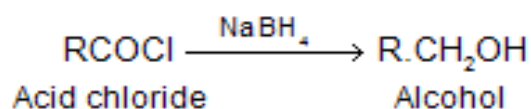
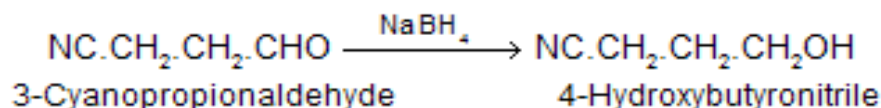
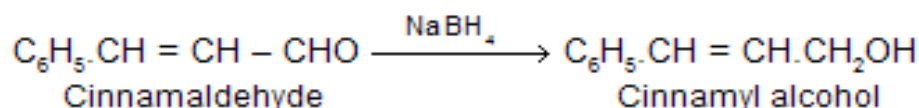
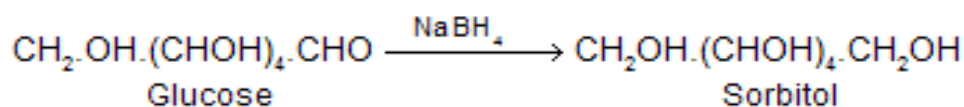
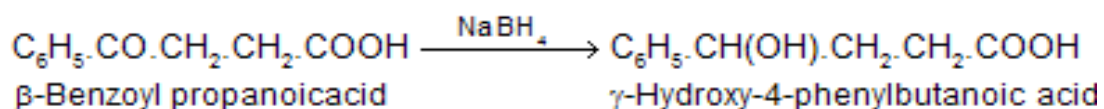
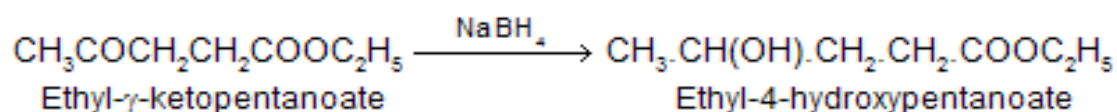
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The following methods are used for the preparation of alcohols:

- 1. Hydrolysis of haloalkanes:** Haloalkanes can be converted to corresponding alcohols using aqueous NaOH, KOH or Ca (OH)<sub>2</sub>. With this method primary and secondary alcohols are formed from a primary and secondary halogenoalkanes. This is a type of nucleophilic substitution reaction (S<sub>N</sub>). This reaction is useful only with reactants that do not undergo E<sub>2</sub> elimination readily.



2. Reduction of carbonyl compounds: Carbonyl compounds (which contain  $\text{-C=O}$  group) such as aldehydes, ketones, carboxylic acids and esters can be reduced to alcohols. Aldehydes give primary alcohols while ketones yield secondary alcohols, either by catalytic hydrogenation or by use of chemical reducing agents like lithium aluminum hydride,  $\text{LiAlH}_4$ . Carboxylic acids and esters also give primary alcohols on reduction with hydride reagents such as  $\text{LiAlH}_4$  and sodium borohydride

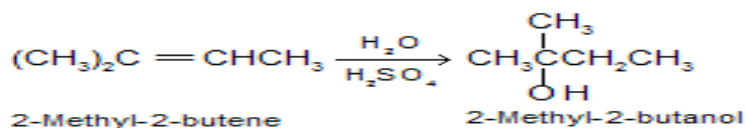
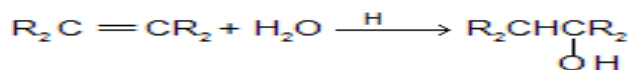
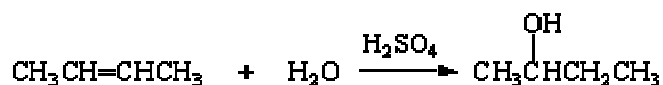
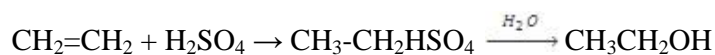


( $\text{NaBH}_4$ ).  $\text{NaBH}_4$  does not reduce carbon-carbon double bonds, not even those conjugated with carbonyl groups, and is thus useful for the reduction of such unsaturated carbonyl compounds to unsaturated alcohols.

In the above reactions it is observed that only the carbonyl group is reduced and the other functional groups remain unaffected. Highly selective behaviour of

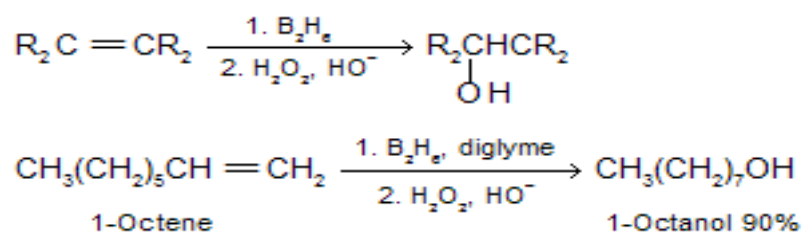
$\text{NaBH}_4$  makes it the preferred reagent for the reduction of carbonyl groups in sensitive polyfunctional group containing compounds.

- 3. From hydration of alkenes:** Hydration i.e.s addition of  $\text{H}^+$  and  $\text{OH}^-$  across a  $\text{C}=\text{C}$  double bond to give alcohols. This is an electrophilic addition of  $\text{H}_2\text{O}$  to the alkene. Alcohols can be prepared by adding water to an alkene in the presence of a strong acid such as co.  $\text{H}_2\text{SO}_4$ . Because these reactions follow Markovnikov's rule, the product of the reaction is often a highly substituted  $2^\circ$  or  $3^\circ$  alcohol.



Ease of preparation is tert. > sec. > prim alcohol; ease of dehydration follows same sequence.

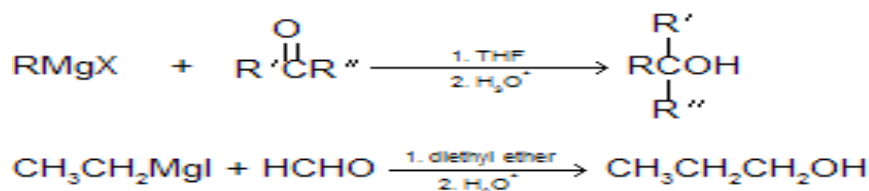
- 4. Oxidation of organoboranes:** When an alkene reacts with  $\text{BH}_3$  (a boron hydride) in THF solution, an organoborane is obtained. Hydroboration followed by oxidation will produce an alcohol. Since  $\text{BH}_3$  has three hydrogens, above addition can occur three times to give trialkylborane. This is oxidised to alcohol by hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) in the presence of aqueous sodium hydroxide. The overall reaction is addition of water across the double bond opposite to that of Markovnikov's rule and the reaction is regioselective producing the least substituted alcohol.



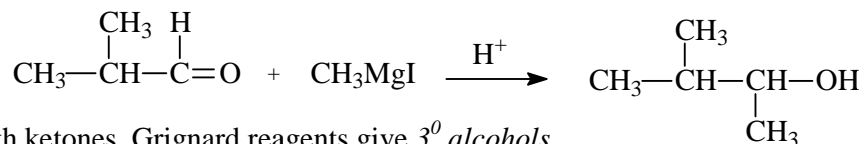
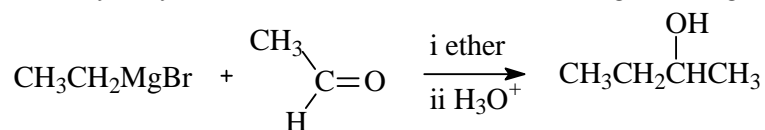
Except ethyl alcohol no other primary alcohol can be obtained by this method, however hydroboration of terminal alkenes give primary alcohols.

**5. From Grignard reagents** – Alcohol can easily be prepared by using Grignard (RMgX) reagent as follow:

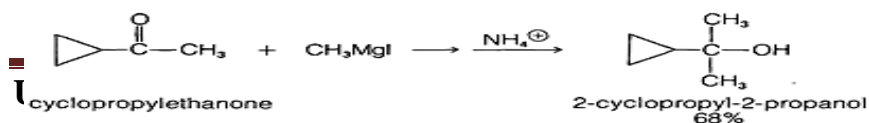
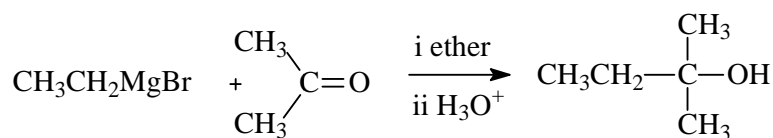
**(a) By reaction with aldehydes & ketones:** The reaction of Grignard reagents with formaldehyde produces a primary alcohol, with other aldehydes, secondary alcohols and with ketones, tertiary alcohols. In this method alcohol is prepared with the formation of new carbon-carbon bonds.



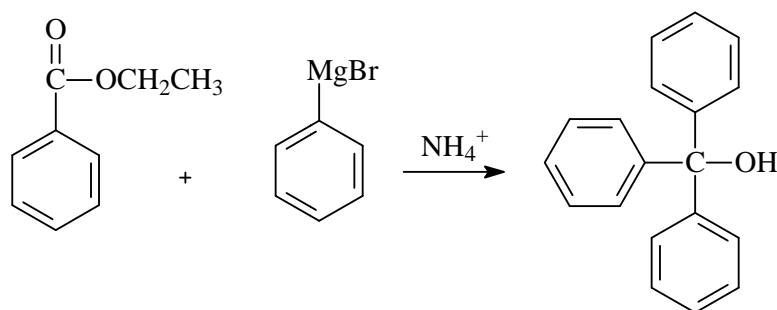
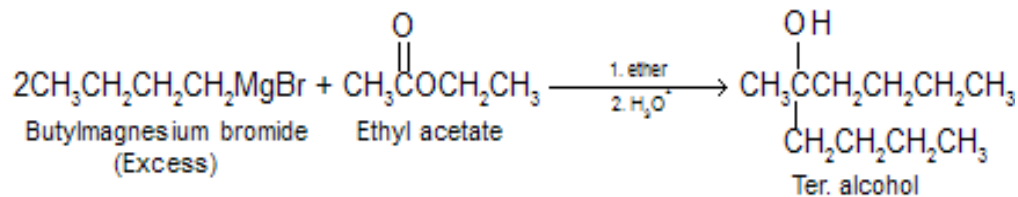
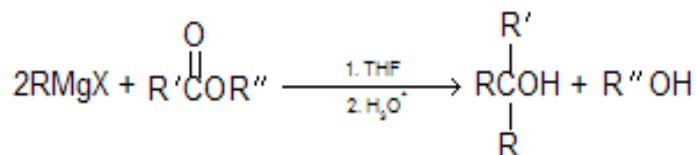
All other aldehydes yield 2<sup>o</sup> alcohols on reaction with Grignard reagents.



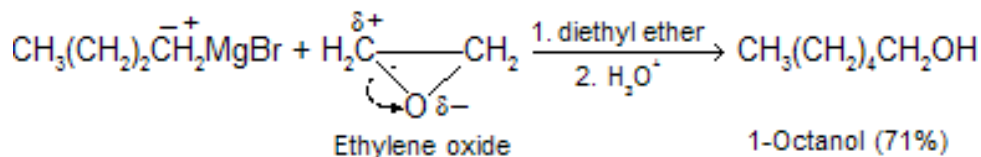
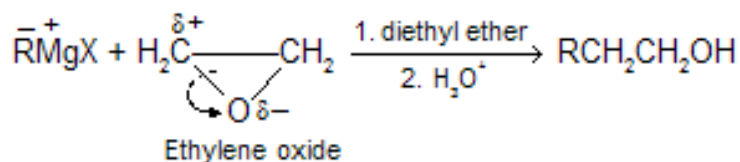
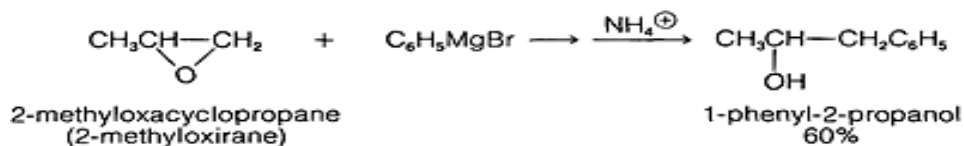
With ketones, Grignard reagents give 3<sup>o</sup> alcohols.



(b) **By reaction with esters:** Produces tertiary alcohols in which two of the substituents on the hydroxyl-bearing carbon are derived from the Grignard reagent.

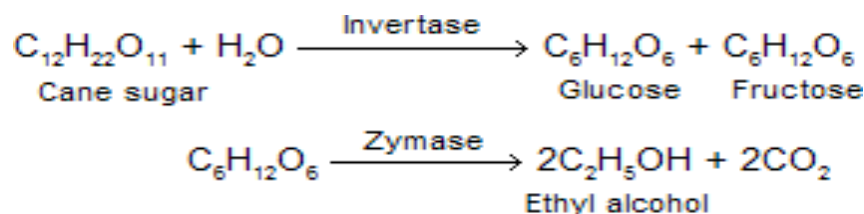


(c) **By reaction with epoxides:** Grignard reagents react with epoxide to yield primary alcohols containing two or more carbon atoms.





5. **Fermentation:** Ethanol is prepared on a large scale using fermentation process. It involves breaking down large molecules into simpler ones using enzymes. Usually, yeast is added as a source of enzymes. Yeast converts the reactant glucose or fructose into ethanol and carbon dioxide in presence of zymase enzyme.



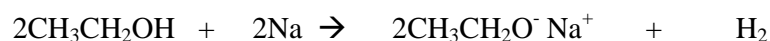

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### 1.6 ACIDIC NATURE OF ALCOHOLS

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Alcohols can act as Brønsted acids as well as Lewis base due to donation of proton and presence of unpaired electron on oxygen respectively. Alcohols are very weak acids because the alkyl group pushes electrons towards the —OH group, so that the oxygen does not strongly attract the electrons in the —OH bond. Furthermore once a RO<sup>-</sup> ion is formed, it cannot be stabilized by the delocalization of the charge. Thus alcohols react only to a very slight extent with alkali, but will react with very electropositive metals under anhydrous conditions to give alkoxide with the general formula RO<sup>-</sup> M<sup>+</sup>.

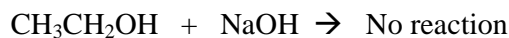
Example: Reaction of ethanol with sodium



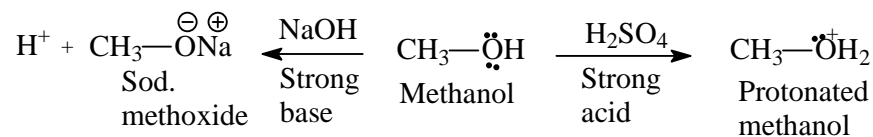
Addition of water will regenerate the alcohol readily.



The reaction is much slower than the reaction of water with sodium. Alcohols tend to be slightly less acidic (pK<sub>a</sub> = 15) compared to water (pK<sub>a</sub> = 14). The higher the pK<sub>a</sub> value the lower is the acid strength. The reaction of alcohol with sodium can be used to deposit the excess sodium in the laboratory. Even alcohols are neutral to litmus and do not react with alkali like NaOH but contain active hydrogen atom so reacts with Na or K metal.



Reactivity of alcohol towards metal:  $1^\circ > 2^\circ > 3^\circ$  alcohol. An electron-releasing group ( $-\text{CH}_3$ ,  $-\text{C}_2\text{H}_5$ ) increases electron density on oxygen tend to decrease the polarity of O-H bond. For example, with methanol:



(i) The lower alcohols are colourless liquids with a characteristic smell and a burning taste. The higher members (with more than 12 carbons) are colourless wax like solids.

(ii) Because of hydrogen bonding, alcohols tend to have higher boiling points than comparable hydrocarbons and ethers of similar molecular weight. Alcohols exist as associated molecules due to the association of molecules in the liquid phase through strong intermolecular hydrogen bond between hydrogen atom of one molecule and oxygen atom of another molecule. The oxygen-hydrogen bond is polar because oxygen is much more electronegative than hydrogen. The lower members have low boiling points. With the increase in molecular weight, the boiling points keep on increasing gradually. For example, the boiling point of butyl alcohol is  $118^\circ\text{C}$  whereas the boiling point of the isomeric diethyl ether is  $36^\circ\text{C}$ .

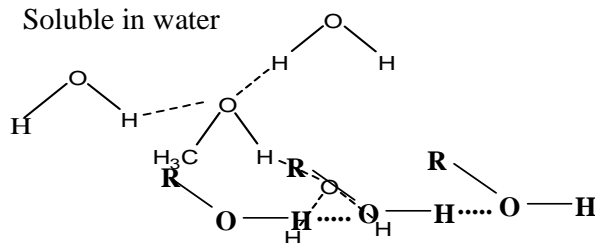
(iii) Solubility: The general rule in solubility is “*like dissolves like.*” The hydroxyl group generally makes the alcohol molecule polar and therefore more likely to be soluble in water. Hydrogen bonding also has an effect on water solubility. The OH groups of an alcohol can hydrogen bond with water, and so this portion of the alcohol is hydrophilic. On the other hand, the alkyl chain in an alcohol is similar to hydrophobic molecules like hydrocarbon that do not mix with water. Compounds like alcohols that have hydrophilic and hydrophobic regions are called amphiphilic (or amphiphilic). The water solubility of a given alcohol depends on whether the hydrophilic OH or the hydrophobic alkyl chain dominates. Alcohols with shorter carbon chains ( $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{CH}_2\text{OH}$ ,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ ) are usually more soluble than those with longer carbon chains because the increasing size of the nonpolar chain disrupts the hydrogen bonding network. Formation of hydrogen bonds with water will increase their

solubility. That is why alcohols are much more soluble in water than their corresponding alkanes, aromatic hydrocarbons, alkyl halides or aryl halides. Amongst isomeric alcohols, the solubility increases with branching.

(iv) The B.P. and M.P. will also increase with carbon chain length. The longer the alcohols carbon chain, the better the chance that the alcohol will be a solid at room temperature. Alcohols show higher boiling points than alkane and ethers of similar mass due to hydrogen bonding. Since there is not any possibility of hydrogen bonding in ether, the forces between the ether molecules are much weaker and can be much more easily vaporized.



Soluble in water



Insoluble in water

Comparison of boiling points among isomeric alcohols

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{CH}-\text{CH}_2\text{OH} \end{array}$	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{C}-\text{OH} \\   \\ \text{CH}_3 \end{array}$
1-butanol	2-methyl 1-propanol	2-methyl 2-propanol
B.P. $118^\circ\text{C}$	B.P. $108^\circ\text{C}$	B.P. $83^\circ\text{C}$
M.Wt = 74	M.Wt = 74	M.Wt = 74

(v) The viscosity of small alcohols is much higher than the viscosity of alkanes.

(vi) Generally alcohols are lighter than water, i.e., less dense than water. Density of alcohols increases with molecular mass.

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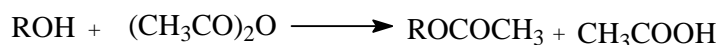
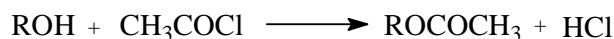
**1.7 CHEMICAL REACTIONS OF ALCOHOLS**

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Alcohols act both as nucleophiles as well as electrophiles. The bond between O-H is broken when alcohols react as nucleophiles and the bond between C-O is broken when they react as electrophiles. The chemical properties of any given aliphatic alcohol depend on the nature of the alkyl group and on the properties of the hydroxyl group. Based on the cleavage of O-H and C-OH bonds, the reactions of alcohols may be divided into two groups:

**(A) Reactions involving cleavage of O-H bond**

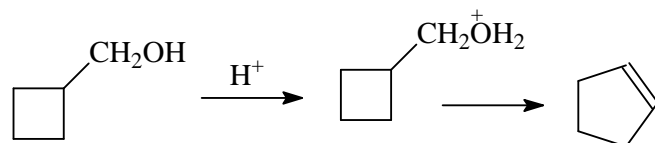
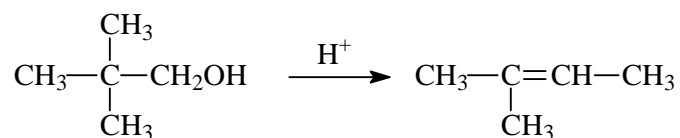
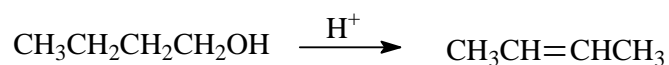
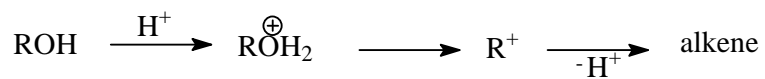
**1. Acylation of alcohol:** When alcohol reacts with acylhalide and anhydride substitution of hydrogen atom by acyl group is known as acylation of alcohols.



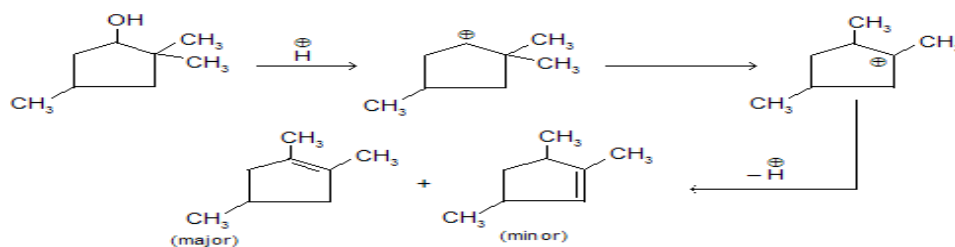
**(B) Reaction involving fission of R—OH bond (cleavage of C—O bond):** The reactions involving R – OH bond with cleavage of C – O bond are as follow

**1. Dehydration: (a) Intramolecular dehydration (forming alkene):** Alcohols undergo dehydration to form unsaturated hydrocarbon on treating with a protic acid e.g., conc.  $\text{H}_2\text{SO}_4$  or  $\text{H}_3\text{PO}_4$ , or catalysts such as anhydrous  $\text{ZnCl}_2$  or  $\text{Al}_2\text{O}_3$ . In this reaction the OH and an H groups remove from adjacent carbons. Since water is removed from the alcohol, this reaction is known as a **dehydration reaction** (or an *elimination reaction*). Secondary and tertiary alcohols are dehydrated under much milder conditions. The conditions for dehydrating alcohols depend closely on the structure of individual alcohols.

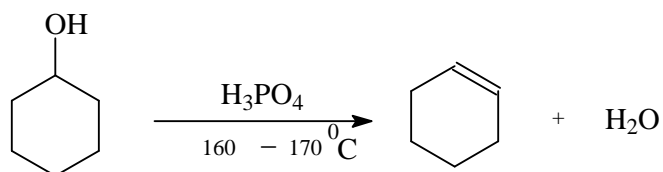
For primary alcohols, the conditions required are conc. sulphuric acid and temperature of  $170^\circ\text{C}$ .



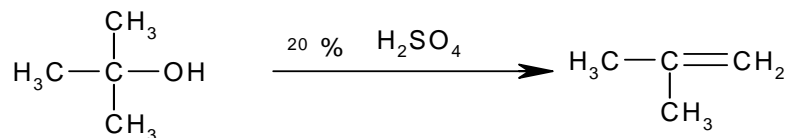
In smaller ring always ring expansion takes place due to molecular strain and they tend to convert to high stability with large ring.



Secondary alcohols dehydrate under milder conditions than primary alcohols.



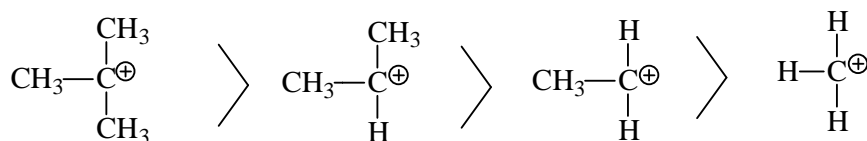
Tertiary alcohols dehydrate under even milder conditions.



The main function of the acid is to transform the poor leaving group —OH into the very good leaving group —OH<sub>2</sub>. The order of the relative ease of dehydration of alcohols is: 3° > 2° > 1°

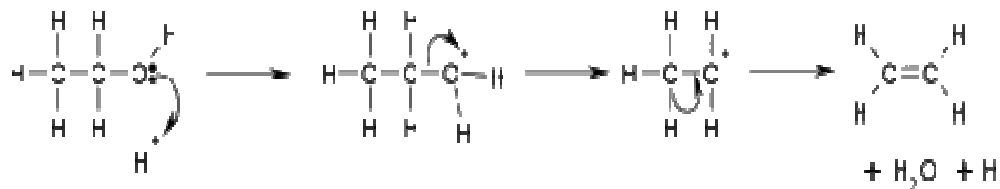
Tertiary carbocations are most stable and therefore are easier to form than secondary and primary carbocations; tertiary alcohols are the easiest to dehydrate.

The order of stability of the carbocations is:



Dehydration of secondary and tertiary alcohols containing more than three carbon atoms will give a mixture of alkenes, the major product can be determined from Saytzeff's Rule:

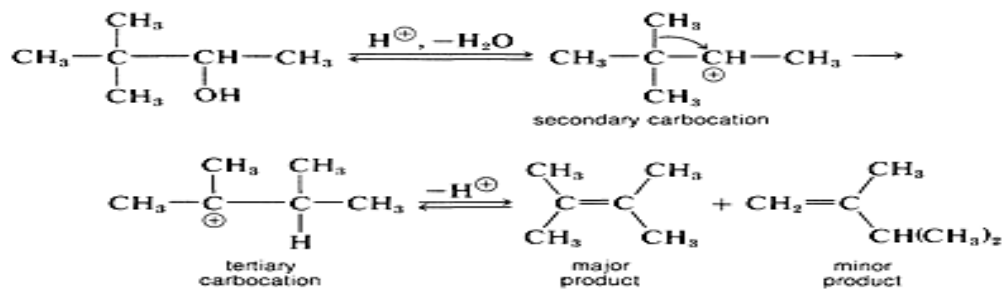
**Saytzeff's Rule**— When an alkene is produced in an elimination reaction, the major product is the one with the more highly substituted double bond i.e., the major product is that contains the higher number of alkyl groups attached to the C=C bond. e.g.



Rearrangement of the alkyl

groups of alcohols is very common in dehydration, particularly in the presence of strong acids, which are conducive to carbocation formation. Typical examples showing both methyl and hydrogen migration follow:

**Mechanism:**



(b)

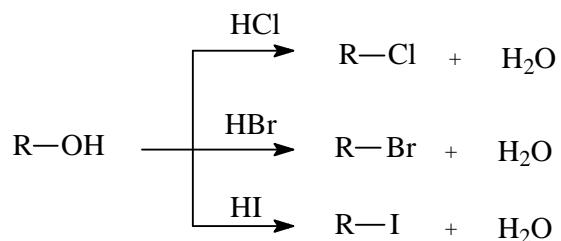
**Intermolecular dehydration (forming ether):**

When the dehydration is carried out at a temperature of  $140^\circ\text{C}$  with an excess of alcohol ether will be formed. This reaction removes a molecule of water from two alcohol molecules, causing the two "R" groups to become attached to an oxygen atom, forming an ether functional group:

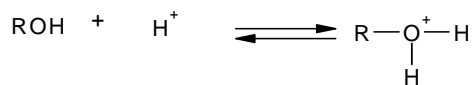


**2. Halogenation:** Alcohols can be converted to alkyl halides using one of three reactions:

**(a) Reaction with hydrogen halides:** Respective alkyl halides are formed by reacting with the appropriate hydrogen halide, HCl for chlorination, HBr for bromination, and HI for iodination. The reaction involves the initial protonation of the hydroxyl group of the alcohol. This improves the leaving group ability of the hydroxyl group.

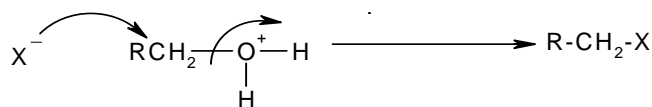
**Mechanism:**

Step1: Protonation of the alcohols: The alcohol acts as a weak base and accepts the proton donated by the hydrogen halide.

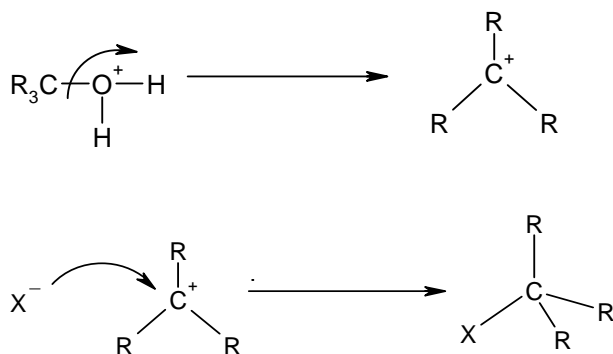


Step 2: Removal of a water molecule and formation of halide through  $\text{S}_{\text{N}}2$  mechanism/  
 $\text{S}_{\text{N}}1$  mechanism as:

(i) For primary and secondary alcohols, it is a  $\text{S}_{\text{N}}2$  reaction.

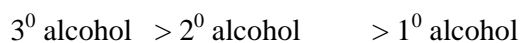


(ii) For tertiary alcohols, it is a  $\text{S}_{\text{N}}1$  reaction.



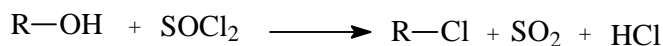
(iii) Rate of the reaction for  $1^\circ$ ,  $2^\circ$  and  $3^\circ$  alcohols:

The order of rates of reaction:



The rate can be shown by the turbidity in the aqueous layer since the chloroalkane formed is immiscible with water.

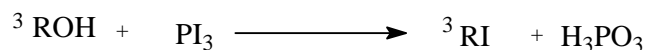
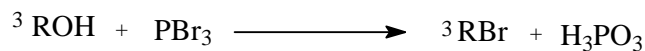
**(b) Reaction with thionyl chloride,  $\text{SOCl}_2$ :** Alcohols will react with thionyl chloride to produce alkyl halides. The reaction involves a nucleophilic attack of the alcohol on a  $\text{SOCl}_2$  molecule displacing one of the chlorides. Then the chloride will act as the nucleophile in a second step and displace the oxygen from the carbinol carbon.



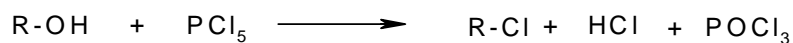


**(c) Reaction with phosphorus halides**

Alcohols will react with phosphorus tribromide or phosphorus pentabromide to form alkyl bromides.

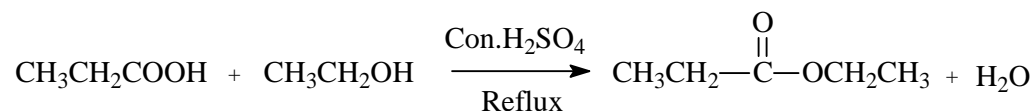


The mechanism is very similar to the thionyl chloride reaction. The alcohol acts as the nucleophile and displaces a halide ion from the  $\text{PX}_3$  or the  $\text{PX}_5$ .



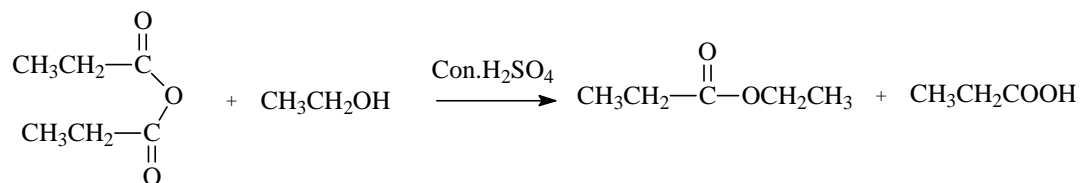
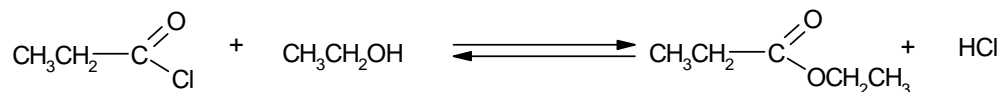
**3. Esterification:** Alcohol reacts with carboxylic acids, acid chlorides and acid anhydrides to form esters. The reaction with carboxylic acid and acid anhydride is reversible, and therefore, water is removed as soon as it is formed. Esterification takes place much faster in the presence of a catalyst such as conc.  $\text{H}_2\text{SO}_4$ .

Example :

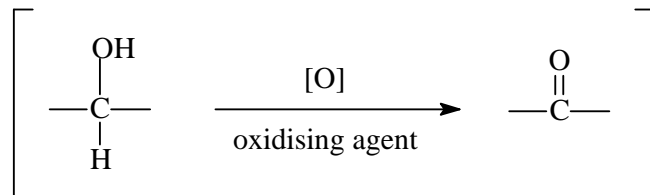


Alcohols can also react with acid chlorides and acid anhydrides to form esters. The introduction of acetyl ( $\text{CH}_3\text{CO}$ ) group in alcohols or phenols is known as acetylation.

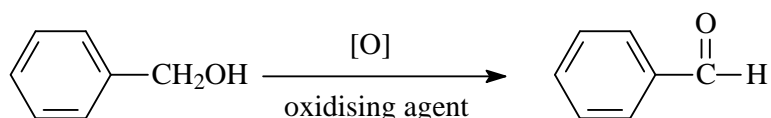
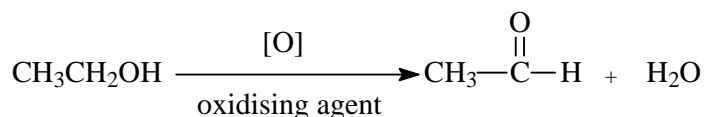
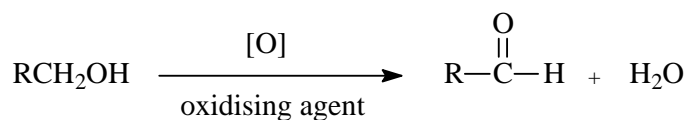
Example:



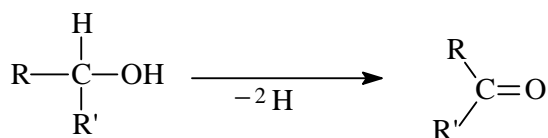
**3. Oxidation:** Alcohols can be oxidized by various oxidizing agents to aldehyde, ketones or carboxylic acids. Oxidation is the gain of oxygens and /or the loss of hydrogens.



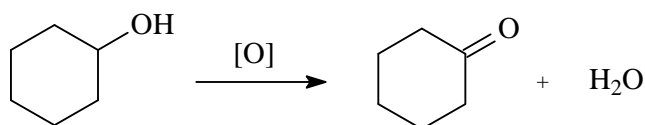
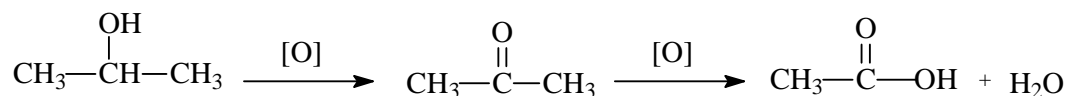
(a) 1<sup>o</sup> alcohol oxidizes readily, first to an aldehyde, then to a carboxylic acid. These two oxidation steps make sense because the primary alcohol functional group has two C-H bonds that can be broken. Primary or secondary alcohols can be oxidized to produce compounds containing the carbonyl group (a carbon-oxygen double bond, C=O). Strong oxidizing agents such as hot alkaline KMnO<sub>4</sub> or CrO<sub>3</sub> in H<sub>2</sub>SO<sub>4</sub> will oxidize primary alcohols right past the aldehyde to the salt of the carboxylic acid in which the acid may be precipitated by acidification. The alcohol, aldehyde and acid retain the same number of carbon atoms.



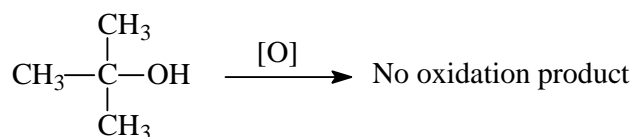
b. 2<sup>o</sup> alcohol has only one C-H bond that can be broken, so it can only oxidize once, to a ketone, which cannot be oxidized any further:

3<sup>o</sup> alcohol

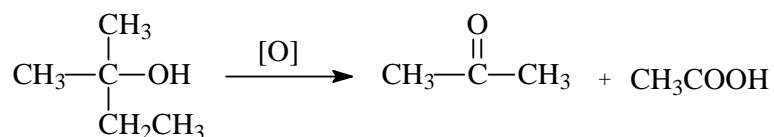
Ketone



c. 3<sup>o</sup> alcohol has no C-H bonds that can be broken, so it is not oxidized, no matter how strong the oxidizing agent because it would involve the breakage of the high energy C—C bonds in the alcohol molecule.



In acidic solutions, 3<sup>o</sup> alcohols can be oxidized to give a mixture of ketone and acid, both with fewer carbon atoms than the alcohol.



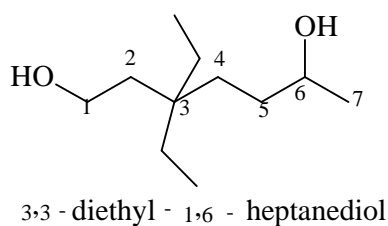
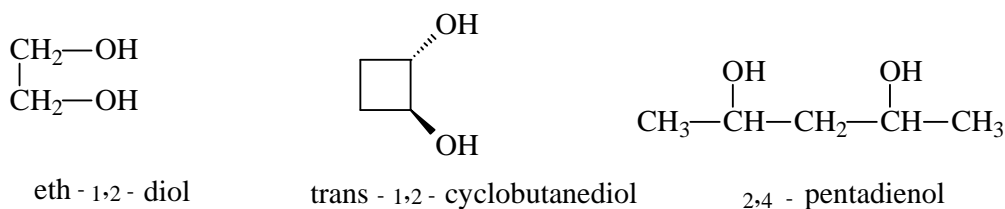
Characterization of the oxidation products of alcohols is a means of distinguishing between primary, secondary and tertiary alcohols.

### 1.8 DIHYDRIC ALCOHOLS

These compounds contain two hydroxyl (–OH) groups in a molecule. These are dihydroxy components of alkanes. Their general formula is  $C_nH_{2n+2}O_2$ . The simplest and most important dihydric alcohol is ethylene glycol. They are classified as  $\alpha, \beta, \gamma, \dots$  glycols, according to the relative position of two hydroxyl groups.  $\alpha$  is 1, 2 glycol,  $\beta$  is 1, 3 glycol.



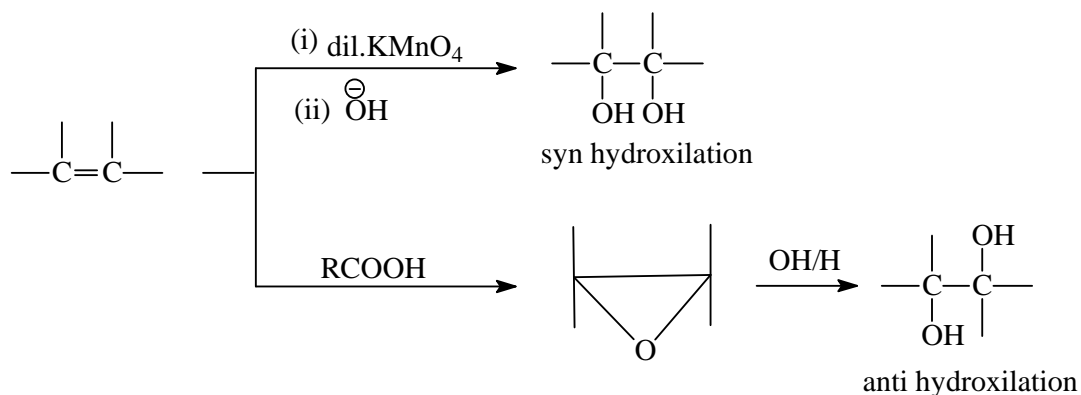
**Nomenclature:** For naming polyhydric alcohols, the name of the alkane is retained and the ending -e is not dropped but add a di- or tri- prefix to the -ol suffix. Thus dihydric alcohols are named as alkane diols and trihydric alcohols are named as alkene triols.



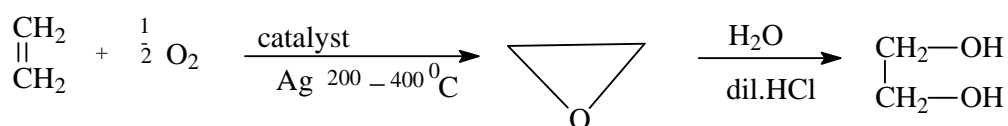
### 1.9 METHODS OF PREPARATION

Dihydric alcohols are prepared by following different methods:

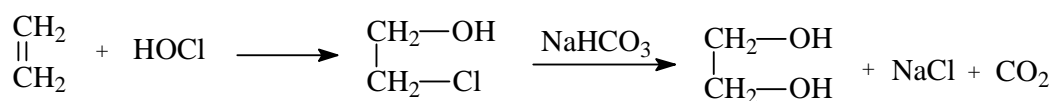
**From ethylene:** (a) through icy dilute alkaline solution of Bayer's reagent.



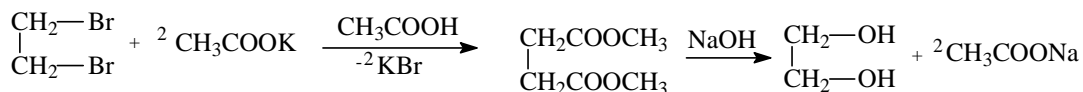
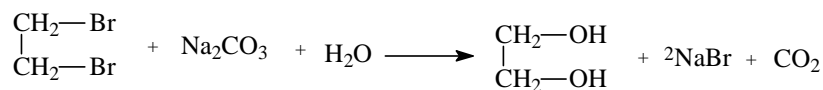
(b) With O<sub>2</sub> in presence of Ag :



(c) With HOCl followed by hydrolysis:



From 1, 2 dibromo ethane :




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### 1.10 PHYSICAL PROPERTIES OF DIHYDRIC ALCOHOL

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Dihydric alcohol viz; glycerol exhibits the following physical properties:

- (i) It is a colourless, syrupy liquid and sweet in taste. Its boiling point is  $197^{\circ}\text{C}$ . melting point  $-11.5^{\circ}\text{C}$
- (ii) It is miscible in water and ethanol in all proportions but is insoluble in ether.
- (iii) It is toxic as methanol when taken orally.
- (iv) It is widely used as a solvent and as an antifreeze agent.

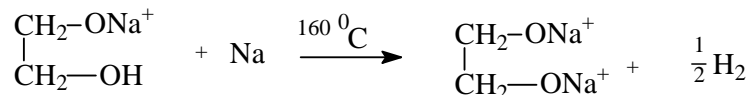
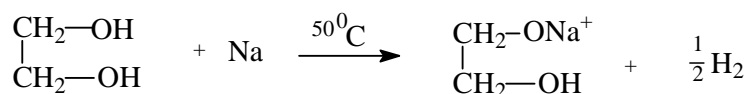
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### 1.11 CHEMICAL REACTIONS OF VICINAL GLYCOLS

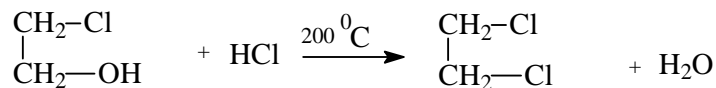
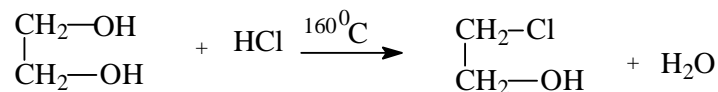
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Glycerol molecule is made up of two  $1^{\circ}$  alcohol groups joined together its chemical reactions are, therefore those of  $1^{\circ}$  alcohols twice over viz;

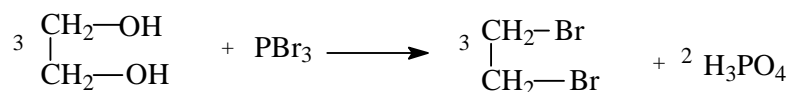
1. Action of Sodium: It reacts with Na at  $50^{\circ}\text{C}$  to form to form mono and dialkoxide at elevated temperature.



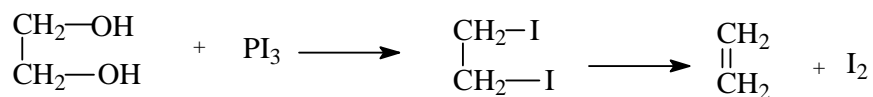
2. Reaction with HCl: Ethylene dichloride is formed in two successive steps at elevated temperature



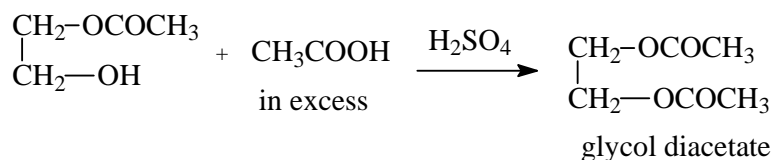
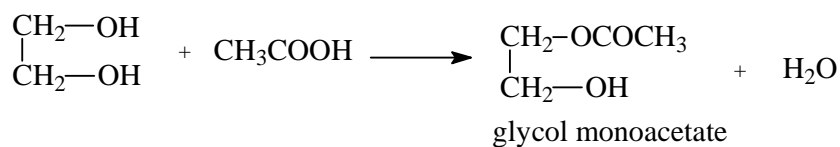
3. Action with phosphorus halides : ethylene dihalides are formed as follow:



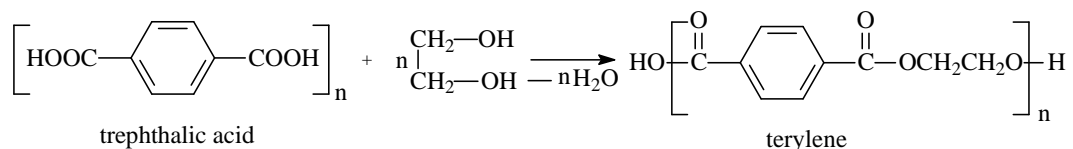
PI<sub>3</sub> produce ethylene diiodide which is unstable and split into I<sub>2</sub> and ethylene



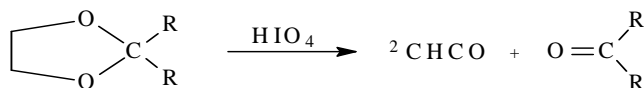
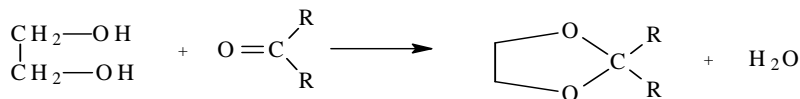
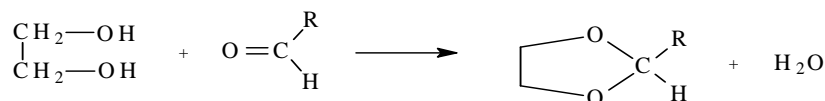
4. Reaction with carboxylic acid: Gives diester depending upon the amount of glycol and acid taken:



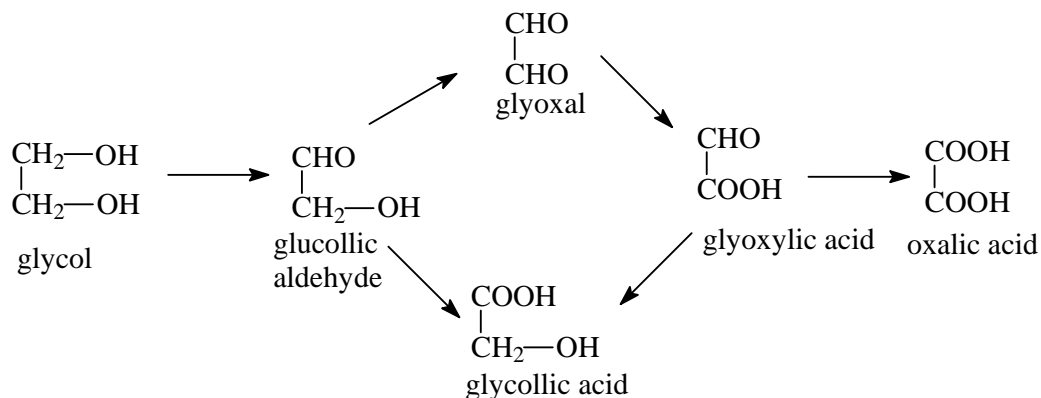
With dibasic acid it form polymer:



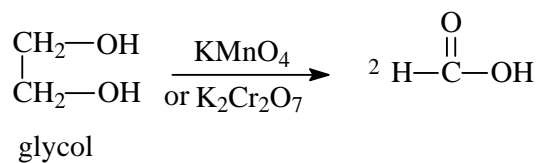
5. Reaction with aldehyde and ketones: Glycol reacts with aldehyde and ketones in presence of p- toluene sulphonic acid to give cyclic acetals/ketals which further may give ketone/aldehyde while treating with HIO<sub>4</sub>. This reaction thus can be useful to protect carbonyl group.



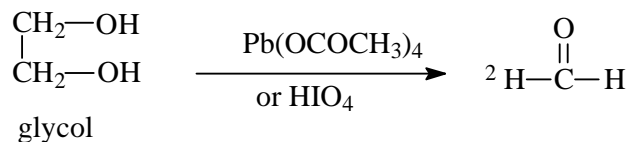
6. (i) The oxidation of ethylene glycol with  $\text{HNO}_3$  to yields a number of substances as follow:



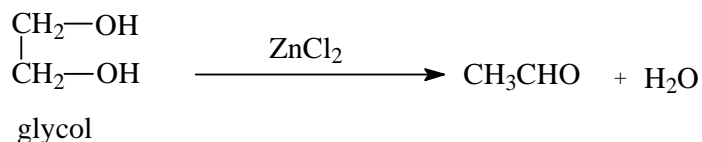
- (ii) Oxidation with  $\text{KMnO}_4$  or  $\text{K}_2\text{Cr}_2\text{O}_7$  to form formic acid:



- (iii) Oxidation with  $\text{Pb}(\text{OCOCH}_3)_4$  or  $\text{HIO}_4$  glycol gives formaldehyde.



7. Dehydration: (i) Heating with  $\text{ZnCl}_2$  glycol gives acetaldehyde

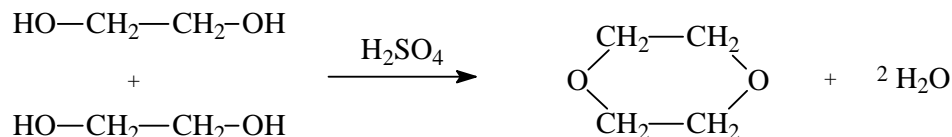


- (ii) When heated alone at  $500^\circ\text{C}$ , it gives ethylene oxide.



- (iii) Dioxane is obtained when glycol is heated with conc.  $\text{H}_2\text{SO}_4$ .





### Uses of ethylene glycol:-

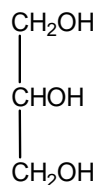
1. It is used as antifreeze substance which prevents the freezing of water in car radiators in cold countries.
2. Due it has a high viscosity, so it is used in the hydrolic break , printing ink ball, pen inks, organic solvents .
3. Used in the manufacture of Dacron, dioxane etc.
4. As a solvent and as a preservatives.
5. As a cooling agent in aeroplanes.
6. As an explosives in the form of dinitrate.
7. Large amounts of ethylene glycol are converted to polymers ( such as polyethylene glycol ) used in The manufacture of dacron fibers ,photographic films and cassette tapes.

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## 1.12 TRIHYDRIC ALCOHOL

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It is a triol. The introduction of third –OH group in diol molecule raises the b.p. about 100<sup>0</sup>C, increase viscosity and make the alcohol more sweet. Viz; glycerol



It is desigbated as prop-1, 2, 3-triol in IUPAC nomenclature. It may be considered as derivative of propane, obtained by replacement of three hydrogen atoms from different

carbon atoms by three hydroxyl group. In industry, it's known as glycerine. It occurs as glycosides in almost all animal and vegetable oils and fats.

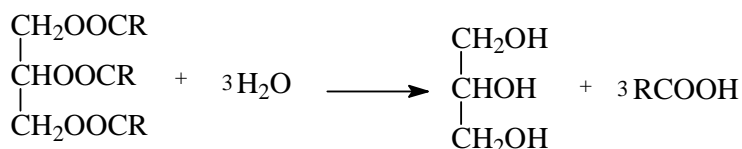
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### 1.13 METHODS OF PREPARATION

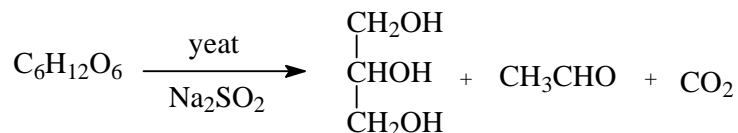
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Glycerol can be synthesized by following different methods:

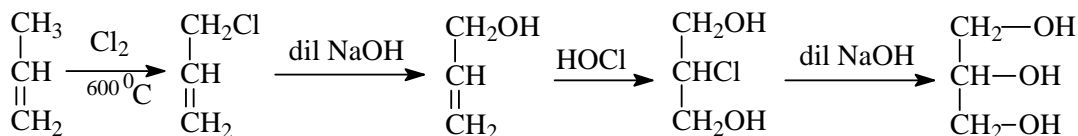
1. **From fats and oil:** On hydrolysis of fats and oils, glycerol and higher fatty acids are formed.



2. **By fermentation of sugars:** Alcoholic fermentation of sugar in the presence of sodium sulphite gives good yield of glycerol.



3. **Synthesis (from propene):** Today much of glycerol is obtained from propene.



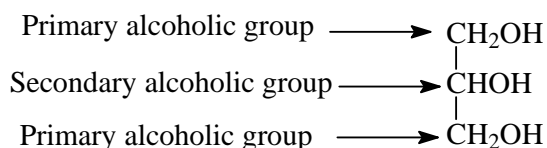
**Physical properties:** Glycerol is a colourless, odourless, viscous and hygroscopic liquid, sweet in taste and non-oxic in nature. It is soluble in water and ethyl alcohol but insoluble in ether. It has high boiling point, i.e., 290°C. The high viscosity and high boiling point of glycerol are due to association through hydrogen bonding purified in the lab by reduced pressure distillation or vacuum distillation.

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### 1.14 CHEMICAL REACTIONS

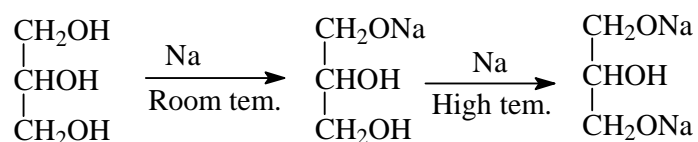
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Glycerol molecule contains two 1<sup>o</sup> – OH groups and one 2<sup>o</sup> – OH group. Thus, it shows characteristics of both primary and secondary alcohols.

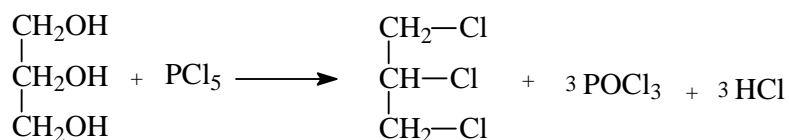


In general,  $1^{\circ}$  – OH groups are more reactive than  $2^{\circ}$  – OH group.

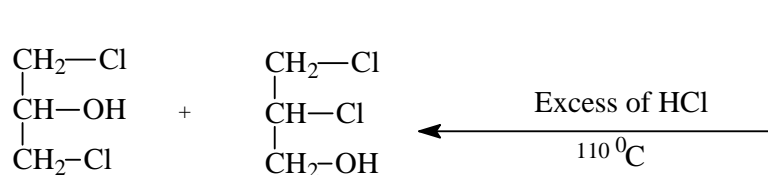
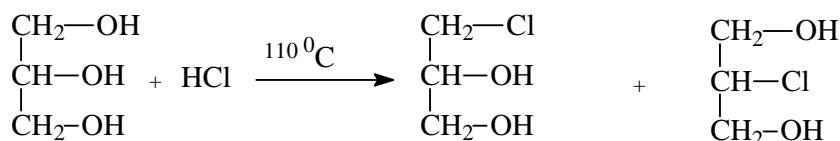
1. Reaction with sodium: Only primary alcoholic groups are attacked one by one and secondary alcoholic group is not attacked, Sodium forms monosodium glycerolate at room temperature and disodium glycerolate at higher temperature.



2. Reaction with  $\text{PCl}_5$ : All three OH groups are replaced by Cl atoms.



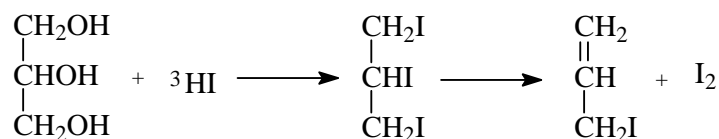
3. Reaction with HCl or HBr: When HCl is passed into glycerol at  $110^{\circ}\text{C}$ , both,  $\alpha$  or  $\beta$  glycerol monochlorohydrins are formed. If the HCl gas is passed for sufficient time, glycerol  $\alpha, \alpha'$  dichlorohydrin and glycerol,  $\alpha, \beta$ - dichlorohydrin are formed.



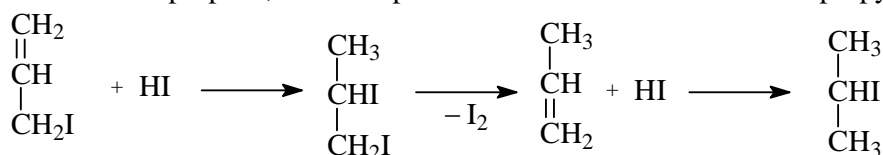
Same reactions occur with HBr.

4. Reaction with HI: Glycerol reacts with HI in two ways:
  - (a) When glycerol is warmed with a small amount of hydrogen iodide, allyl iodide is

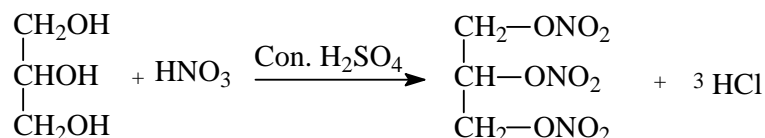
formed. First tri iodide is formed but due to large size of iodine atom  $I_2$  comes out from product.



(b) When glycerol is heated with a large amount of HI, the allyl iodide first formed is reduced to propene, which in presence of excess of HI forms iso-propyl iodide.

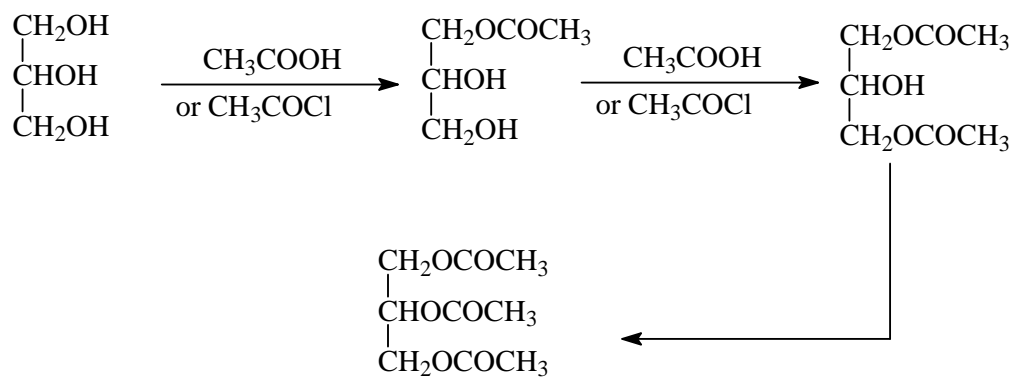


5. Reaction with  $\text{HNO}_3$ : When one part of glycerol in a thin stream is added to three times conc.  $\text{HNO}_3$  and five parts of concentrated sulphuric acid, nitro-glycerine (glyceryl trinitrate) is formed.



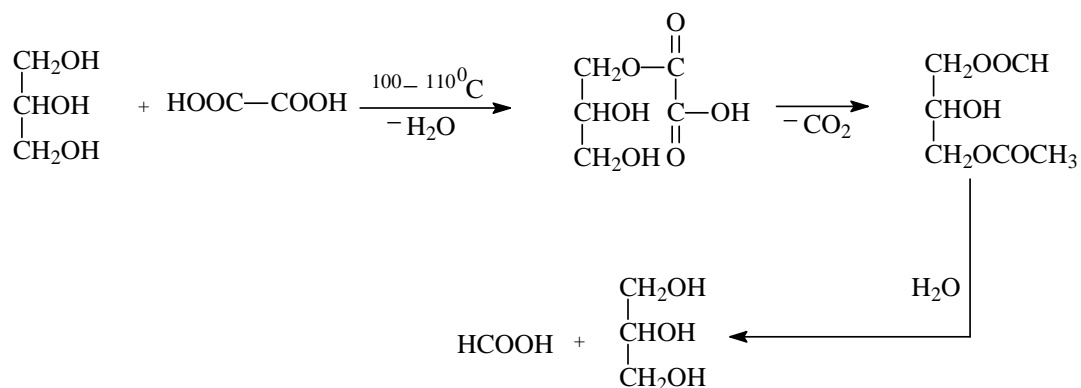
Glyceryl trinitrate is a yellow oily liquid. It is poisonous and causes headache. It explodes violently when heated rapidly or subjected to sudden shock. It becomes a safer explosive when absorbed on kieselguhr. In this form, it is known as **dynamite**. Dynamite was discovered by Alfred Nobel in 1867.

6. Reaction with acetic acid, acetic anhydride or acetyl chloride: Mono-, di- and tri-esters are formed.

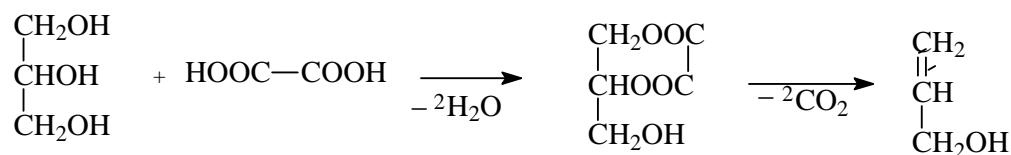


7. **Reaction with oxalic acid:** Different products are formed under different conditions.

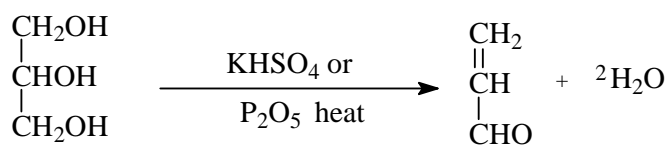
(a) At 100<sup>0</sup>C and with excess of oxalic acid, formic acid is formed



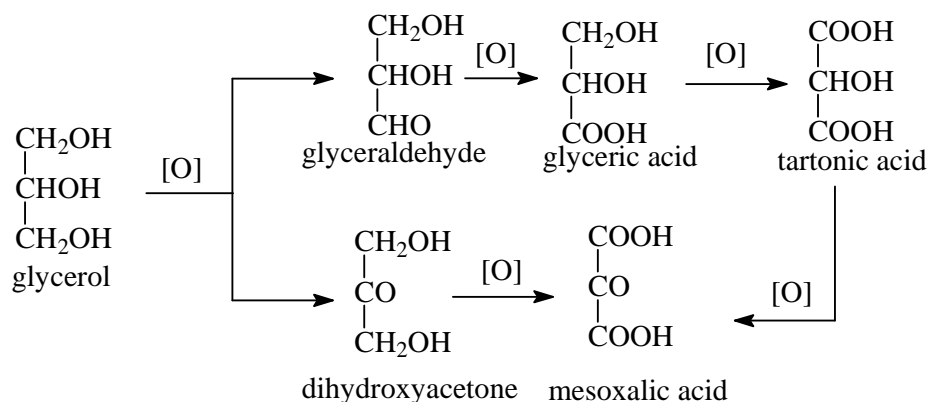
(b) At 260<sup>0</sup>C allyl alcohol is formed



8. **Dehydration:** Glycerol when heated alone or with dehydrating agents such as potassium hydrogen sulphate or phosphorus penta oxide or conc. sulphuric acid, acrolein or acrylaldehyde is formed which has a characteristic bad smell. This reaction can be used as a test of glycerol.

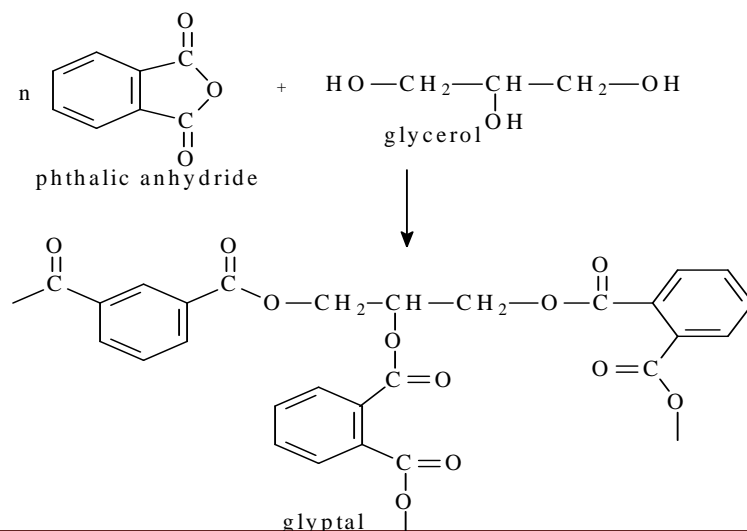


9. **Oxidation:** Glycerol gives different oxidation products depending on the nature of oxidizing agent. The following products may be obtained during oxidation of glycerol.



- (a) Dilute HNO<sub>3</sub> gives mainly glyceric acid.
- (b) Conc. HNO<sub>3</sub> oxidises glycerol into glyceric acid and tartronic acid.
- (c) Bismuth nitrate gives mainly meso oxalic acid.
- (d) Fenton's reagent (H<sub>2</sub>O<sub>2</sub> + FeSO<sub>4</sub>) or NaOBr or Br<sub>2</sub>- water in presence of Na<sub>2</sub>CO<sub>3</sub> oxidises glycerol into a mixture of glyceraldehyde and dihydroxy acetone (or glycerose).

10. Formation of resin: Glycerol reacts with phthalic anhydride forming polyesters known as glyptals. Each of the three -OH groups in glycerol forms an ester linkage with the anhydride, giving a thermosetting polymer (plastic) used for making synthetic fibers.



**Uses:** Glycerol is used: Glycerol is used as a sweetening agent in confectionery, beverages and medicines being non-toxic in nature. It is used as antifreeze in automobile radiators, in the preparation of good quality of soap, hand lotions, shaving creams, tooth pastes and cosmetics and as a lubricant in watches and preservative.

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### 1.15 SUMMARY

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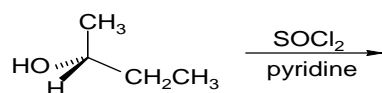
In this unit we have learnt that: Alcohols are compounds in which a hydrogen of alkane has been replaced by an –OH group and are classified as monohydric, dihydric, trihydric or polyhydric on the basis of –OH group present. The monohydric alcohols can be classified into 1°, 2° and 3° alcohols. In IUPAC name alcohols are designated as alkannol by replacing ‘e’ with –ol from the corresponding alkane. This unit also describes the methods of preparation of alcohols by using different methods like; hydrolysis of halogenoalkanes, hydration of alkene, reduction of aldehydes and ketones using Grignard reagents (RMgX), LiAlH<sub>4</sub>, NaBH<sub>4</sub>, by fermentation of carbohydrates etc. The amphoteric nature of alcohols has also been described in this unit. As an acid, it ionizes to form an alkoxide ion (RO<sup>-</sup>) and hydrogen ion, H<sup>+</sup> in the presence of a base, while in presence of an acid, the alcohol may function as a base and can accept a proton. This unit makes the readers aware about methods of preparation, physical properties and chemical reactions along with applications of dihydric alcohol glycol and trihydric alcohol glycerol.

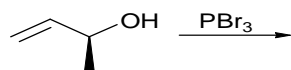
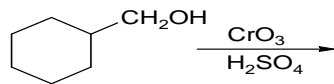
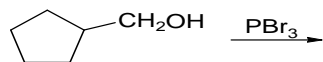
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### 1.16 TERMINAL QUESTION

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- Q. 1. Explain why Alcohols are acidic in nature.
- Q. 2. Write the mechanism of dehydration of ethyl alcohol with conc. H<sub>2</sub>SO<sub>4</sub>.
- Q. 3. Why boiling point of alcohols is higher than that of alkanes of corresponding molecular weight.
- Q. 4. Explain why polarity of primary alcohol is maximum? Q.5. Write the major product(s) of the following reaction.





Q.6. Write short note on:-

1. Saytzeff's rule
2. Glyptal
3. Amphoteric nature of alcohols
4. Synthesis of glycerol
5. Applications of glycol and glycerol
6. Classification of monohydric alcohols
7. Oxidation of glycol and glycerol

Q.8. Tick the appropriate option (MCQs)

1. Ethanol containing some methanol is called

- |                    |                      |
|--------------------|----------------------|
| A. Absolute spirit | B. Rectified spirit  |
| C. Power alcohol   | D. Methylated spirit |

2. Glycerol is a:

- |                      |                       |
|----------------------|-----------------------|
| A. Primary alcohol   | B. Monohydric alcohol |
| C. Secondary alcohol | D. Trihydric alcohol  |

3. Which of the following can work as a dehydrating agent for alcohols?

- |                            |                            |
|----------------------------|----------------------------|
| A. $\text{H}_2\text{SO}_4$ | B. $\text{Al}_2\text{O}_3$ |
|----------------------------|----------------------------|



C.H<sub>3</sub>PO<sub>4</sub>

D. All.

4. Primary and secondary alcohols on action of red hot copper give

A. Aldehydes and ketons respectively

B. Ketones and aldehydes respectively

C. Only aldehydes

D. Only ketones

5. Which one has highest boiling point?

A. Butan-2-ol

B. Ethane

C. Butane

D. Pentane

6. Which of the following has maximum hydrogen bonding?

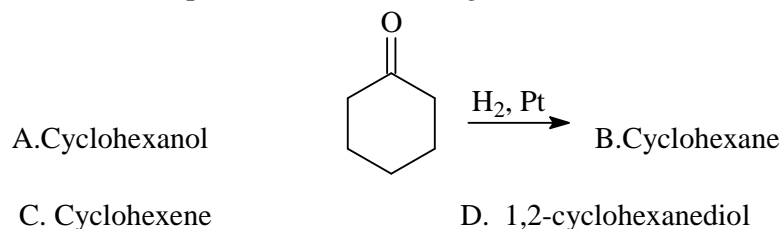
A. Ethyl amine

B. Ammonia

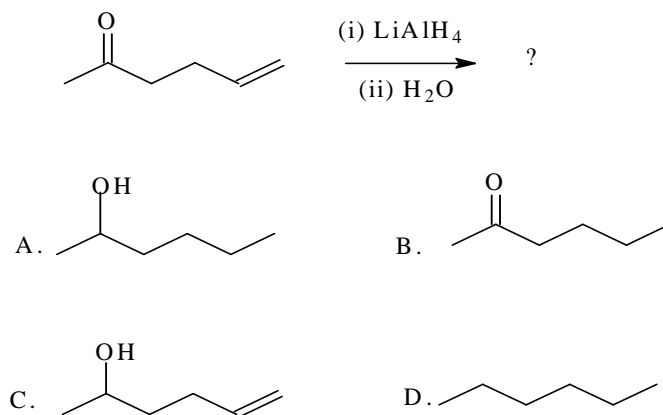
C. Ethyl alcohol

D. Diethyl ether

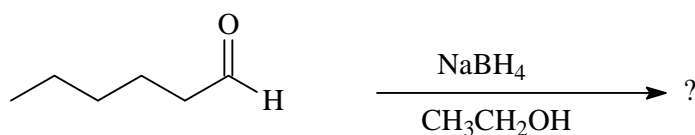
7. What is the product of the following reaction?



8. What is the product of the following reaction?

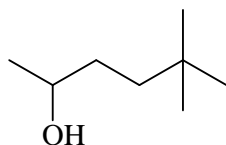


9. What is the product in following reaction?.



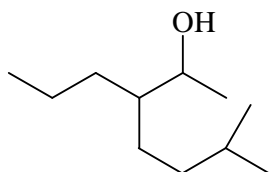
- A. CCCCCC(=O)O      B. CCCCCC=C  
 C. CCCCCCO      D. CCCCCC

10. What is the IUPAC name of the compound below?



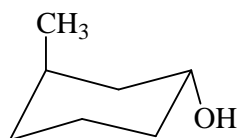
- A. 5,5 – dimethyl-2-hexanol      B. 5,5-dimethyl- 2- pentanol  
 C.2,2- dimethyl-5-hexanol      D. 2,2-dimethyl-5-pentanol

11. What is IUPAc name of the following compound ?



- A. 3-isobutyl-2-hexanol      B. 2-methyl-5-propyl-6-heptanol  
 C. 2-methyl-5-(1-hydroxyethyl)octane      D. 6-methyl-3-propyl-2-heptanol

12. What is the IUPAC name of the following compound?



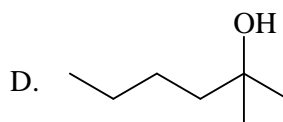
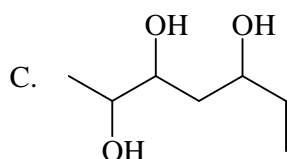
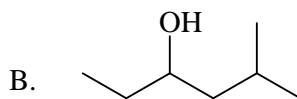
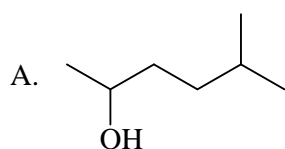
A. *cis*-3-methylcyclohexanol

B. *cis*-5-methylcyclohexanol

C. *trans*-3-methylcyclohexanol

D. *trans*-5-methylcyclohexanol

13. Identify the tertiary alcohol.



14. What is the hybridization of the oxygen atom in alcohols?

A.  $sp$

B.  $sp^2$

C.  $sp^3$

D.  $sp^3d$

15. The compound found in Whisky, Brandy & Beer:

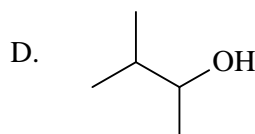
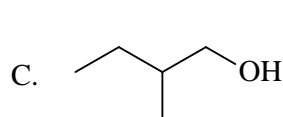
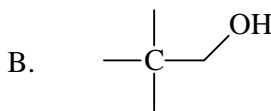
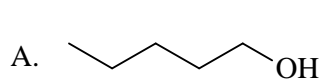
A.  $CH_3OH$

B.  $CH_3CH_2OH$

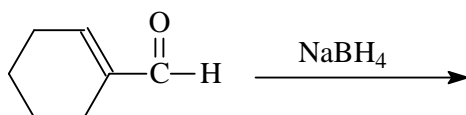
C.  $CH_3CH_2CH_2OH$

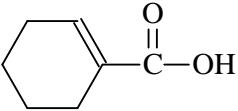
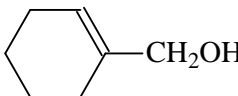
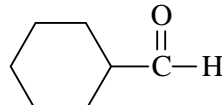
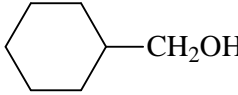
D.  $CH_3CH_2CH_2CH_2OH$

16. Which of these five-carbon alcohols would you expect to be most water soluble?

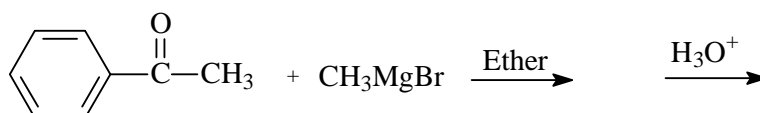


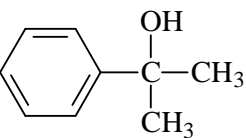
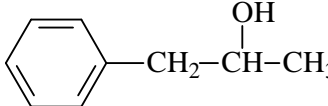
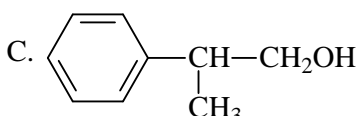
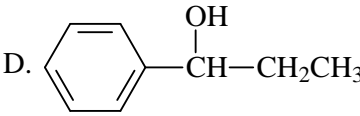
17. Which is the major product of the following reaction?



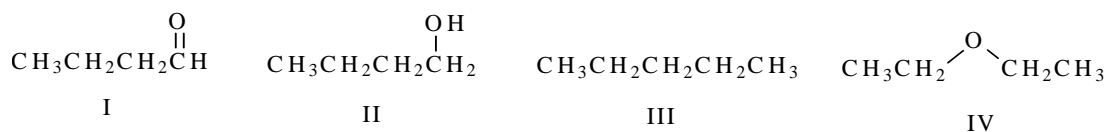
- A.  B. 
- C.  D. 

18. Which is the major product of the following reaction?



- A.  B. 
- C.  D. 

19. Arrange the compounds in order of increasing solubility in water (least first).



- A. II, I, IV, III      B. I, II, IV, III
- C. III, IV, I, II      D. II, I, IV, III

20. Dynamide is:

- A. Nitroderivative of glycerol                      B. Nitro derivative of glycol  
C. Acetyl derivative of glycerol                      D. Acetyl derivative of glycol

---

**1.17 ANSWERS(MCQs):**

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2.D	2.D	3.D	4.A	5.A	6.C	7.C	8.C
9.C	10.A	11.D	12.C	13.D	14.C	15.B	16.B
17.B	18.A	19B	20.B				

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**1.18 REFERENCES**

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2. P.S. Kalsi, Organic Reactions and their Mechanisms, 2<sup>nd</sup> edition, New age International Publishers. 2017
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**UNIT -2 PHENOLS**

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**CONTENTS:**

- 2.1 Objectives
- 2.2 Introduction
- 2.3 Nomenclature
- 2.4 Methods of preparation of phenols
- 2.5 Commercial preparation of phenols
- 2.6 Physical properties of phenols
- 2.7 Acidic character of phenols
- 2.8 Chemical reactions of phenols
- 2.9 Substituted phenols
- 2.10 Summary
- 2.11 Terminal questions
- 2.12 Answers (MCQs)
- 2.13 References

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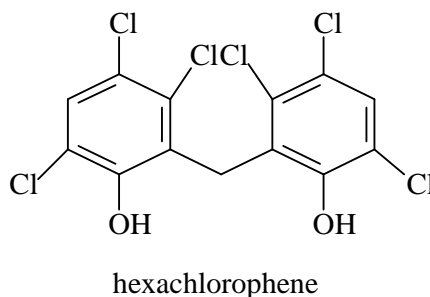
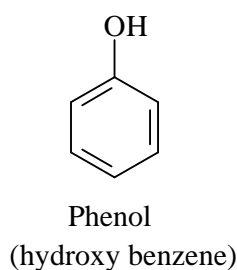
***OBJECTIVES***

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The objectives of this unit are to study the structure and bonding of phenol. To study physical and chemical properties of phenols, their acidic characters. Besides these objectives this unit will make aware the students about general methods of preparation of phenols, comparative acidic characters with alcohols, various chemical reactions, characteristic electrophilic substitution reactions and some name reactions involving phenols.

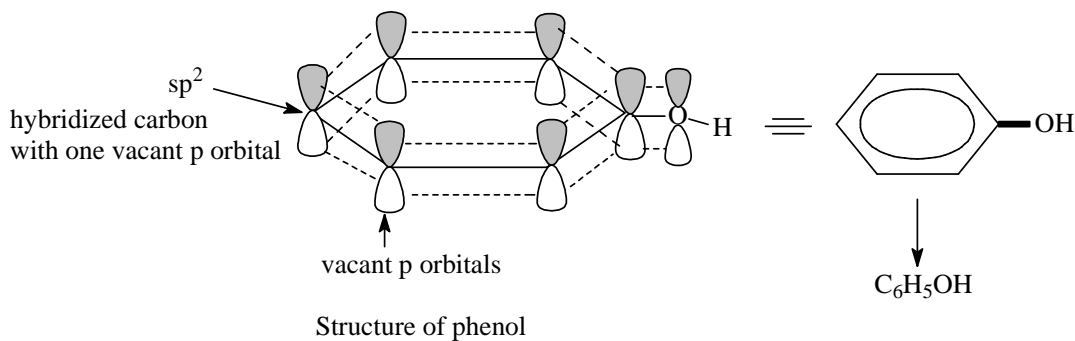
## 2.2 INTRODUCTION

Phenols are compounds in which the -OH group is directly attached to an aromatic carbon like benzene ring. Although they share the same functional group with alcohols, where the -OH group is attached to an aliphatic carbon, the chemistry of phenols is very different from that of alcohols. The simplest phenol is hydroxybenzene also called phenol with formula  $C_6H_5OH$ . Simple phenol is an antiseptic. A phenolic compound hexachlorophene is a constituent of several mouthwashes, deodorant soaps and medicinal skin cleansers.

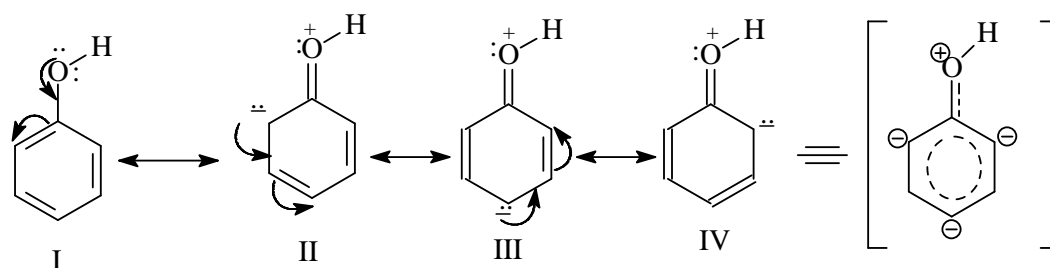


The -OH group consists of an **O** atom bonded to a  $sp^2$ -hybridised aromatic **C** atom and a **H** atom via  $\sigma$  bonds as follow. Both the **C-O** and the **O-H** bonds are polar due to the high electronegativity of the **O** atom. Conjugation exists between an unshared electron pair on the oxygen and the aromatic ring.

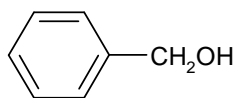
This results in, compared to simple alcohols: - A shorter carbon-oxygen bond distance,  
a more basic hydroxyl oxygen, a more acidic hydroxyl proton (-OH)



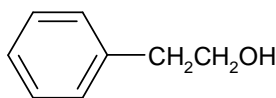
The electronic structure of phenol can be represented as resonance hybrid of the following canonical forms.



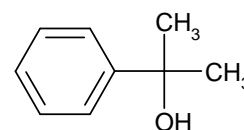
It must be noted that the aromatic compounds in which -OH group is not directly attached to benzene ring are not phenols but are called aromatic alcohols. These may be regarded as aryl derivatives of aliphatic alcohols.



Benzyl alcohol



2-Phenylethanol



2-Phenylpropanol

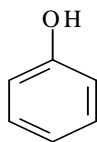
## 2.3 NOMENCLATURES

Functional group suffix = *-common - phenol, systematic - benzenol*

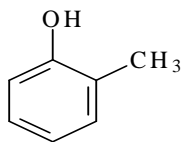
Functional group prefix = *hydroxy*

The hydroxyl derivatives of toluene have been given the name CRESOLS. If a phenolic moiety is included in a molecule which is named by IUPAC system, the -OH group is specified as a substituent according to the order of precedence. In such a case a substituent (COOH or -CHO) is assigned number-1. The systematic and common names of some phenols have been illustrated as follow.

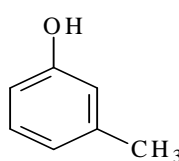
### MOHOLYDRIC PHENOLS:



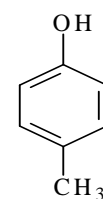
phenol



2 - methylphenol

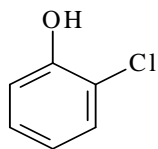


3 - methylphenol

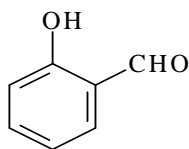


4 - methylphenol

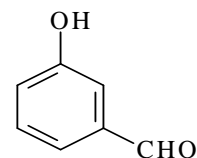




2-chlorophenol  
2-chloro-1-hydroxybenzene

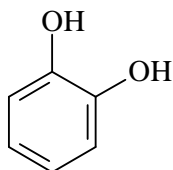


2-hydroxybenzaldehyde  
ortho hydroxybenzaldehyde

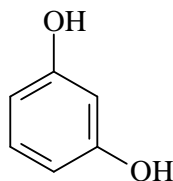


3-hydroxybenzaldehyde  
meta hydroxybenzaldehyde

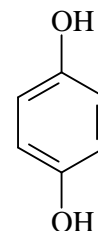
**DIHYDRIC PHENOLS:**



1,2-dihydroxybenzene  
catechol

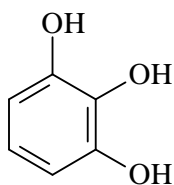


1,3-dihydroxybenzene  
resorcinol

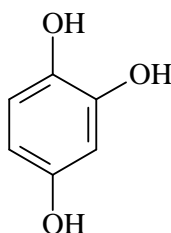


1,4-dihydroxybenzene  
hydroquinone

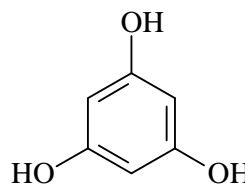
**TRIHYDRIC PHENOLS:**



1, 2, 3-trihydroxybenzene  
pyrogallol

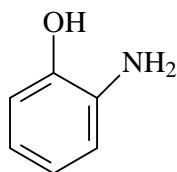


1, 2, 4-trihydroxybenzene  
hydroxyquinone

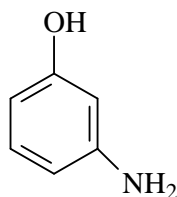


1, 3, 5-trihydroxybenzene  
phloroglucinol

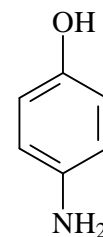
The prefix ortho, meta and para are also used in place of 2, 3 and 4 while naming monohydrin substituted phenols or cresols



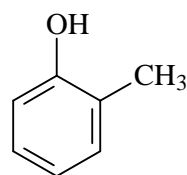
ortho amino  
phenol



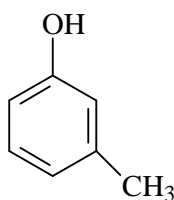
meta amino  
phenol



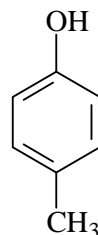
para amino  
phenol



ortho cresol



meta cresol



para cresol

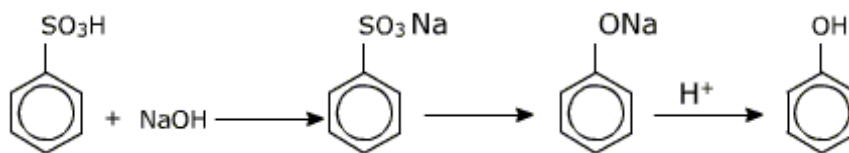
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## 2.4 METHODS OF PREPARATION OF PHENOLS

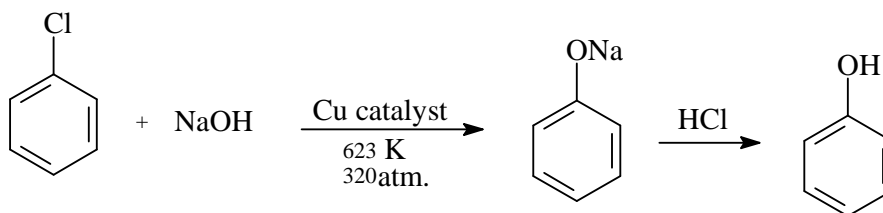
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There are many methods which are used to prepare phenols viz;

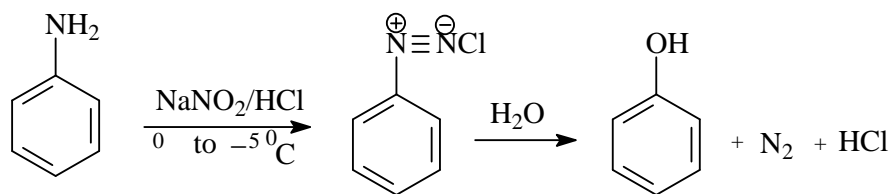
**1. From aryl sulphonic acids:** An aryl sulphonic acid yields the corresponding phenol on heating it with molten sodium hydroxide at 570 - 620<sup>0</sup> K. The sodium salt is obtained which is hydrolysed with acid to obtain free phenol.



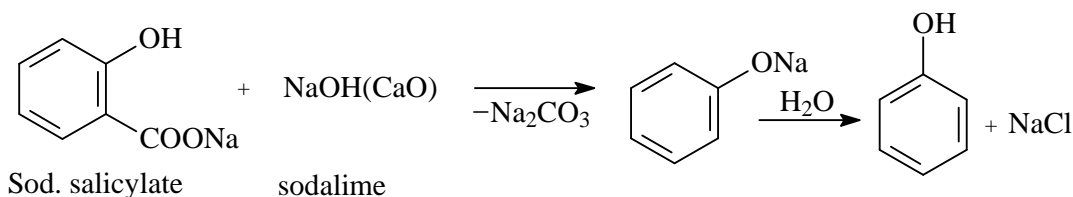
**2. From haloarenes:** Chlorobenzene (an haloarene) is hydrolysed by treating it with 10% NaOH at 623<sup>0</sup> K and 320 atmospheric pressure in presence of Cu catalyst. Phenol is obtained by acidification of sodium phenoxide.



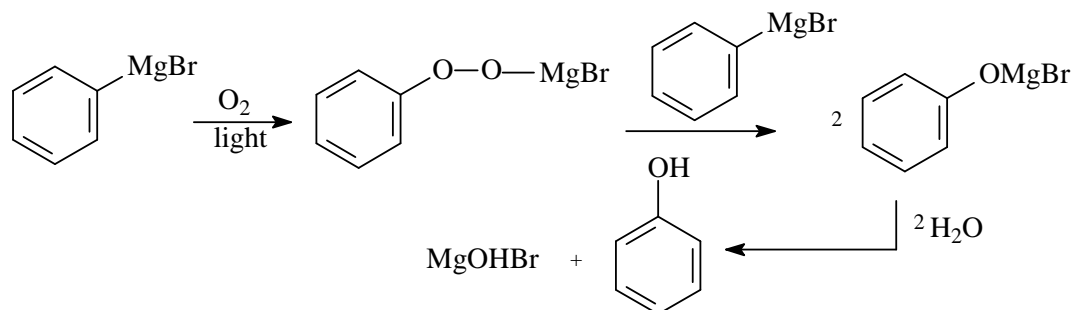
**3. Hydrolysis of diazonium salts:** A diazonium salt is formed by treating an aromatic primary amine with nitrous acid (obtained from a mixture of NaNO<sub>2</sub> and HCl) at low temperature of 273<sup>0</sup> K to 278<sup>0</sup> K. Diazonium salts are hydrolysed to phenols treating with dilute acids.



**4. Decarboxylation of phenolic acids:** Phenolic acids upon distillation with sodalime are decarboxylated to form sodium phenoxide, which upon hydrolysis gives phenols.



**5. Oxidation of Grignard reagent followed by hydrolysis:** Aromatic Grignard reagent on treating with  $\text{O}_2$  in presence of light followed by hydrolysis in presence of mineral acid gives phenol.

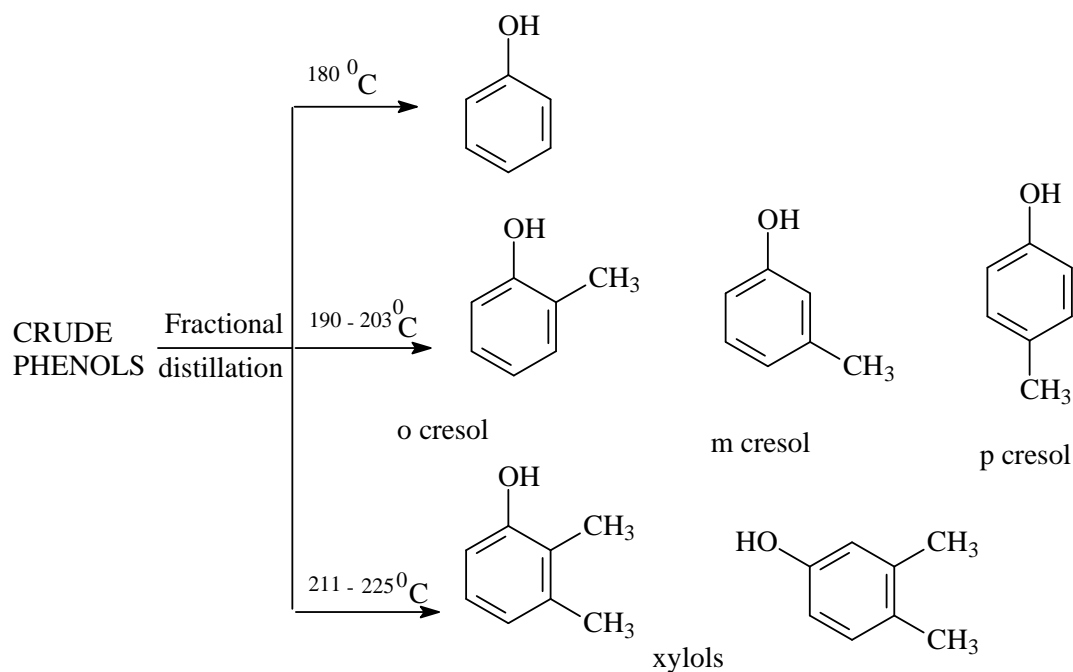
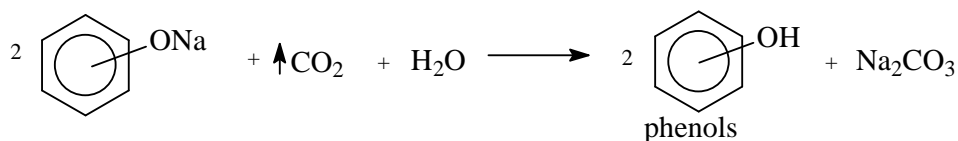
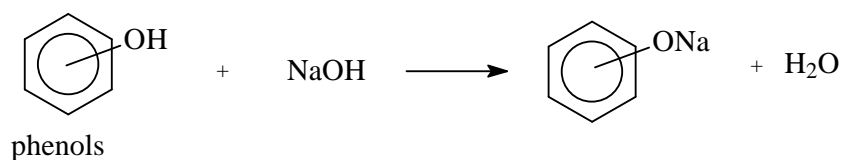


## 2.5 COMERCIAL PREPARATION OF PHENOLS

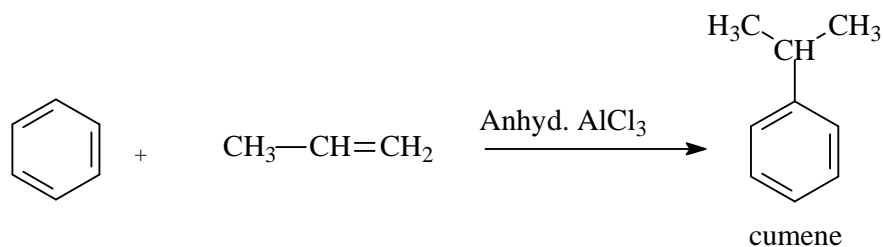
Phenols are important class of compounds used commercially for many purposes and need commercial synthesis in pilot scale. Still some amount of phenols are obtained from coal-tar, however about 90% are produced synthetically in industries.

1. From coal-tar: generally heavy and middle oil containing phenols and naphthalene in crude oil are subjected to extra cooling as a result the naphthalene crystals are separated and are removed by filtration. The remaining fraction is treated with NaOH, which dissolves the phenols by making phenoxides. Ultimately carbon dioxide gas is blown through the solution in order to liberate phenols. The water layer containing  $\text{Na}_2\text{CO}_3$  is

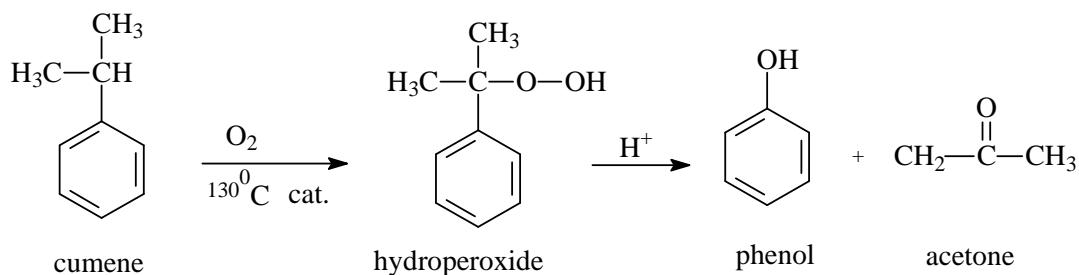
drawn off, leaving crude phenol behind, which is fractionated to recover the individual phenols as follow



2. From cumene: Commercially phenol can be synthesised from cumene, which in turn is prepared from petroleum using Friedal Craft reaction as follow.

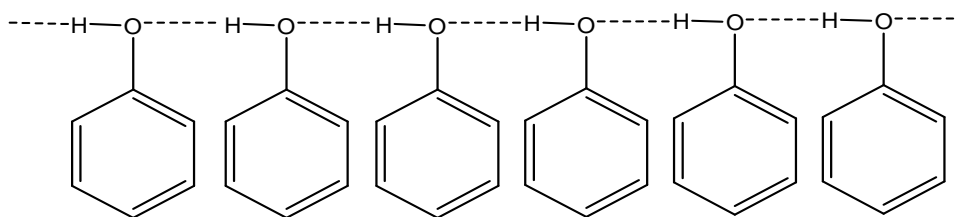


The cumene obtained from petroleum as above is oxidised at  $130^{\circ}\text{C}$  in presence of metal catalyst, which gives phenol as the ultimate product by involving the intermediate compounds in sequence as follow.



## 2.6 PHYSICAL PROPERTIES OF PHENOLS

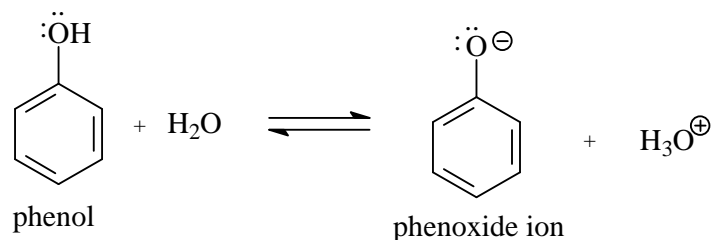
Phenol has higher boiling point than the arenes or haloarenes or ethers of same molecular weight. It is due to the formation of intermolecular hydrogen bond. Pure phenol is a white crystalline solid, smelling of disinfectant. It has to be handled with great care because it causes immediate white blistering to the skin. The crystals are often rather wet and discolored. Phenols are sparingly soluble in water but readily soluble in organic solvents such as alcohol and ether. The boiling points of phenols increase with increase in the number of carbon atoms (increase in van der Waals forces). The -OH group in alcohols and phenols is involved in intermolecular hydrogen bonding which is responsible for the high boiling point that is lacking in ethers and hydro carbons.



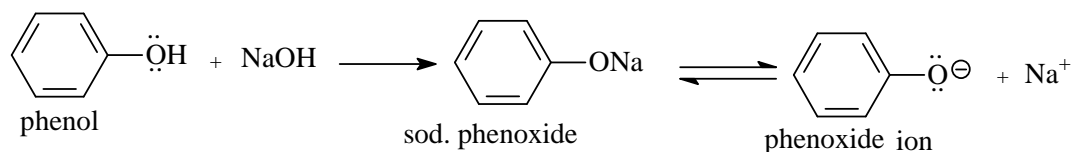
## 2.7 ACIDIC CHARACTER OF PHENOLS

Unlike alcohols (which also contain an -OH group) phenol is a strong acid. Phenols turn blue litmus red and react with metals liberating hydrogen. Phenols behave as acids because of the presence of more polar O-H group in them. They ionise in aqueous solutions and give  $\text{H}^+$  ions to a base. However they do not react with carbonates or bicarbonates.

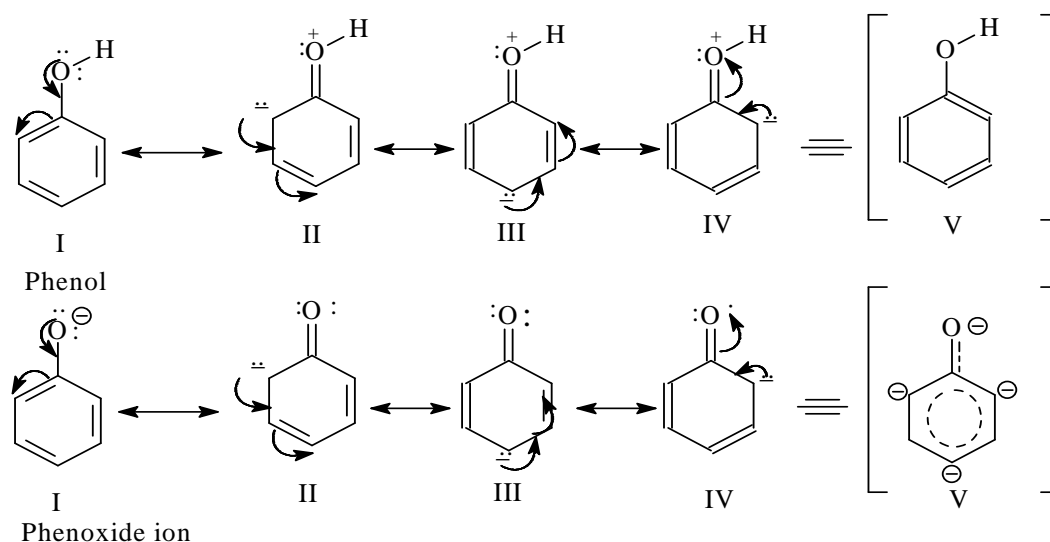
The greater acidity of phenols can be attributed to the resonance stabilisation of the phenoxide ion formed after losing hydrogen ion. The delocalisation of the negative charge over the benzene ring stabilises the phenoxide ion. No such stabilisation is possible, in case of alkoxide ions. Phenol is a very weak acid than carboxylic acid and the position of equilibrium lies well to the left.



Phenols as well as phenoxide ion both are resonance stabilised. The negative charge on the oxygen atom is delocalised around the ring. The benzene ring helps to stabilise a negative charge on the phenoxide ion,  $\text{C}_6\text{H}_5\text{O}^-$ , and this makes phenol appreciably acidic (unlike ethanol, which is neutral, a solution of phenol in water has a pH of about 5). The more stable the ion is, the more likely it is to form. Phenol reacts with aq. sodium hydroxide solution to give a colourless solution containing sodium phenoxide.

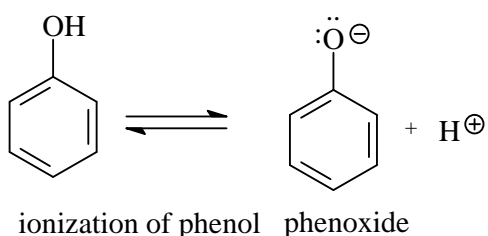
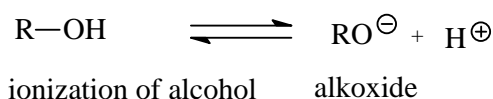


The various contributing structures of phenol and phenoxide ion are given below:



## Comparative acidic character of alcohols and phenols

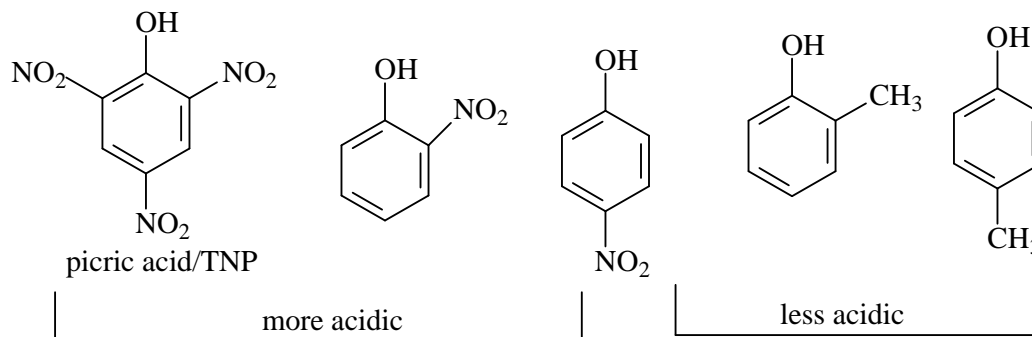
The ionisation of an alcohol and a phenol takes place as shown in equation:



In alkoxide ion, the negative charge is localised on oxygen while in phenoxide ion, the charge is delocalised. The delocalisation of negative charge (structures I-V) makes phenoxide ion more stable and favours the ionisation of phenol. The hydroxyl group, in phenol is directly attached to the  $sp^2$  hybridised carbon of benzene ring which acts as an electron withdrawing group. Due to this, the charge distribution in phenol molecule, as depicted in its resonance structures, causes the oxygen of -OH group to be positive. A compound in which hydroxyl group directly attached to an aromatic ring is more acidic than the one in which hydroxyl group is attached to an alkyl group. Acids react with the more reactive metals to give hydrogen gas. Alcohols and phenols react with active metals like Na, K, Al etc to liberate hydrogen gas. The reactions of phenol with metals as well as NaOH indicate it is relatively more acidic than alcohols and also water. The  $sp^2$  carbon of phenol attached to 'O' being more electronegative than  $sp^3$  carbon of alcohols, it decreases the electron density on oxygen. Because of this oxygen develops still more electron seeking character and releases proton by taking the shared pair of electrons with it.

**Effect of substituents on acidity of phenol:** In substituted phenols, the presence of electron withdrawing groups such as nitro group enhances the acidic strength of phenol. This effect is more pronounced when such a group is present at ortho and para positions. It is due to the effective delocalisation of negative charge in phenoxide ion. On the other hand, electron releasing groups, such as alkyl groups, in general, do not favour the

formation of phenoxide ion resulting in decrease in acid strength. Cresols, for example, are less acidic than phenol.

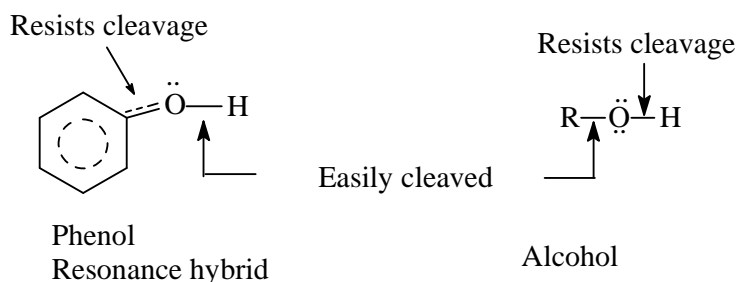


Electron releasing groups like alkyl groups increase the electron density on oxygen and decrease the polarity of O-H bond. This decreases the acidic strength. Hence alkylphenols have greater  $pK_a$  values as compared to phenol itself.

On the other hand, electron withdrawing substituents increase the acidity and phenols having these substituents ( $-\text{Cl}$ ,  $-\text{NO}_2$ , etc.) have lower  $pK_a$  values than phenol. In fact, 2,4,6-trinitrophenol / picric acid (TNP) is more acidic than many carboxylic acids.

## 2.8 CHEMICAL REACTIONS OF PHENOLS

Alcohols and phenols both contain  $-\text{OH}$  group attached with carbon but in case of phenols the carbon atom is member of phenyl ring as also shown above in resonating structures in phenols the C-O bond acquires double bond character because of delocalization of electrons from oxygen to phenyl ring, which results the C-O stronger than O-H  $\sigma$  bond. The increased electron density in the phenyl ring activates it and gives electrophilic substitution reaction.





In alcohols no resonance is possible and the non bonded electron pairs remain localized on the oxygen atom. The C-O linkage thus retains its  $\sigma$ -bond character and is weak as compared to that in phenol.

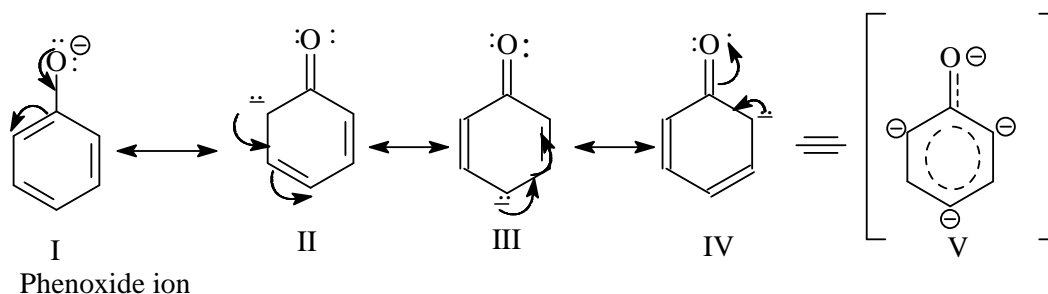
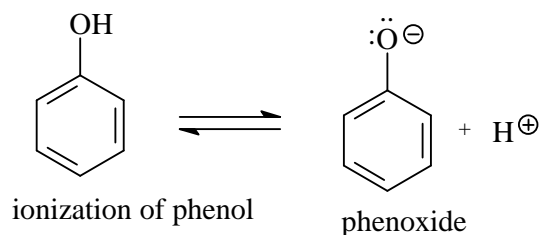
Phenols thus undergo two types of reactions:

A. Reaction involving the  $-OH$  group

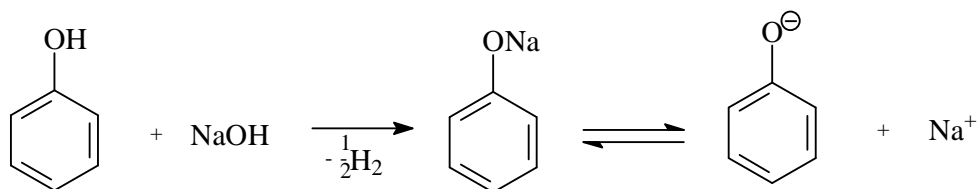
B. Reaction involving aromatic ring

A. Reactions involving  $-OH$  group:

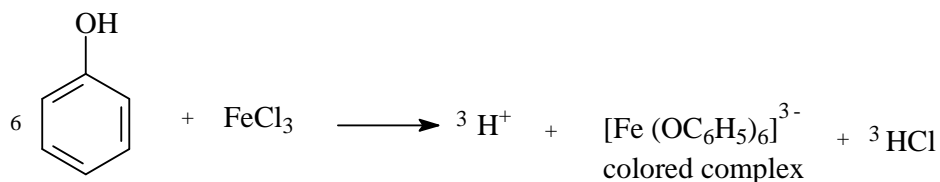
1. Acidic character: Phenols are acidic compared to alcohols as they furnish proton to form phenoxide ion which is stabilized by resonance. Acidity of phenol is less than carboxylic acids.



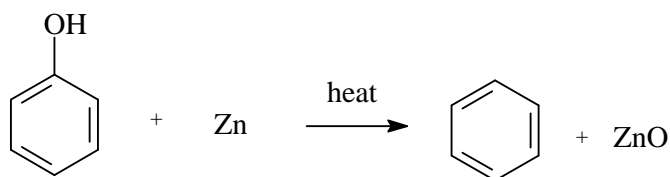
Phenols when react with aq.  $\text{NaOH}$  or  $\text{KOH}$  (but with  $\text{Na}_2\text{CO}_3$ ) to form soluble sodium salt known as phenoxides.



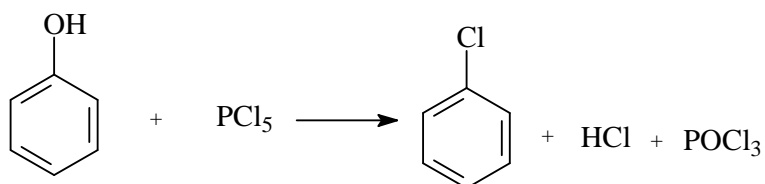
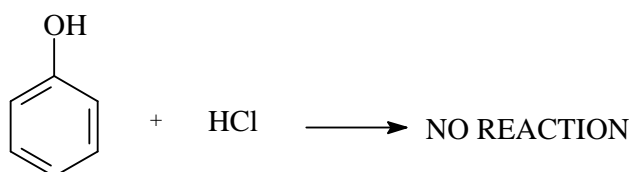
2. Reaction with  $\text{FeCl}_3$ : Phenols give colored complex when react with ferric neutral chloride solution



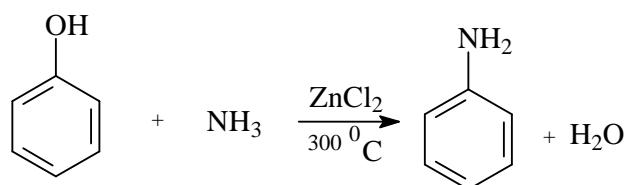
3. Replacement of  $-\text{OH}$ : When distilled with Zn dust, the  $-\text{OH}$  group is replaced by hydrogen atom.



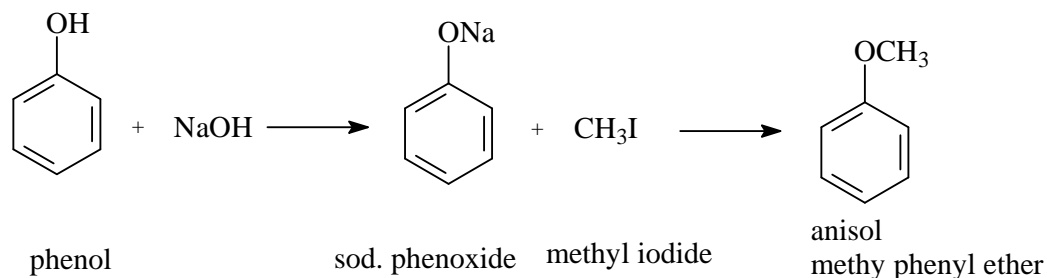
4. Replacement of  $-\text{OH}$  by halogens: unlike alcohols  $-\text{OH}$  group cannot be replaced by alkyl halids; however halogen derivatives are obtained by treating with  $\text{PBr}_3$  or  $\text{PCl}_5$



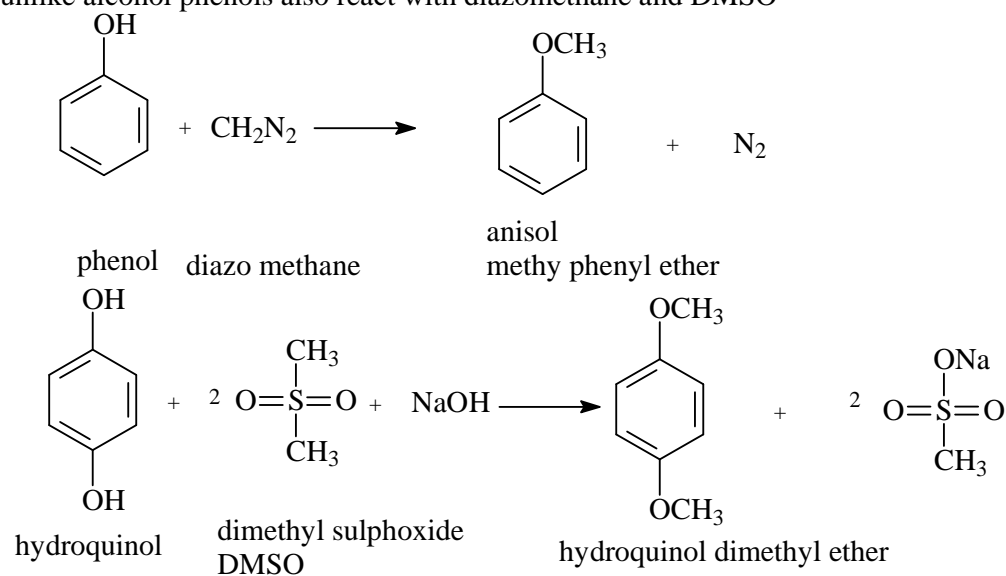
5. Replacement by  $-\text{NH}_2$  function:



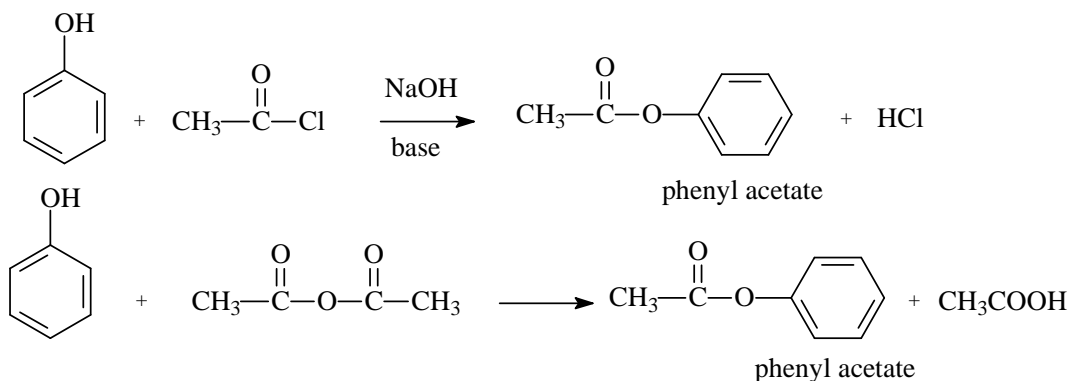
6. Ether formation: The sodium phenoxide of phenol undergoes Williamson synthesis and reacts with alkyl halides to give ether.



unlike alcohol phenols also react with diazomethane and DMSO

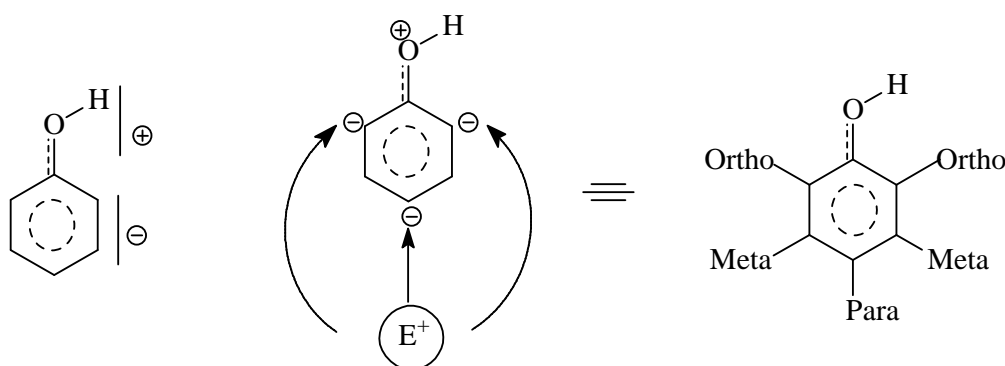


7. Esterification:



Phenols cannot be esterified directly by using carboxylic acid in presence of mineral acids. This is because of less nucleophilic oxygen of the phenol compared to alcohols

B. Reactions involving aromatic ring: The aromatic ring in phenols generally undergo electrophilic substitution reaction in which the hydroxyl group is a powerful activating group and hence phenols readily undergo electrophilic substitution reactions. Phenol is more reactive than benzene towards electrophilic reagents because there is an interaction between the lone pairs on the oxygen atom in —OH or —O and the ring; which increase the availability of electrons in the aromatic ring. Also, it directs the incoming group to ortho and para positions in the ring as these positions become electron rich due to the resonance effect caused by -OH group. In this reaction, an **electrophile** (electron loving species) attacks the benzene ring and replaces one of its hydrogen atoms. Since the *ortho* and *para* positions of the phenol are electron rich, the substitution takes place at these positions.



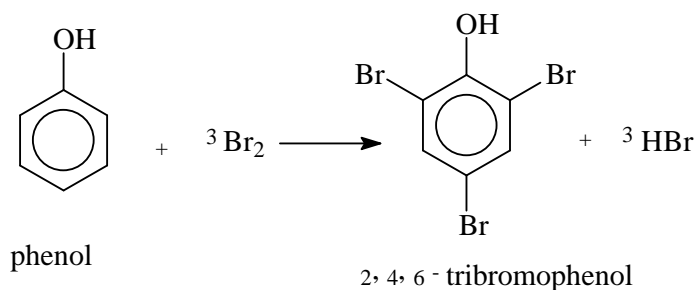
Electrophile attack at ortho and para positions

Common electrophilic aromatic substitution reactions taking place in phenol are as follow:

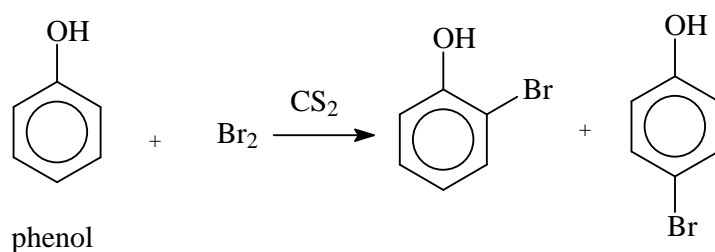
**1.Halogenation (Bromination):** The -OH group in phenol can donate electrons back to the delocalised  $\pi$ -system, helping to stabilise the intermediates of electrophilic substitution and so making phenol much more reactive than benzene. It will react immediately with bromine water, decolorising it and forming a white precipitate of 2,4,6-tribromophenol. If bromine water is added to a solution of phenol in water, the bromine water is decolourised and a white precipitate is formed. The usual halogenation of benzene takes place in the presence of a Lewis acid, such as  $\text{FeBr}_3$ , which polarises the halogen molecule. The faster reaction in water is due to the presence of phenoxide ions.

In case of phenol, the polarisation of bromine molecule takes place even in the absence of Lewis acid.

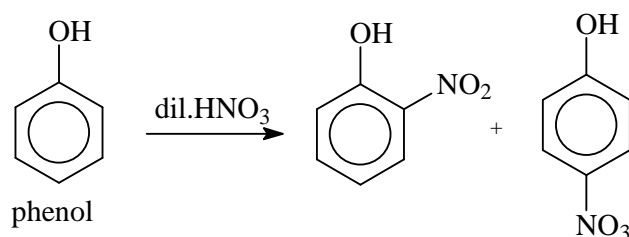
It is due to the highly activating effect of -OH group attached to the benzene ring. Chlorine, in the absence of solvent, gives 2 and 4-chlorophenol. Bromine, in a nonpolar solvent (e.g. CS<sub>2</sub> or CCl<sub>4</sub>) gives 2, 4-bromophenol.



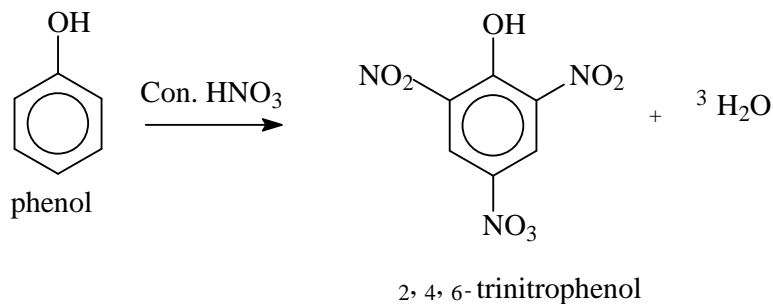
Bromination can be limited to monobromination to give mainly 4-bromophenol using low temperature and less polar solvent such as carbon disulphide. The other product formed in minor quantity is 2-bromophenol.



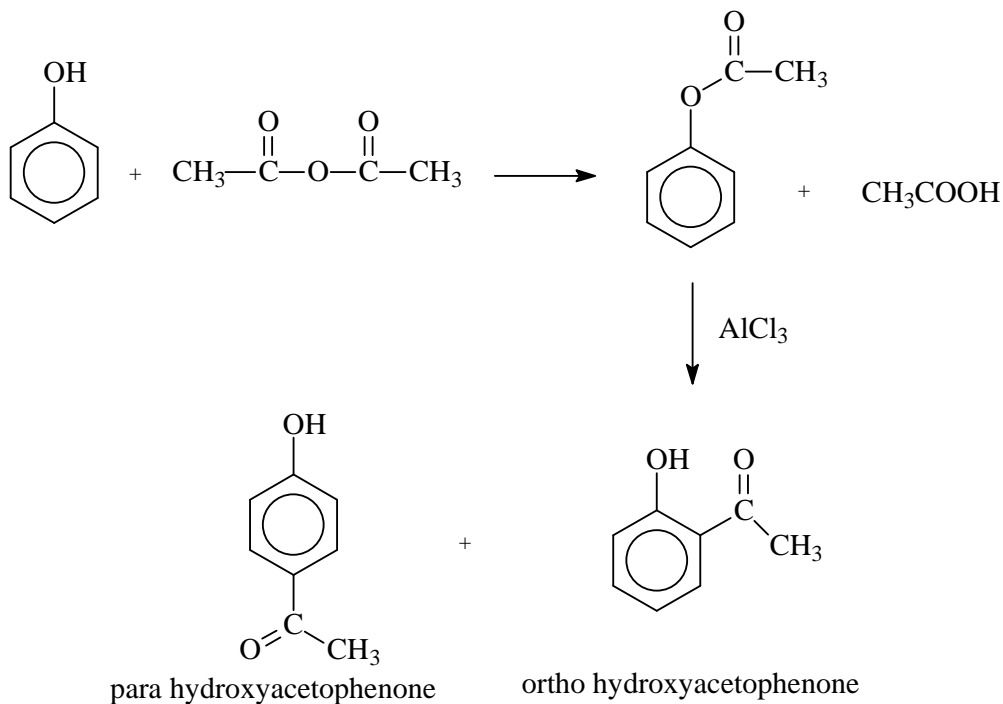
**2. Nitration of Phenol:** Phenol can be nitrated with dilute nitric acid. Monosubstituted compound is obtained with dilute nitric acid at room temperature. Phenol reacts with dilute nitric acid at room temperature to give a mixture of 2-nitrophenol and 4-nitrophenol.



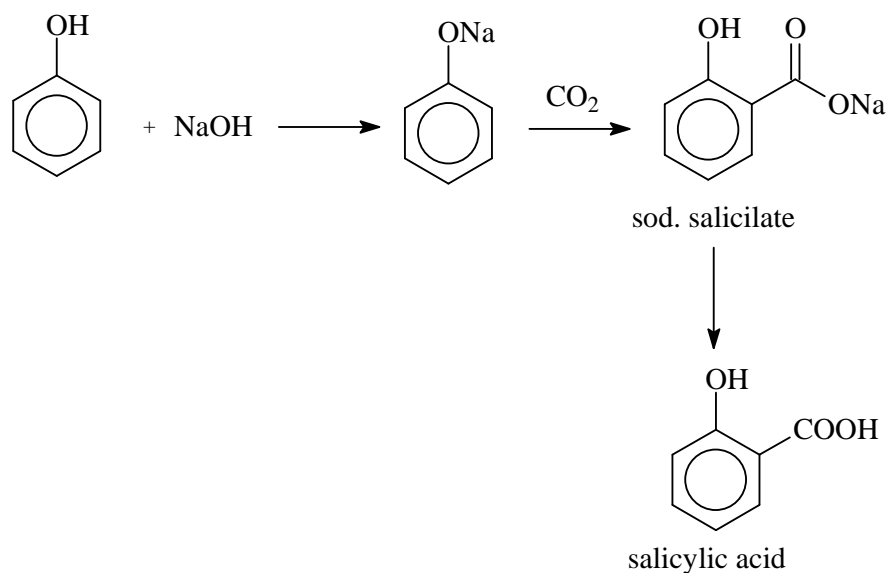
With concentrated nitric acid trisubstituted product product, 2,4,6-trinitrophenol (picric acid) is obtained readily.



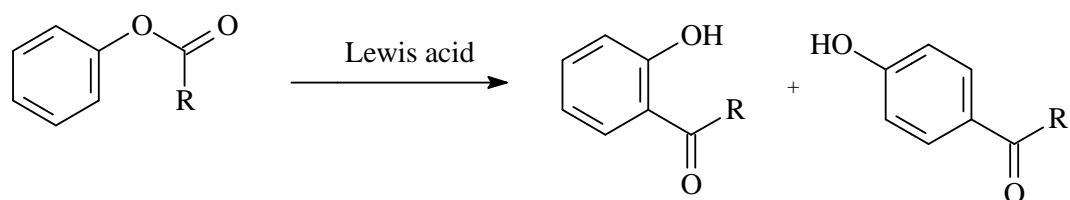
**3. Acylation and caboxylation:** Ester of phenols are obtained on treatment with anhydrous aluminium chloride, which further treating with Lewis acid like AlCl<sub>3</sub> yields ketones of phenols (Fries rearrangement)



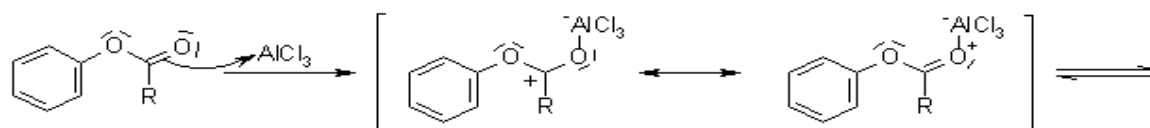
**4. Kolbe's reaction:** On reaction sodium salt of phenol with carbon dioxide gas, ortho hydroxy benzoic acid is formed as the main product. The temperature is 400 K and a pressure of 4-7 atm is required. Sodium salicylates formed which an acidification yields salicylic acid (ortho hydroxy benzoic acid).

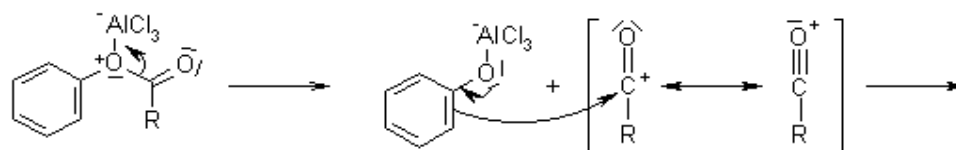


**5. Fries Rearrangement:** The Fries Rearrangement enables the preparation of acyl phenols. The reaction is catalyzed by Bronsted or Lewis acids such as HF, AlCl<sub>3</sub>, BF<sub>3</sub>, TiCl<sub>4</sub> or SnCl<sub>4</sub>. The acids are used in excess of the stoichiometric amount, especially the Lewis acids, since they form complexes with both the starting materials and products. The reaction is *ortho*, *para*-selective so that, for example, the site of acylation can be regulated by the choice of temperature.



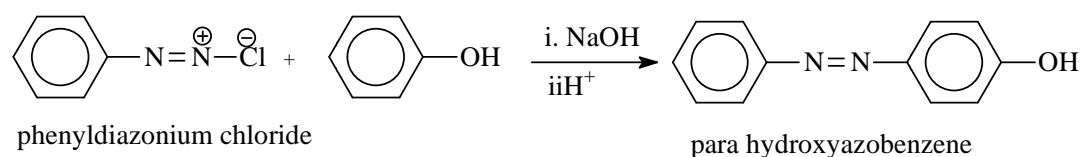
#### Mechanism



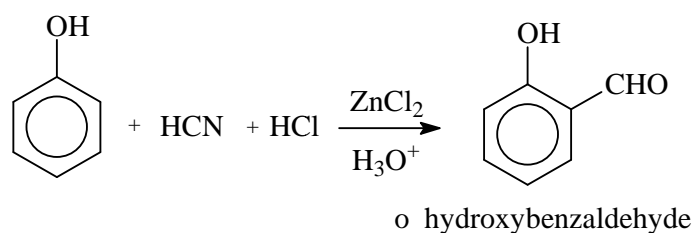


The complex can dissociate to form an acylium ion, which act as an electrophile. After hydrolysis, the product is liberated.

**6. Coupling reaction:** Phenols form azo compounds by coupling with aryldiazonium salts in presence of alkali.



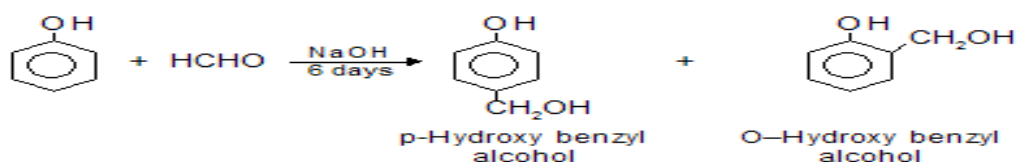
**7. Gattermann Reaction:** Introduction of  $-CHO$  group ortho to  $-OH$  group by treating phenol with  $HCN$ ,  $HCl$  and  $ZnCl_2$  catalyst is known as Gattermann reaction.



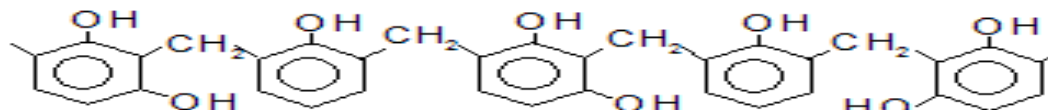
This reaction is used for formylation of aromatic ring

**8. Lederer Manasse's Reaction:** When phenol is treated with 40% aqueous solution of formaldehyde (formalin) in the presence of a dilute acid or alkali at low temperature, a mixture of o-and p-hydroxy benzyl alcohol is formed.

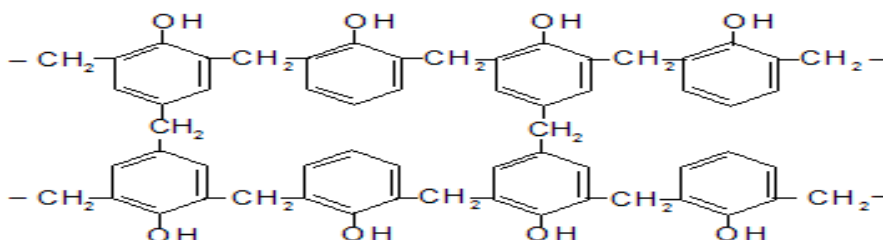




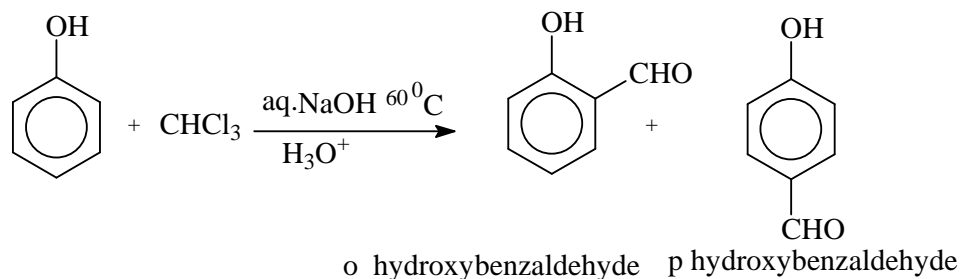
This reaction is called **Lederer-Manasse reaction**. On heating these compounds condense with themselves and give linear polymers by elimination of water.



These reactions are the basis of the preparation of phenol formaldehyde resins. These materials were developed by Backland and are hence called **bakelite**. They are thermoplastic solids soluble in many organic solvents. When warmed with hexa methylene tetramine,  $(\text{CH}_2)_6\text{N}_4$ , which splits up to formaldehyde and ammonia, further methylene bridges are formed and a three-dimensional polymer results.

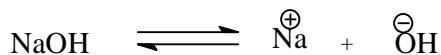


**9. Reimer Tiemann Reaction:** Process of formylation of phenols with chloroform in alkaline solution is known as **Reimer-Tiemann reaction**. Phenols react with chloroform in the presence of sodium hydroxide (or potassium hydroxide) solution followed by acidification to give hydroxy aldehydes.

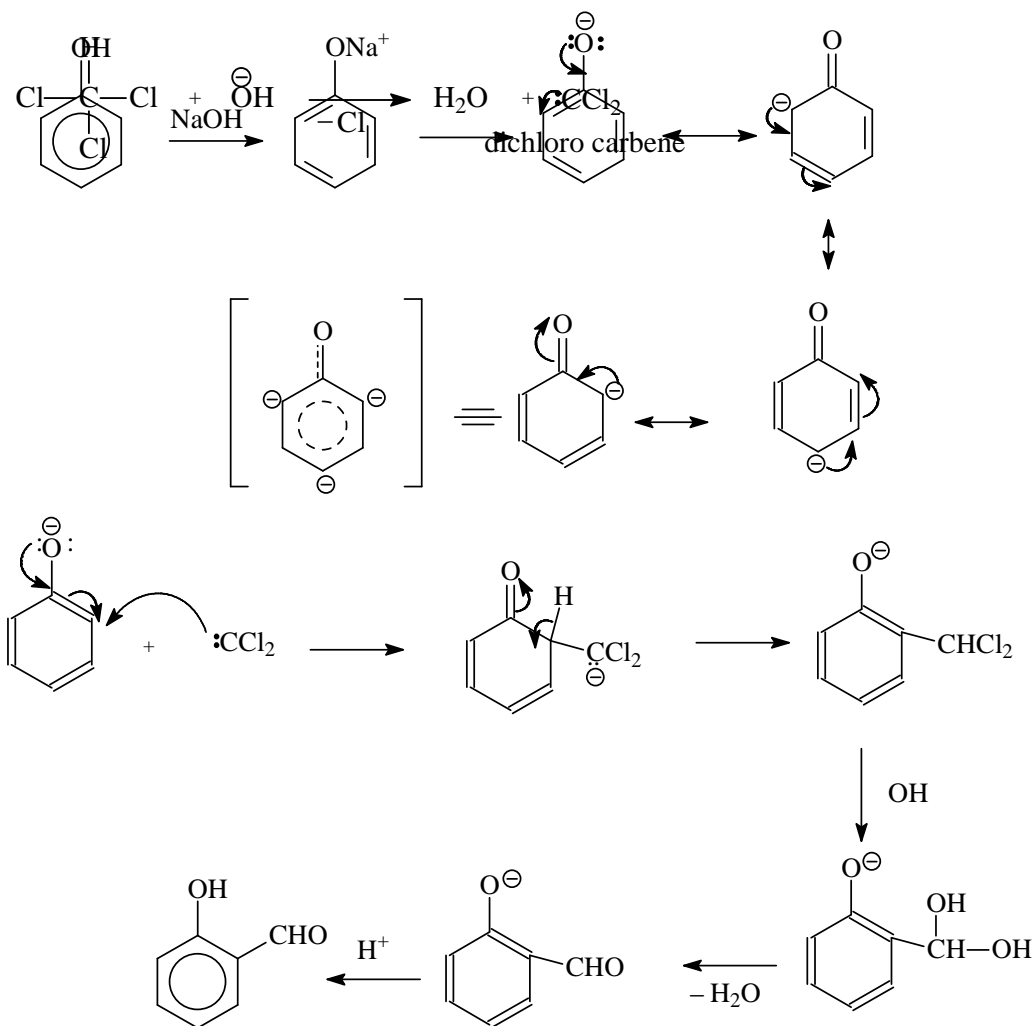


**Mechanism:** Reimer Tiemann reaction is an electrophilic substitution reaction. The first step is generation of electrophile.

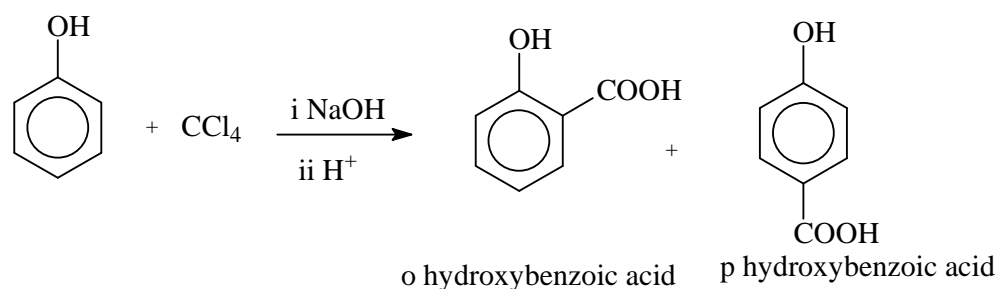
A Generation of dichloro carbene (electrophile)



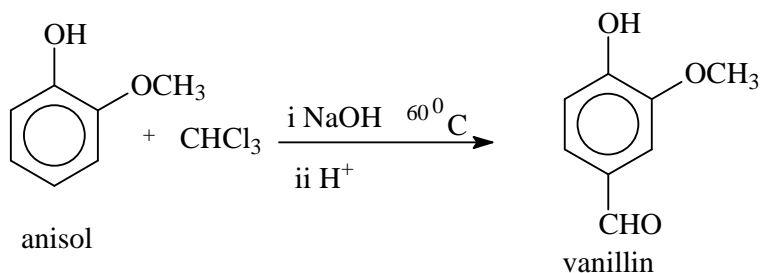
B Electrophilic substitution in phenol ring



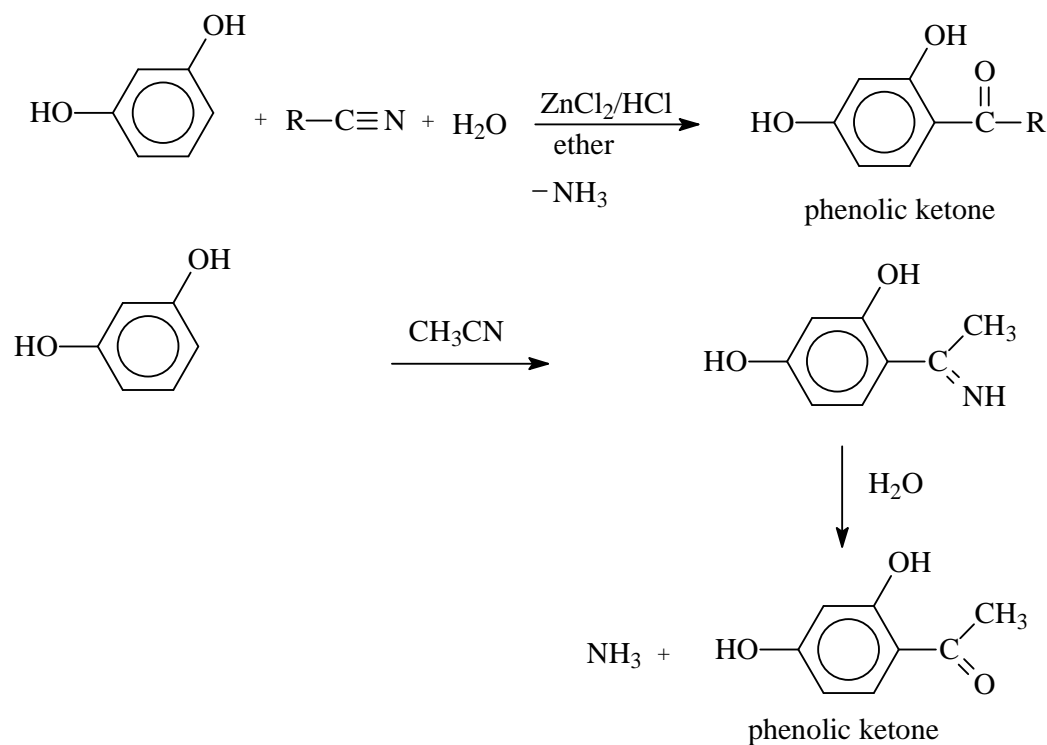
Use of carbon tetrachloride in place of chloroform gives salicylic acid. A mixture of ortho-and para-isomers is obtained in which the ortho isomer predominates due to more thermodynamical stability. If one of the ortho positions is occupied the para-isomer is the major product.



When anisol is treated with  $\text{CHCl}_3$  in presence of alkali a commercial edible product vanillin is formed as major product

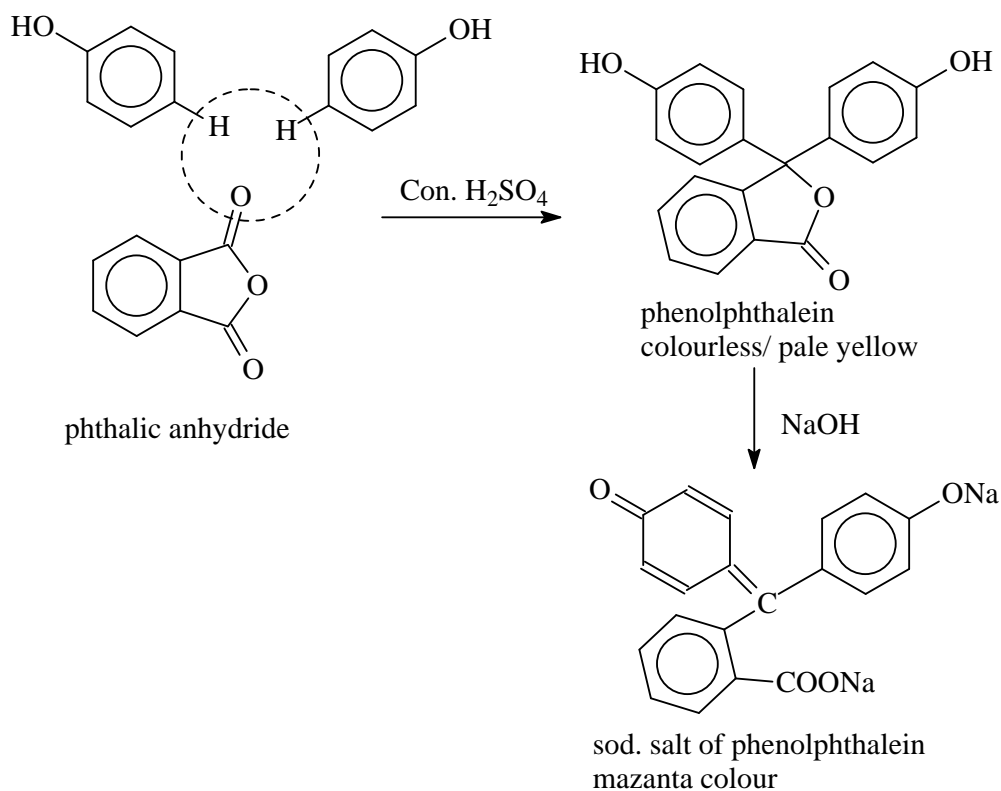


**10. Houben –Hoesch reaction:** Reactive polyhydric phenols in which  $-\text{OH}$  groups are *meta* to another may be acylated by treating with alkyl cyanides in the presence of  $\text{ZnCl}_2$  and  $\text{HCl}$ . This reaction is known as Houben-Hoesch reaction. The product of the reaction is phenolic ketone.

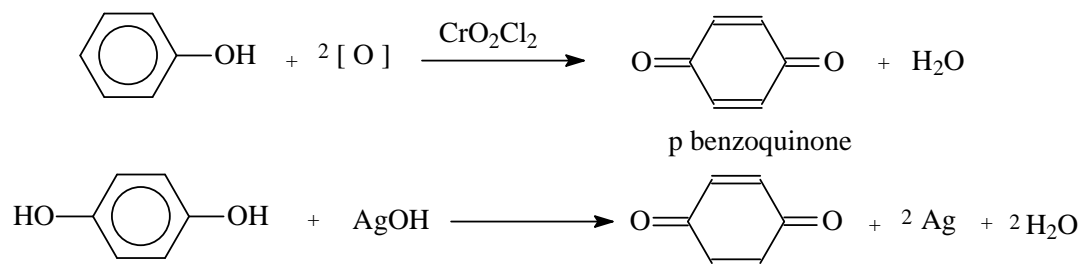


Phenol does not respond to Houben- Hoesch reaction

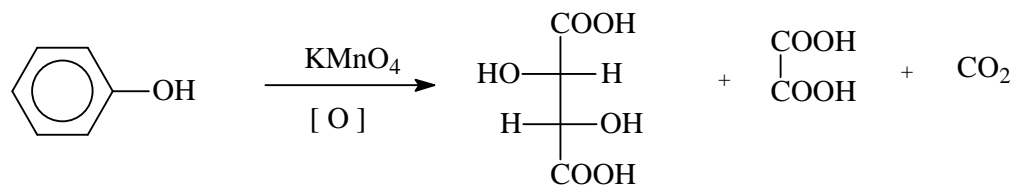
**11. Condensation with phthalic anhydride:** Phenol when treated with phthalic anhydride in presence of  $\text{H}_2\text{SO}_4$  gives phenolphthalein, a colourless compound which produces pink color with alkali solution due to the formation of colored sodi salt. It is a popular indicator used in acid base titrations.



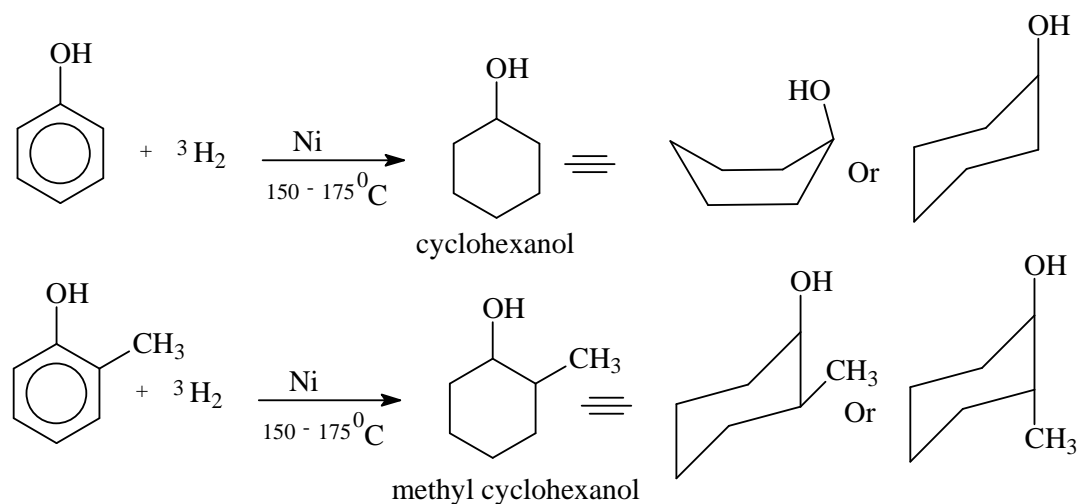
**12. Oxidation:** Phenol is easily oxidized to p-benzoquinone and similarly hydroquinone on oxidation with silver salt gives p- benzoquinone. This reaction leads to the use of hydroquinone as a photographic developer.



Under drastic condition upon oxidation phenol gives tartaric acid, oxalic acid and carbondioxide



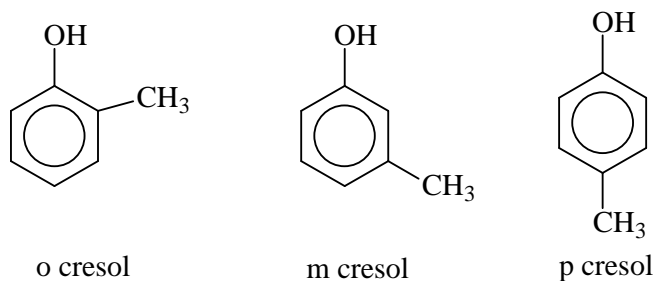
**13. Reduction:** The -OH group is stable and the catalytic reduction of phenol yields cyclohexanol, Substituted phenols would in same fashion form substituted cyclohexanol



**Uses of phenols:** Phenol, in dilute solution, was the first successful antiseptic used by Lister (called *carbolic acid*). Now substituted phenols are used both as **antiseptics** (to keep surfaces free of pathogens) and as **disinfectants** (to kill pathogens already present).

## 2.9 SUBSTITUTED PHENOLS

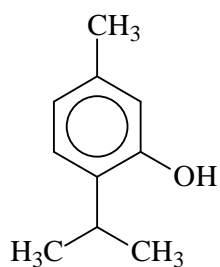
**Cresols / hydroxytoluene:**



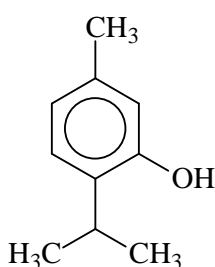
**Properties:** Cresols are colourless liquids with phenolic smell. Their B.P are o-  $191^{\circ}\text{C}$ , m-  $201^{\circ}\text{C}$  and p-  $202^{\circ}\text{C}$ . They are less toxic than phenol but have greater germicidal activity. Can be oxidized to corresponding carboxylic acid if  $-\text{OH}$  group is protected.

**Uses:** As preservative for timber railway sleepers etc. for making Lysol (a mixture of cresol in soapy water). For the synthesis of dyes, resin, plasticisers and explosive etc.

**Thymol and carvacrol:** These are two isomeric forms of phenol and are extensively used in perfumery and as antiseptics. Thymol occurs in the essential oil of thyme (*Thymus linearis*) carvacrol is obtained by heating camphor with iodine while naturally it occurs in *Mentha spicata* (mint)

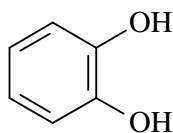


thymol



carvacrol

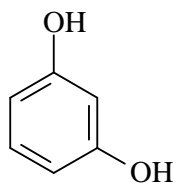
**Dihydric member:** catechol: it occurs in Indian catechu (*Acasia catechu*) hence is designated as catechol



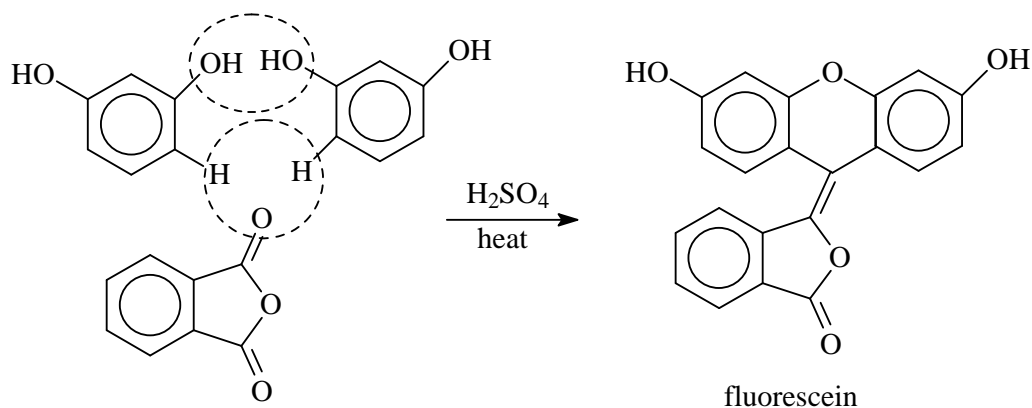
**Properties:** It is white crystalline solid M.P.  $104^{\circ}\text{C}$ . Soluble in  $\text{H}_2\text{O}$  ethanol and ether. Gives green color with  $\text{FeCl}_3$  while condensed with phthalic anhydride it gives alizarin

**Uses;** As a photographic developer. To manufacture alizarin. As antioxidant in gasoline

**Resorcinol:**



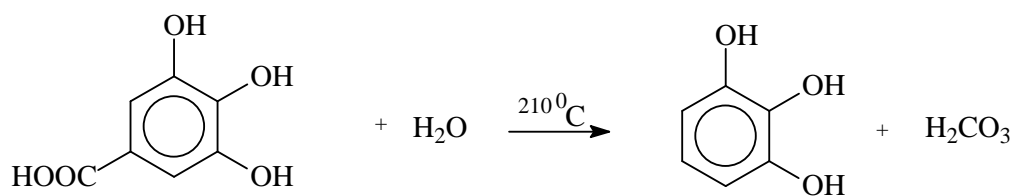
**Properties:** White solid M.P. 110°C Turns gray in air, soluble in water, forms 2,4,6-tribromoresorcinol when treated with bromine water. It couples diazonium salts to form azo dye and condense with phthalic anhydride to produce fluorescence which show intense green fluorescence when alkaliized



**Uses:** Used as antiseptic in ointments, for the manufacture of dyes like azo dyes, fluorescein, eosin etc, for preparing drugs used for curing hookworm and urinary disorders etc.

**Trihydric phenols:**

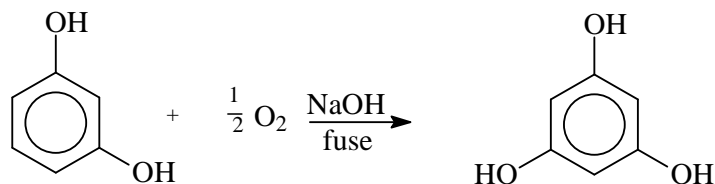
**Pyrogallol:** obtained by heating gallic acid



**Properties:** White crystalline solid, M.P. 133°C, soluble in water, alkaline solution turns to brown, most powerful reducing agent.

**Uses:** Excellent photographer developer, for preparing ointments and antiseptic for skin, as hair dyes, for absorbing oxygen in gas analysis

**Phloroglucinol:** prepared by fusing resorcinol with NaOH in air



**Properties:** White crystalline solid, M.P.  $218^{\circ}\text{C}$ , soluble in water alkaline solution readily darkens on exposure to air due to oxidation.

**Uses:** Used for detecting carbohydrates, producing a red coloration with in presence of  $\text{H}_2\text{SO}_4$ .

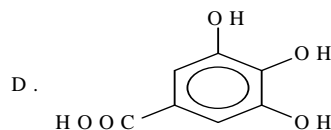
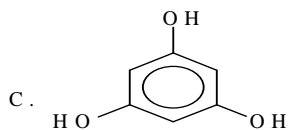
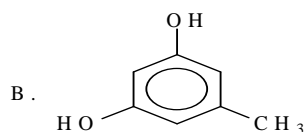
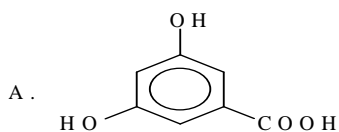
## 2.10 SUMMARY

In this unit emphasis has been given to the introduction properties structure, physical properties, chemical properties of phenols. This unit also describes the difference between phenols and alcohols. Acidic character of phenols in comparison to alcohols and carboxylic acids has been described. In chemical reactions both types of reactions, due to  $-\text{OH}$  group and due to aromatic ring which are basically electrophilic in nature have been described in detail. The important name reactions involving phenols have been described in this unit. Besides simple phenol, substituted phenols like cresols, pyrogallol, catechol, thymol, carvacrol, resorcinol, flurogocinol etc have been described with their properties and industrial application.

## 2.11 TERMINAL QUESTION

Q.1 Tick the correct option (MCQs):

i. Structure of gallic acid is:

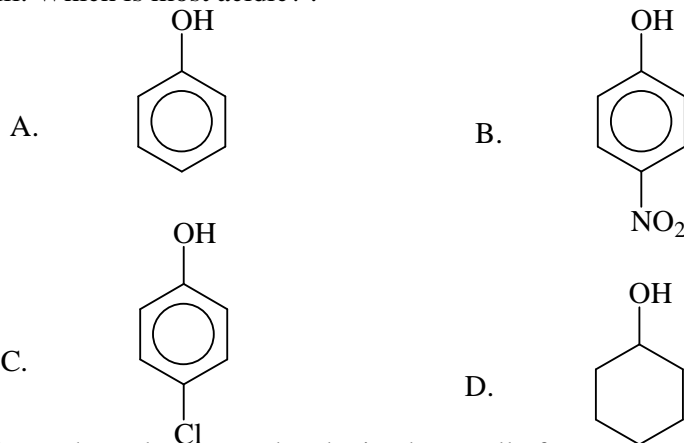


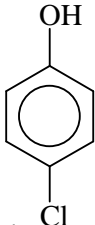


ii. Vanillin is obtained by using:

- A. Reimer-Teiman Reaction      B. Hoffman bromide Reaction  
 C. Houben-Hosches Reaction      D. Gatterman Reaction

iii. Which is most acidic? :



iv. Thymol  can be obtained naturally from:

- A. Thymus      B. Acasia  
 C. Rose      D. None of them

v. Commercially phenols can be obtained from:

- A. Coal- tar      B. Benzene  
 C. Gasoline      D. Wood

vi. Phenol when treated with ZnO gives.

- A. Cyclohexanol      B. Benzene  
 C. Cyclohexanone      D. hydroquinone

vii. Phenol undergoes ionization to become more stable by reacting with

- A. negative ions      B. positive ions  
 C. both A and B      D. neutral atoms

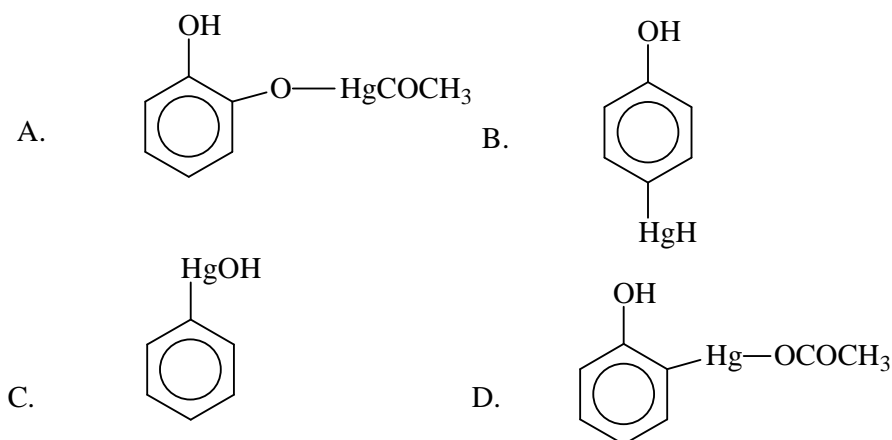
viii. Condensation of phenol with HCHO to produce Bakelite is an example of:

- A. Aldol condensation      B. Lederer-Manasse reaction  
 C. Beckmann reaction      D. Knoevengal reaction

ix. Which of the following groups will increase the acidity of phenol?

- A.  $\text{NO}_2$       B. CN  
 C. halogens      D. all

x. Upon refluxing phenol with  $(\text{CH}_3\text{COO})_2\text{Hg}$  we get.



Q.2. Write the Mechanism of following name reactions

1. Kolbe reaction
2. Fries rearrangement
3. Reimer Tiemann
4. Reimer –Teiman reaction

Q.3. Arrange the following in order of increasing acidic strength. Giving reason:

p- Nitro phenol, m-Nitro phenol, o-Nitro phenol.

Q.4. Explain why phenols do not undergo substitution of OH group like alcohol.

Q.5 Explain why phenols are more acidic than alcohols.

Q.6. How will you convert phenol to:-

1. Salysilic acid
2. Phenolphthalein
3. Picric acid
4. Ethoxy benzene
5. Azo dye
6. Catechol

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**2.12 ANSWERS (MCQs)**

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1-D	2- A	3- B	4- A	5- A
6- B	7- A	8- B	9- D	10- D

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**2.13 REFERENCES**

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**UNIT -3 ETHERS AND EPOXIDES**

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**CONTENTS:**

- 3.1 Objectives
- 3.2 Introduction
- 3.3 Nomenclature of ethers
- 3.4 Methods of preparation
- 3.5 Physical properties
- 3.6 Chemical properties
- 3.7 Summary
- 3.8 Terminal questions
- 3.9 Answers (MCQs)
- 3.10 References

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***3.1 OBJECTIVES***

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The objectives of this unit are to make aware the students about ethers, to state the IUPAC name of ethers, to name ethers either as alkoxyalkanes or as dialkyl ethers, to name epoxides as oxiranes or as epoxyalkanes, to state the means to prepare ethers from 1° alcohols, to draw the mechanism for the preparation of an ether from the reaction of an alkene and an alcohol in the presence of an acid catalyst, to draw the mechanism for the preparation of an ether from the reaction of a 1° alkyl halide and an unhindered alkoxide, to draw the mechanism and discuss about the major product of the reaction of an ether with excess HX, to draw the mechanism and give the major product of the reaction of a vicinal halohydrin with hydroxide, including stereochemistry, to draw the mechanism and give the major product of the reaction of an epoxide with a strong nucleophile and to draw the mechanism and give the major product of the reaction of an epoxide with either ROH/H<sup>+</sup>, HX, or H<sub>2</sub>O/H<sub>2</sub>SO<sub>4</sub>

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***3.2 INTRODUCTION***

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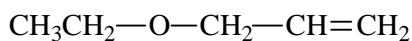
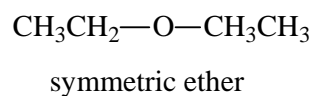
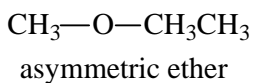
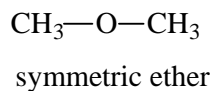
Ethers are compounds that containing single oxygen atom bonded to two alkyl groups, two aryl groups or one aryl and one alkyl group. The general formula, of ethers is C<sub>n</sub>H<sub>2n+2</sub>O. They are isomeric with the aliphatic monohydric alcohols with the general

formula  $C_nH_{2n+1}OH$ . Thus, ethers can be represented as  $R-O-R'$ , where R and R' may be alkyl or aryl groups. When the two substituent groups (R and R') are identical, then the ether is called a simple or symmetrical ether, otherwise if these two groups are different, then the ether is known as a mixed or unsymmetrical ether. Diethyl ether,  $C_2H_5OC_2H_5$ , is symmetrical ether whereas  $C_2H_5OCH_3$  and  $C_2H_5OC_6H_5$  are unsymmetrical ethers. The symmetrical diethyl ether is commonly also referred simply as *ether* because of its wide use as a solvent for reactions and extraction of organic compounds. It was also used as an anaesthetic for over hundred years. Ethers are distinguished from other organic compounds because they lack a continuous chain of carbons.

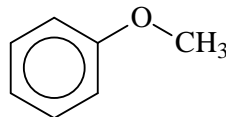


Ethers are thought of as alkyl analogues of water.

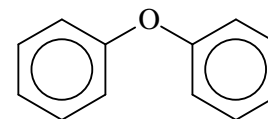
Substitution of the hydroxyl hydrogens of alcohols by hydrocarbon groups gives compounds known as ethers. These compounds may be classified further as open-chain, cyclic, saturated, unsaturated, and aromatic, and so on. The oxygen atom of the ether can also be part of a ring, in which case the ether is known as cyclic ether or also called epoxide. Epoxides are formed when an oxygen atom is linked to carbon atoms of a carbon chain forming a three membered ring. Epoxides are heterocyclic compounds containing oxygen atom as a hetero atom. Epoxides have considerable ring strain. Epoxides are special kinds of ethers. These compounds are special because they have a three member ring that contains an oxygen atom. They are far more reactive than typical ethers. Tetrahydrofuran is one such cyclic ether which is used as a solvent. Ethers are commonly used as solvents for organic reactions.



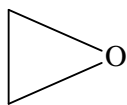
unsaturated ether



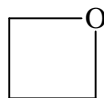
aryalkyl ether



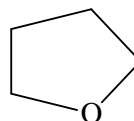
aryl ether



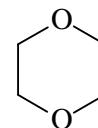
ethylene oxide



trihydrofuran



tetrahydrofuran



dioxane

Cyclic ethers

### 3.3 NOMENCLATURE OF ETHERS

There are two methods of naming ethers. The first is the common method and is most useful with simple ethers. Common names “trivial names” of ethers add the suffix ether after naming the two groups on either side of the oxygen. The alkyl groups are listed in alphabetic order. There are spaces between the names of the alkyl groups and the word ether. If the two groups are the same, the prefix “di-” is used, although sometimes this is simply dropped (“ethyl ether”).

e.g.  $\text{H}_3\text{COCH}_2\text{CH}_3$  Ethylmethyl ether

$\text{C}_2\text{H}_5\text{—O—C}_2\text{H}_5$  Diethyl ether

$\text{C}_6\text{H}_5\text{—O—C}_6\text{H}_5$  Diphenyl ether

$\text{C}_2\text{H}_5\text{—O—C}_6\text{H}_5$  Ethyl phenyl ether.

In IUPAC nomenclature, the larger alkyl (or aryl) group is used as the root name as the *alkane*. Treat the oxygen and the remaining carbons as a side chain and the smaller alkyl group is named as an *alkoxy* (—OR = alkoxy group) substituent on this alkane. The *-yl* ending of alkyl substituents is replaced by *-oxy*.

— $\text{CH}_3$  methyl

— $\text{OCH}_3$  methoxy

—CH<sub>2</sub>CH<sub>3</sub> ethyl    —OCH<sub>2</sub>CH<sub>3</sub> ethoxy

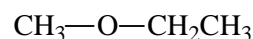
For example, in ethyl methyl ether having ethyl and methyl groups, the ethyl group is larger than methyl group and hence this ether is treated as the ethane derivative.



Ethylmethyl ether

The remaining portion, *i.e.*, —OCH<sub>3</sub> part in this case, is called the methoxy substituent. Hence, the above ether is called methoxyethane. The numbering of the parent chain is done so that the carbon atom linked to the -O-atom gets the lowest number. Some more examples of IUPAC names of ethers are given below:

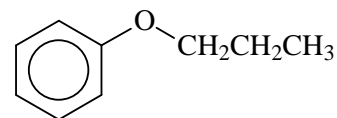
Examples:



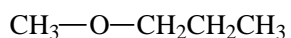
ethylmethyl ether  
methoxy ethane



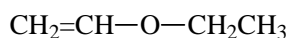
butylethyl ether  
1 ethoxy butane



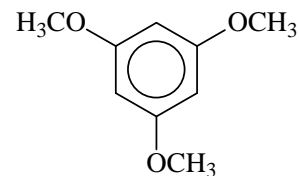
phenylpropyl ether  
1 phenoxypropane



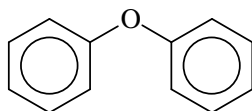
1 methoxypropane



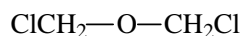
ethoxyethene



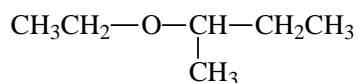
1, 3, 5 trimethoxybenzene



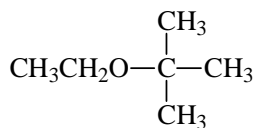
diphenyl ether



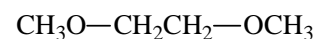
bis(chloromethyl)ether



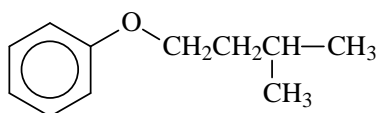
2 ethoxybutane



2 ethoxy 2 methylpropane

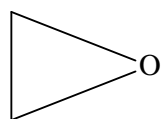


1, 2 dimethoxyethane



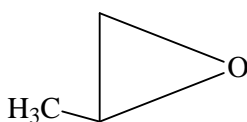
3 methylbutoxybenzene

Cyclic ethers generally termed as epoxides in IUPAC system. Epoxide contains a 3-membered ring between oxygen and two carbons ethers.



epoxyethane

ethylene oxide



propylene oxide

1,2 epoxypropane

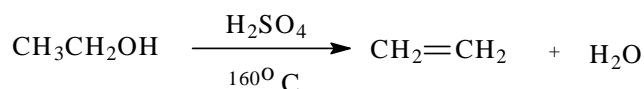
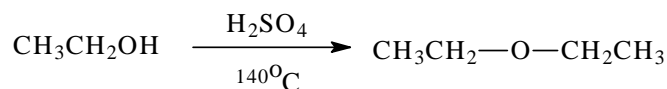
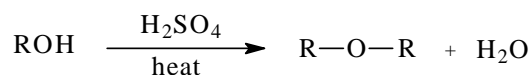
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### 3.4 METHODS OF PREPARATION

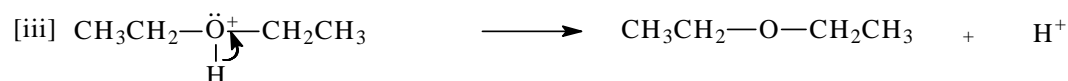
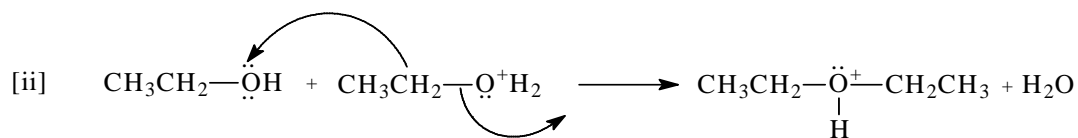
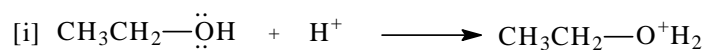
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There are different methods for the synthesis of ethers some of which are being described as follow:

- 1. By Dehydration of alcohols:** (a) The formation of reaction product, alkene or ether depends on the reaction conditions. This method involves heating of excess of primary alcohol with concentrated sulphuric acid and the temperature has to be maintained around 413<sup>0</sup> K to get symmetrical ether. If alcohol is not used in excess or the temperature is higher, the alcohol will preferably undergo dehydration to yield alkene.

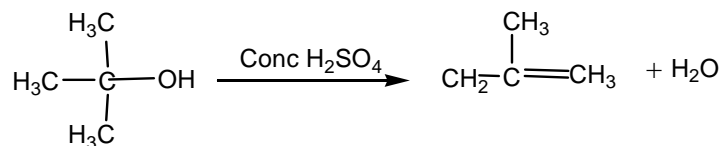


Mechanism:





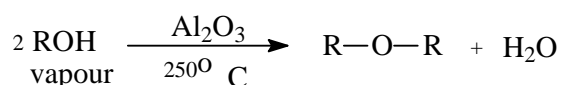
If ethanol is dehydrated to ethene in presence of sulphuric acid at 433K but as 410K ethoxyethane is the main product. The dehydration of secondary and tertiary alcohols to get corresponding ethers is unsuccessful as alkenes are formed easily in these reactions.



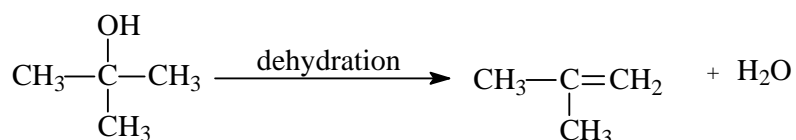
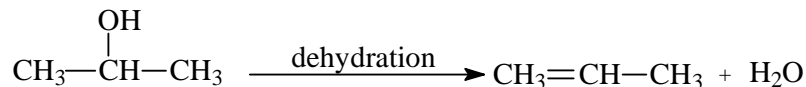
t -butyl alcohol

Iso-butylene

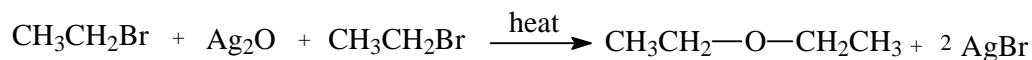
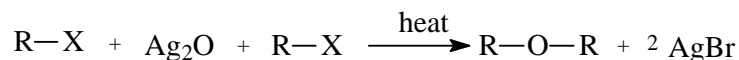
(b) On passing alcohol vapours over heated alumina at 250°C, dehydration of alcohols leads to the formation of ethers.



The secondary and tertiary alcohols on dehydration lead to the formation of alkene as main product.

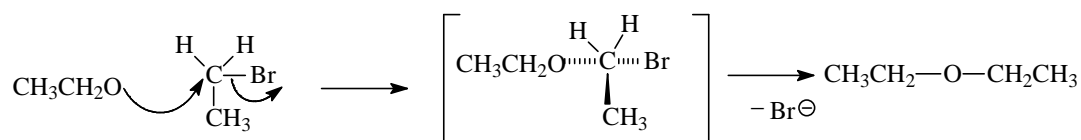
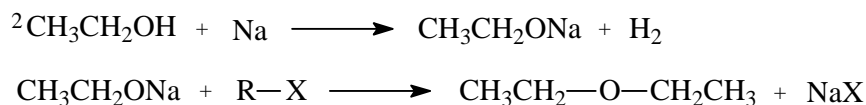


**2. By alkyl halides:** Alkyl halides on heating with dry Ag<sub>2</sub>O (in ether) give ethers.



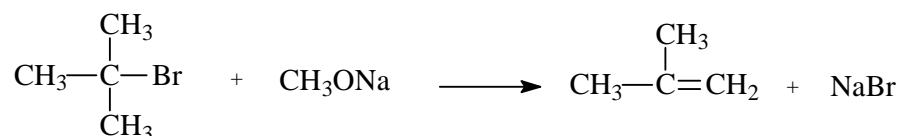
**3 Williamson syntheses of ethers:** It is an important laboratory method for the preparation of symmetrical and unsymmetrical ethers. The method involves the treatment of an alkyl halide with sodium or potassium salt of alcohol or phenol. This is

a good method to get better yield of mixed ethers in comparison to above methods. This reaction obeys  $S_N2$  mechanism. Ethers containing substituted alkyl groups (secondary or tertiary) may also be prepared by this method. The reaction involves a nucleophilic substitution of halide ion by an alkoxide ion.



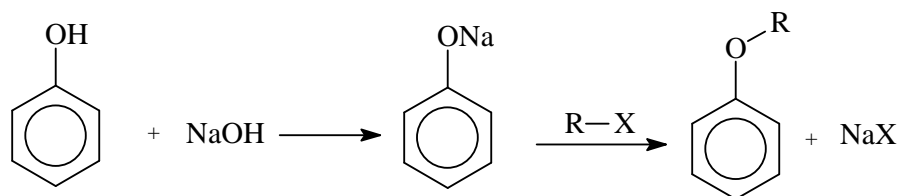
Good results are obtained if the alkyl halide is primary. If a tertiary alkyl halide is used, an alkene is the only reaction product and no ether is formed.

For e.g., the reaction of  $\text{CH}_3\text{ONa}$  and  $(\text{CH}_3)_3\text{C-Br}$  gives exclusively 2-methyl propene.

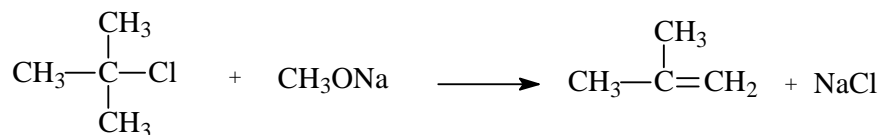


This is because alkoxides are not only nucleophiles but also strong bases as well. They react with alkyl halides leading to elimination reaction.

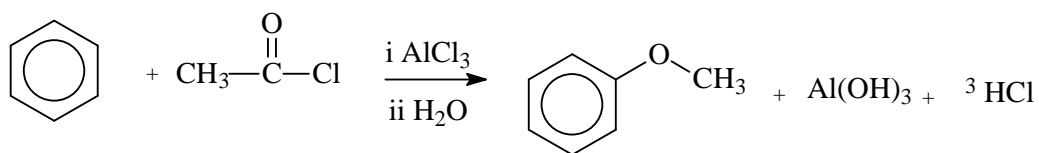
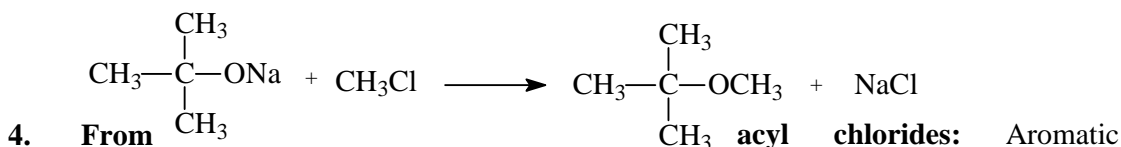
Phenols are also converted to ethers by this method.



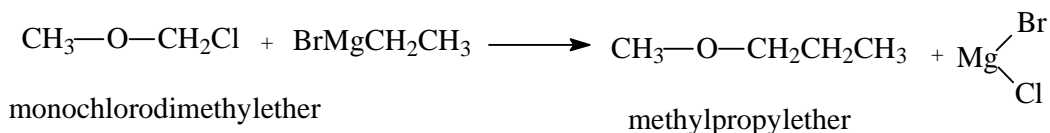
Tertiary alkyl halides undergo elimination reaction with sodium alkoxide to produce



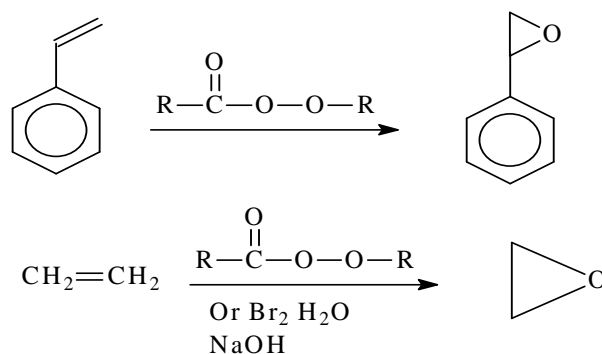
Therefore to prepare t- alkyl-alkyl ether, one must take an alkyl halide with tertiary alkoxide.



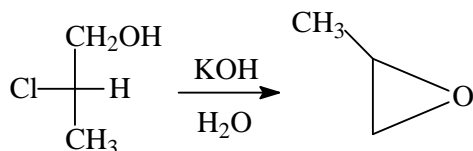
5. **From Grignard reagent:** This is a good method for the preparation of higher ether from lower members, in which a lower halogenated ethers when heated with Grignard reagent we get higher ethers.



6. **Epoxides formation from olefinic peroxidation:** The cyclic ether like epoxide can be synthesized by the reaction of peroxides on olefinic compounds to get epoxides or are synthesized by treating alkene with bromine water followed treatment with NaOH.



7. By intramolecular  $\text{S}_{\text{N}}2$  reaction: The  $\text{S}_{\text{N}}2$  intramolecular reaction of halohydrin in presence of  $\text{KOH}/\text{H}_2\text{O}$  gives epoxide.

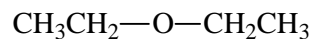


### 3.5 PHYSICAL PROPERTIES

**a) Physical state:** Dimethylether and ethyl methyl ether are gases at ordinary temperature. The other lower homologues are colourless, pleasant smelling, volatile liquids with typical ether smell.

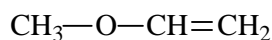
**b) Boiling points:** The C - O bonds in ether are polar and thus ethers have a net dipole moment. The weak polarity of ethers does not appreciably affect their boiling points which are comparable to those of the alkenes of comparable molecular mass. Ethers have much lower boiling points as compared to isomeric alcohols. This is because alcohols molecules are associated by hydrogen bonds while ether molecules are not.

Boiling point order: alcohols > ethers > alkanes



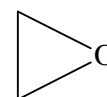
diethylether  
ethoxyethane

b. p  $35^\circ\text{C}$



methoxy ethene  
methyl ethenyl ether

b. p  $12^\circ\text{C}$



epoxide

b. p  $11^\circ\text{C}$

c) **Solubility:** Ethers are slightly polar, and can hydrogen-bond to water, although very weakly, through the oxygen atom. Because ethers have no O-H bonds, they cannot participate in hydrogen bonding to the same extent that alcohols do. Nevertheless, the oxygen in the ether can form a hydrogen bond to the hydrogen in water. The presence of only single site on the ether for a limited kind of hydrogen bonding interaction means that ethers generally have significantly smaller solubilities in water than do alcohols. Still they have higher solubilities than any hydrocarbon. These are extremely volatile and highly flammable (easily oxidized in air).

Ethers containing upto three carbon atoms are soluble in water, due to their hydrogen bond formation with water molecules.



The solubility decreases with increase in the number of carbon atoms. The relative increase in the hydrocarbon portion of the molecule decreases the tendency of H-bond formation. Ethers are appreciably soluble in organic solvents like alcohol, benzene, acetone etc.

Water solubility order: alcohols > ethers > alkanes

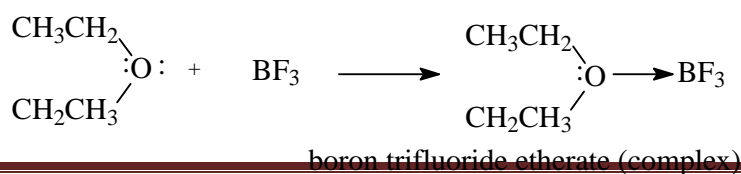
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### 3.6 CHEMICAL PROPERTIES:

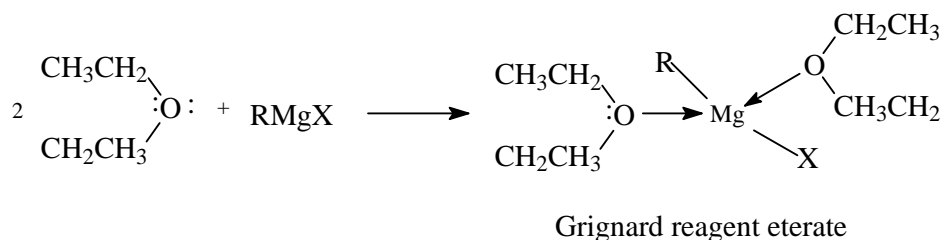
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Ethers have geometry similar to water and alcohols. The oxygen atom is  $sp^3$  hybridised. Since the carbon-oxygen bond is polar and the molecule has a bent structure, there is a net dipole moment and the ether molecule is polar in nature. Ethers, thus, act as polar solvents. Ethers are quite stable compounds. These are not easily attacked by alkalies; dilute mineral acids, active metals, reducing agents or oxidising agents under ordinary conditions.

**1. Reaction with acids:** Being Lewis bases, ethers form complexes with Lewis acids such as  $BF_3$ ,  $AlCl_3$ ,  $FeCl_3$ , etc. These complexes are called etherates.



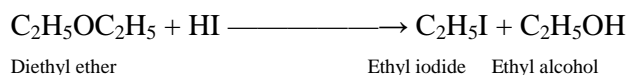
Similarly, diethyl ether reacts with Grignard reagent forming Grignard reagent etherate.



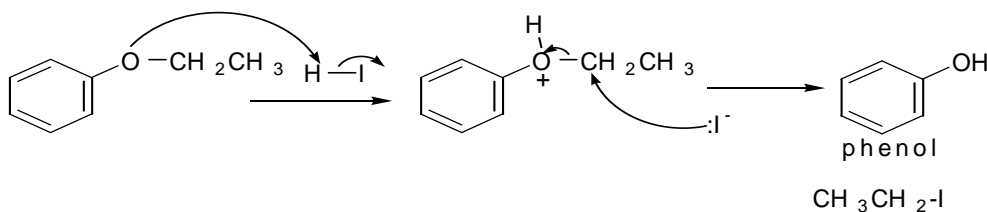
Due to the formation of the etherate, Grignard reagents dissolve in ether. That is why Grignard reagents are usually prepared in ethers. However, they cannot be prepared in benzene, because benzene has no lone pair of electrons and therefore, cannot form complexes with them.

**2. Action of hydroiodic acid:** Following reactions takes place when ethers are treated with haloacids.

(a) With cold HI

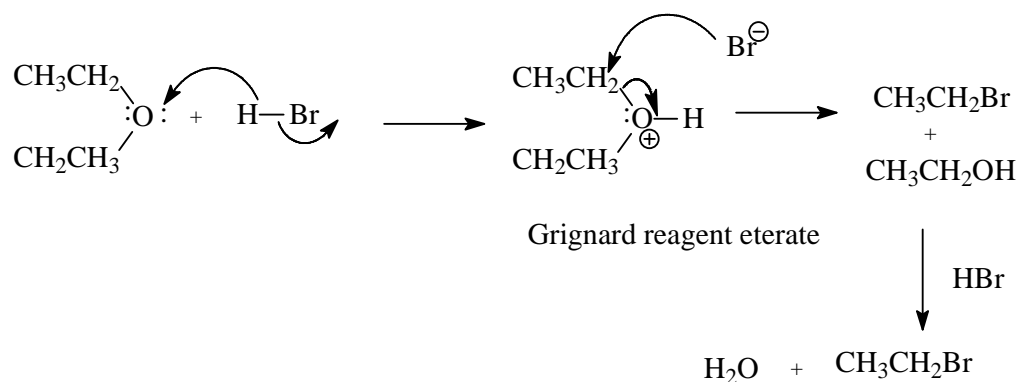


(b) With hot HI



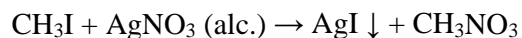
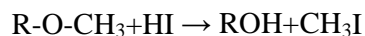
Phenyl ethers are slightly different, and cleave to give alkyl halides and phenols. The reaction stops at the phenol stage since the sp<sup>2</sup> carbon of the C-O bond does not allow the required S<sub>N</sub>1 or S<sub>N</sub>2 reactions to generate the second molecule of aryl halide.

**3. Reaction with HBr:** Since the oxygen atom of ethers contains lone pairs of electrons, they can accept a proton from the acids. Thus, ethers are basic in nature. Ethers are stable to bases, but acidic conditions leads to the protonation of the ether oxygen, which then can undergo substitution reactions.

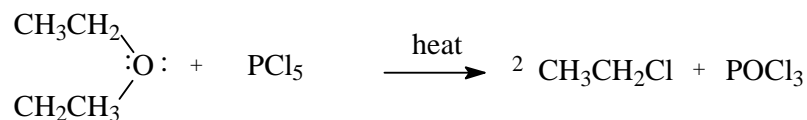
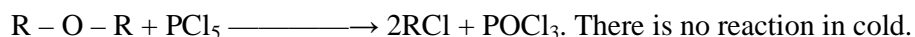


**4. Zeisel method:** The compound is heated with excess hydriodic acid, forming an alcohol and iodomethane. The iodomethane is distilled off and led into an alcoholic solution of silver nitrate, where it precipitates silver iodide.

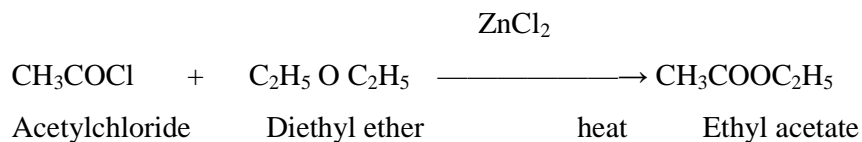
The silver iodide thus formed can be detected and estimated. This is the basis of Zeisel method for the detection and estimation of methoxy (–OCH<sub>3</sub>) groups in an organic compound. The method was developed by S. Ziesel in 1886.



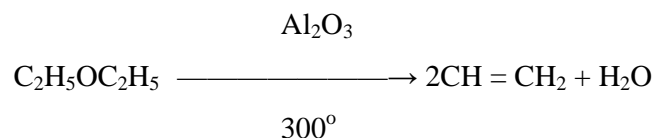
**5. Action of PCl<sub>5</sub>:** Alkyl halides are obtained



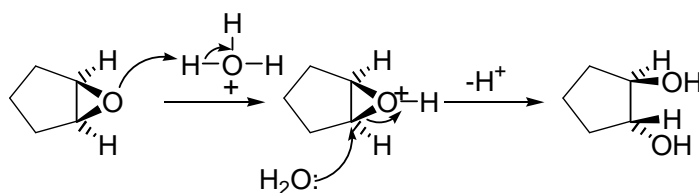
**6. Reaction with acetyl chloride:** Esters are obtained while treating with acyl halides



**7. Dehydration:** Upon dehydration at elevated temperature ethers provide alkenes



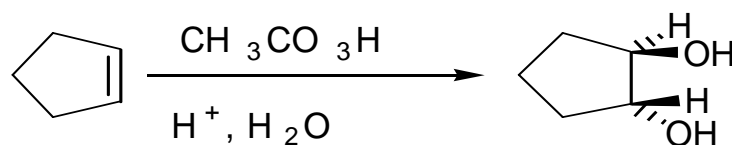
**8. Acid and base catalyzed ring opening:** Unlike straight chain ethers, epoxides are very reactive and are useful intermediates because of their chemical versatility. Epoxides react to release their considerable strain energy. The acidic hydrolysis of epoxides gives



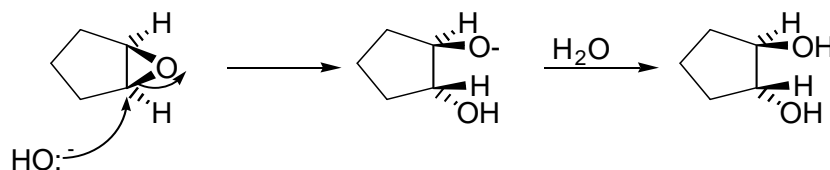
*trans*-cyclopentane-1,2-diol

anti diols. Proton transfer from the acid catalyst generates the conjugate acid of the epoxide, which is attacked by nucleophiles such as water. The result is anti-hydroxylation of the double bond. This hydration of an epoxide does not change the oxidation state of any atoms or groups.

Epoxides ring can also be opened by alcohols with acidic catalysis to generate alkoxy alcohols with anti stereochemistry.



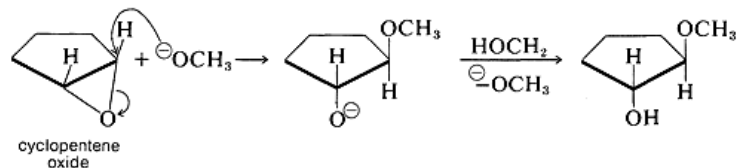
The reaction of hydroxide (or alkoxide) with a symmetric epoxide generates anti diols (or alkoxy alcohols) identical to those produced under acidic conditions.



**9. Orientation of ring opening:** Unlike most ether, oxacyclopropanes react readily with nucleophilic reagents. These reactions are no different from the nucleophilic

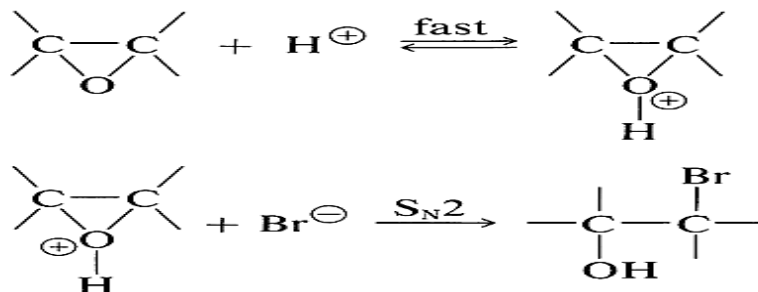


displacements, except that the leaving group, which is the oxygen of the oxide ring, remains a part of the original molecule. The stereochemistry is consistent with an  $S_N2$  mechanism because inversion of configuration at the site of attack occurs. Thus cyclopentene oxide yields products with the trans configuration:

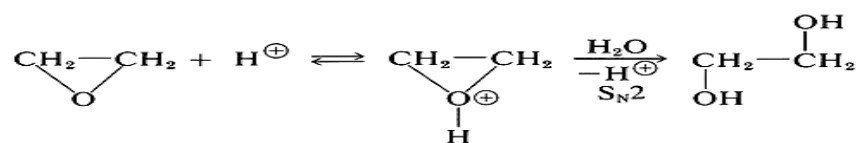


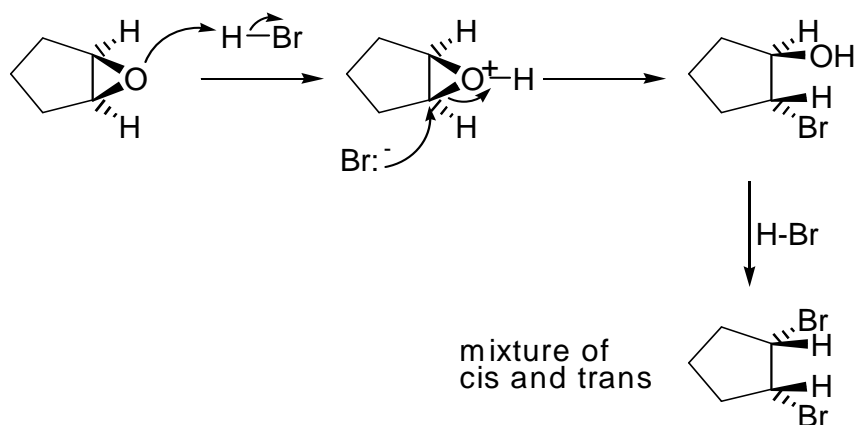
Acidic conditions

also can be used for the cleavage of oxacyclopropane rings. An oxonium ion is formed first, which subsequently is attacked by the nucleophile in an  $S_N2$  displacement or forms a carbocation in an  $S_N1$  reaction. Evidence for the  $S_N2$  mechanism, which produces inversion, comes not only from the stereochemistry but also from the fact that the rate is dependent on the concentration of the nucleophile. An example is ring opening with hydrogen bromide:



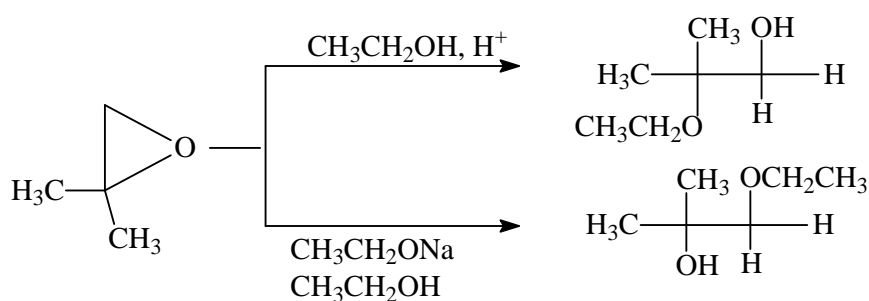
The same kind of mechanism can operate in the formation of 1,2-diols by acid-catalyzed ring-opening with water as the nucleophile.



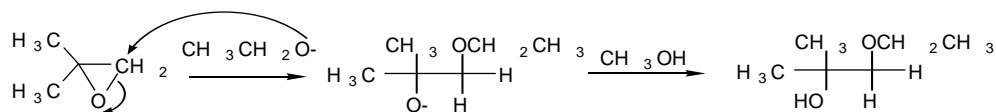


Epoxides react with H-X to produce halohydrins, which react further with H-X to generate 1, 2-dihalides.

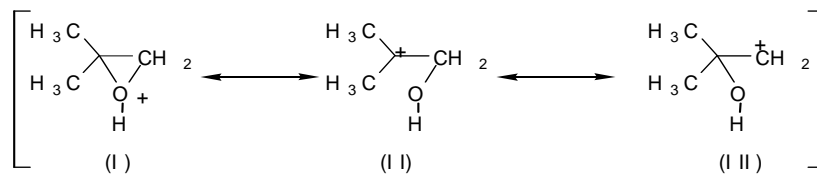
Unsymmetrical epoxides give products with different regiochemistry with basic opening compared to acidic opening.



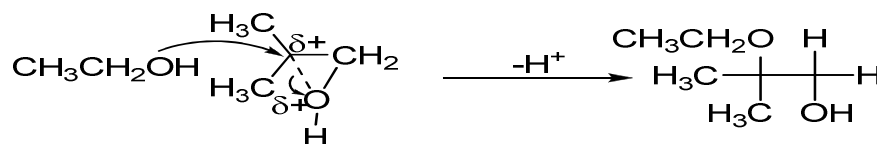
Under basic conditions, the alkoxide simply attacks the least sterically hindered epoxide carbon in an  $S_N2$  displacement.



Under acidic conditions, the alcohol *seems* to attack the more hindered carbon, but it is more complicated. The protonated epoxide has several resonance structures.

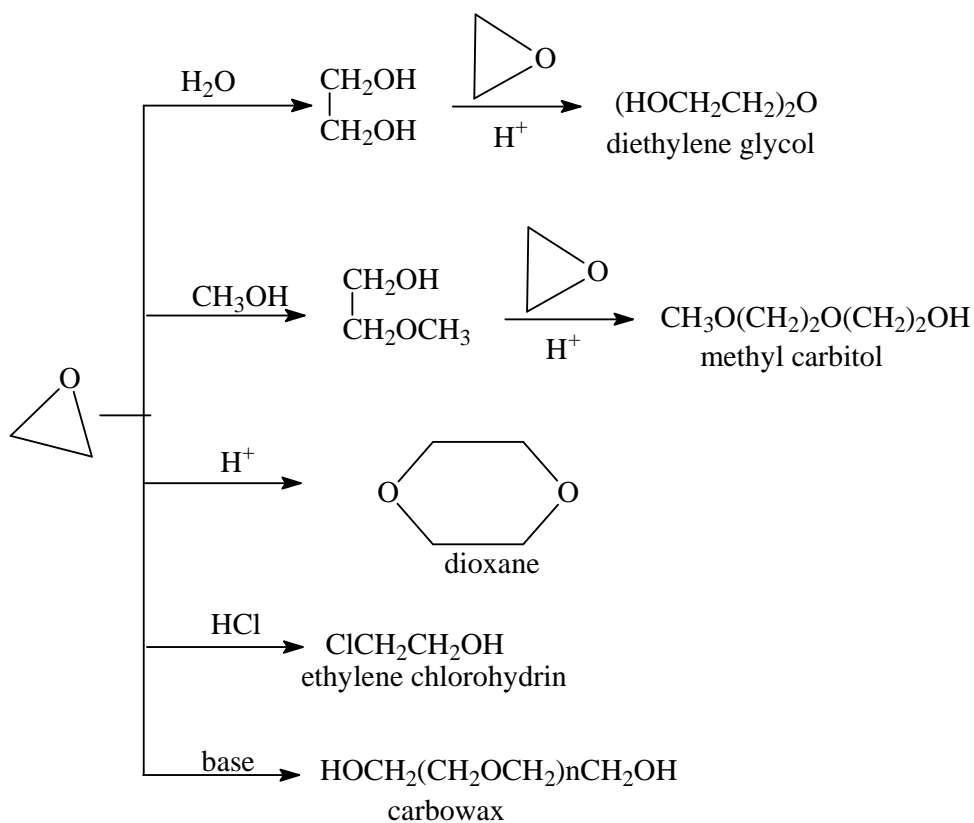


Structure II is a major contributor since the cation is more highly substituted and



Therefore more stable. The nucleophile attacks the carbon with greatest positive partial charge.

Some important chemical reactions of epoxide are summarized as follow.



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### 3.7 SUMMARY

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In this unit we learnt that. Ethers possess the structure: R – O – R' and are compounds having the general formula  $C_nH_{2n+2}O$ . Ethers are isomeric with the aliphatic monohydric alcohols with the general formula  $C_nH_{2n+1}OH$ . We learnt that epoxides are the three membered cyclic ethers. This unit also made us aware that the symmetrical or simple ethers have R and R' being identical while unsymmetrical or mixed ethers have different R and R' groups. We learnt that ethers are characterized by the C-O-C bond and can be classified into linear and cyclic compounds. This unit described that in comparison to alcohols, ethers are fairly unreactive except to very strong acids such as HI or HBr. This low reactivity makes them useful as solvents, *e.g.* diethyl ether,  $(C_2H_5)_2O$  and tetrahydrofuran (THF),  $C_4H_8O$ . The more reactivity of epoxides over simple ethers due to some ring strain and capability to react with nucleophiles resulting in ring opening reaction has also been described in this unit. It has been described in this unit that under acidic conditions, epoxides open by  $S_N1$  way with the nucleophile attacking the more substituted end. The general modoe of synthesis of ethers and cyclic ethers have been described in this unit besides their important reactions.

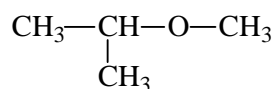
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### 3.8 TERMINAL QUESTIONS

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Q.1 Tick the correct option (MCQs)

i. IUPAC name of the following compound is



A. 1-methoxy-1-methylethane

B. 2-methoxy-2-methylethane

C. 2-methoxypropane

D. isopropylmethyl ether

ii. Ethers can exhibit isomerism

A. Metamesism

B. Functional isomerism

C. Both A and B

D. Geometrical

iii. Ethers have:

- A. Pungent odour  
 B. Pleasant odour  
 C. Fishy odour  
 D. Vinegar odour

iv. When diethyl ether is treated with hot HI, it forms:

- A. Ethyl iodide  
 B. Acetyl iodide  
 C. Propyl iodide  
 D. Ethyl alcohol

v. Ethylisopropyl ether reacts with cold HI gives:

- A.  $\text{CH}_3\text{CH}_2\text{CH}_2\text{I} + \text{CH}_3\text{CH}_2\text{OH}$   
 B.  $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{I} + \text{CH}_3\text{CH}_2\text{OH}$   
 C.  $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{OH} + \text{CH}_3\text{CH}_2\text{I}$   
 D.  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{CH}_3\text{CH}_2\text{I}$

vi. Because of following properties ether are used as inert (reaction) medium.

- A. Neutral and good solvent  
 B. Neutral and bad solvent  
 C. Acidic and good solvent  
 D. Basic and good solvent

vii. Ethoxy ethane is hydrolysed by using

- A.  $\text{KOH}_{\text{aq}}$   
 B.  $\text{H}_2\text{O}$   
 C.  $\text{NaHCO}_3$   
 D. dil  $\text{H}_2\text{SO}_4$  under pressure

viii Which of the following cannot be considered as use of ether?

- A. Inert solvent  
 B. Anaesthetic  
 C. Antipyretic  
 D. Solvent of oil, fats and resins

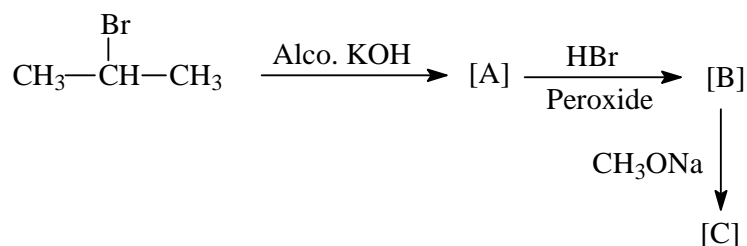
ix. When a mixture of ethyl alcohol and con.  $\text{H}_2\text{SO}_4$  are heated at  $413^\circ\text{K}$  gives diethyl ether. This reaction is:

- A. Dehydration  
 B. Desulphonation  
 C. Intermolecular dehydration  
 D. Intramolecular dehydration

x. With boiling water or steam diethylether gives.

- A.  $(\text{C}_2\text{H}_5)_2\text{SO}_4$   
 B.  $\text{C}_2\text{H}_5\text{OH}$   
 C.  $\text{CH}_2=\text{CH}_2$   
 D.  $\text{C}_2\text{H}_5\text{OH} + \text{C}_2\text{H}_5\text{HSO}_4$

xi. In the reaction:



C is:

- |                      |                     |
|----------------------|---------------------|
| A. Diethylether      | B. 1-methoxypropane |
| C. Isopropyl alcohol | D. Propylene glycol |
- xii. The preparation of ether by diazomethane method is known as:
- |                           |                      |
|---------------------------|----------------------|
| A. Etherification         | B. De-etherification |
| C. Methylation of alcohol | D. methylation       |

xiii. Sodium phenoxide reacts with methyl iodide and give anisol. The reaction is known as:

- |                           |                           |
|---------------------------|---------------------------|
| A. Kolbe's reaction       | B. Williamson's reaction  |
| C. Friedel-Craft reaction | D. Reimer-Teiman reaction |

xiv. From the formula  $\text{C}_4\text{H}_9\text{OH}$ , the number of isomers of ethers obtained is as follow.

- |          |        |
|----------|--------|
| A. Four  | B. Two |
| C. Three | D. One |

xv. Which of the following is ametamer of methyl isopropyl ether /

- |                  |                       |
|------------------|-----------------------|
| A. Butan-2-ol    | B. 2-methylbutan-1-ol |
| C. Diethyl ether | D. Butan-1-ol         |

Q.2 Draw structural formulas for these compounds.

- |   |                                      |
|---|--------------------------------------|
| (a) 2-(1-Methylethoxy)propane           | (b) <i>trans</i> -2,3-Diethyloxirane |
| (c) <i>trans</i> -2-Ethoxycyclopentanol | (d) Ethenyloxyethene                 |
| (e) Cyclohexene oxide                   | (f) 3-Cyclopropyloxy-1-propene       |
| (g) 1,1-Dimethoxycyclohexane            |                                      |

Q.3 Predict the products of the following reaction. An excess of acid is available.  
ethoxycyclohexane + HBr

Q.4. Write the names of reagents and equations for the preparation of the following ethers by Williamson's synthesis:

- (i) 1-Propoxypropane

(ii) Ethoxybenzene

(iii) 2-Methoxy-2-methylpropane

(iv) 1-Methoxyethane

Q.5. Discuss polarity of ethers and compare it with the polar characters of alcohols.

Q.6. Why Grignard reagent is prepared in ether discuss with reaction and reason.

Q.7. Write a note on: Williamson's synthesis.

Q.8. How is diethyl ether prepared in laboratory? How does it react with (i)  $\text{PCl}_5$  (ii)  $\text{O}_2$  (iii) cold concentrated  $\text{H}_2\text{SO}_4$  (iv) Con. HI

Q.9. Discuss different properties and uses of ether

Q.10. Give general methods of preparation and properties of epoxides.

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### **3.9 ANSWERS (MCQs)**

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i-C	ii- C	iii-B	iv -A	v- B
vi - A	vii- B	viii.- C	ix.- D	x.- B
xi - B	xii- C	xiii -B	xiv- C	xv- D

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### **3.10 REFERENCES**

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3. S.M. Mukherji and S.P. Singh, Reaction Mechanism in Organic Chemistry Trinity Press, 2017
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## UNIT 4: ALDEHYDES

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### CONTENTS:

- 4.1 Objectives
- 4.2 Introduction
- 4.3 Structure and nomenclature of the carbonyl group
- 4.4 Preparation of aldehydes
- 4.5 Physical properties of aldehydes.
  - 4.5.1 Relative reactivity of carbonyl compounds
- 4.6 Chemical properties of aldehydes
  - 4.6.1 Addition reactions
  - 4.6.2 Addition reactions followed by elimination
  - 4.6.3 Reduction reactions of aldehydes
  - 4.6.4 Oxidation reactions of aldehydes
  - 4.6.5 Other reactions:
- 4.7. Summary
- 4.8. Self assessment
  - 4.8.1 Fill in the blanks
  - 4.8.3 True/false
  - 4.8.3 Short answer questions
  - 4.8.4 Questions related to important reactions:

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### ***4.1 OBJECTIVES***

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Objectives of this unit are to Study about:- Carbonyl Functional groups; molecular orbital structure of functional group, reactivity of carbonyl group, nucleophilicity vs. basicity, nucleophilicity of carbonyl group, types of reactions carbonyl group undergoes, mechanism of name reactions, effect of conjugation on carbonyl group reactivity.

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### ***4.2 INTRODUCTION***

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An aldehyde alkanals are an important class of an organic compounds containing a functional group with the structure  $-\text{CHO}$ , consisting of a carbonyl center (a carbon

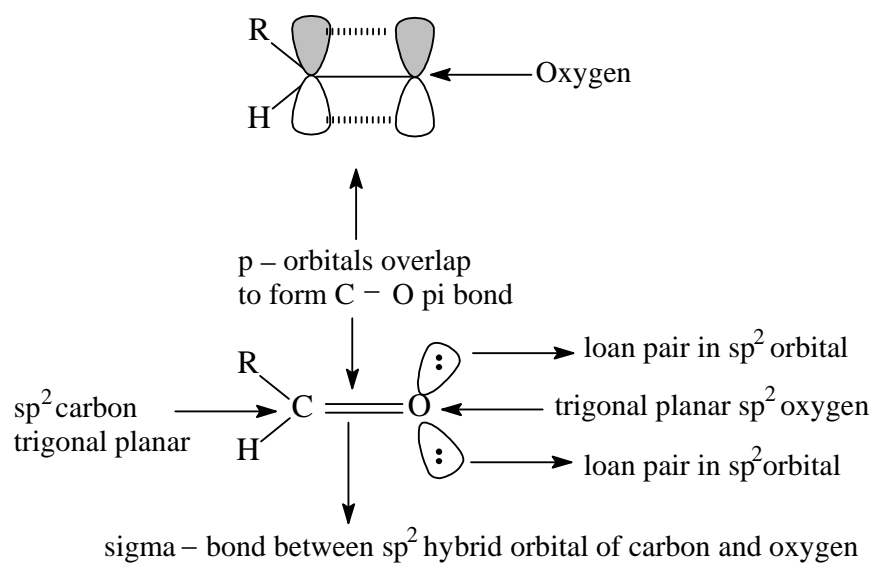


double-bonded to oxygen) with the carbon atom also bonded to hydrogen and to an alkyl/aryl group(s). The group—without alkyl/aryl moiety, also known as the formyl group. Aldehydes are common in organic chemistry. Industrially aldehydes are produced in large scale as starting material for synthesis of other important chemicals. viz HCHO is produced more than 1.4 million tons/year for the preparation of formalin. Traces of many aldehydes are found in essential oils (terpenoids) and often contribute to their favorable odors, e.g. cinnamaldehyde, cilantro, and vanillin. Possibly because of the high reactivity of the formyl group, aldehydes are not common in several of the natural building blocks: amino acids, nucleic acids, lipids. Most sugars, however, are derivatives of aldehydes. These aldoses exist as hemiacetals, a sort of masked form of the parent aldehyde. For example, in aqueous solution only a tiny fraction of glucose exists as the aldehyde.

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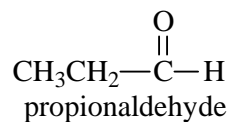
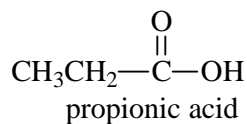
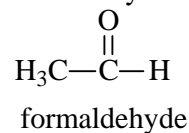
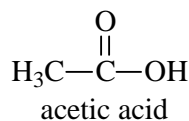
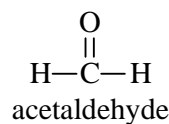
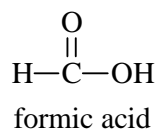
### 4.3 STRUCTURE AND NOMENCLATURE OF THE CARBONYL GROUP

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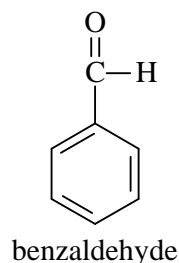
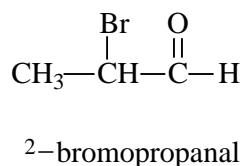
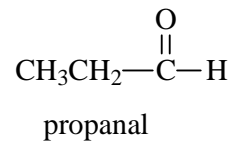
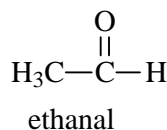
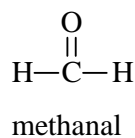
Carbonyl compounds have planar structure. It has a  $\text{sp}^2$  hybridized carbon atom and an  $\text{sp}^2$  hybridized oxygen atom. The carbon uses two  $\text{sp}^2$  hybridized orbitals to form  $\sigma$ -bonds to the substituents. Two lone pairs of electrons are accommodated in  $\text{sp}^2$  hybridized orbital of oxygen.

**Nomenclature:** - Common name for aldehydes are obtained from the names of the corresponding carboxylic acids.



IUPAC names for aldehydes are obtained by replacing the ending -e of the corresponding alkane with -al-. Aldehyde functional group is always terminal in chain.

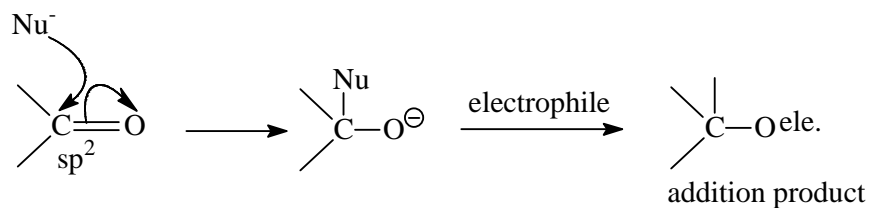
When other substituents are present, the carbonyl carbon is assigned number 1.



The electronegativity of carbon and oxygen is 2.5 and 3.5 respectively.

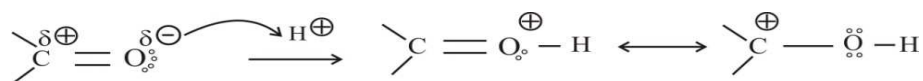
Bond energy of C = O bond is  $720 \text{ kJ mol}^{-1}$ , Bond length of C = O bond is  $1.21 \text{ \AA}$ .

Carbonyl group C = O double bond is shorter than C – O single bond and stronger. C = O bond is polarized and carbon atom has some degree of positive charge and this charge attracts negatively charged nucleophiles and supports nucleophilic addition reaction.

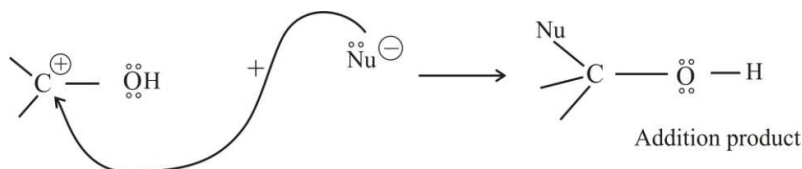


Nucleophilic addition reactions of Aldehydes may be catalysed by acids or bases.

**Acid catalysis** - Electrophilic protonation Addition :



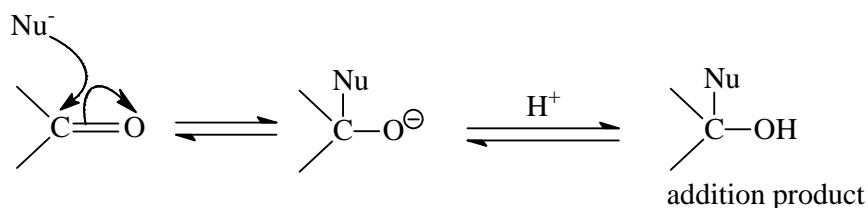
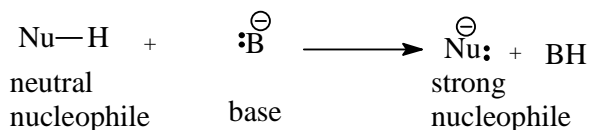
Hydrogen ion of acid attacks negatively charged carbonyl oxygen to give protonated carbonyl group. Protonated carbonyl which is resonance stabilized.



The nucleophile attacks the protonated carbonyl group to form the addition product.

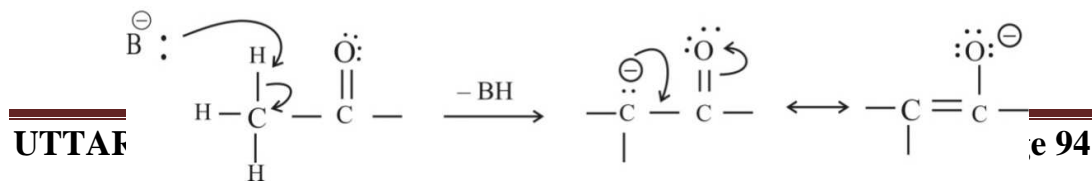
**Base catalysis – nucleophilic addition – protonation**

Bases convert weak nucleophile to a strong one by deprotonation.



So, in carbonyl carbon two areas of reactivity, i.e. Lewis basic oxygen and electrophilic carbonyl carbon lead to addition of carbonyl  $\pi$  bond.

**$\alpha$ -hydrogen :-** A carbon next to the carbonyl group is called  $\alpha$ - carbon and the hydrogen attached with it is referred to as an  $\alpha$ -hydrogen.  $\alpha$ -hydrogens of carbonyl carbon are acidic in nature with some  $pK_a$  values. Abstraction of  $\alpha$  hydrogen by a base ( $B^-$ ) results in the formation of anion (enolate ion) which is resonance stabilized by delocalisation of charge onto electronegative oxygen.

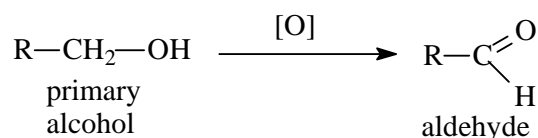


$\alpha$ - carbon of the enolate ion is an ambident ion. It can act as nucleophile and attack at electrophilic carbonyl carbon of other carbonyl group containing molecules and leads to condensation. Enolate ion can attach an alkyl group to the reactive carbon and it is called **C-alkylation**. Alkylation at oxygen is uncommon but protonation leads to **alkenol**.

#### 4.4 PREPARATION OF ALDEHYDES

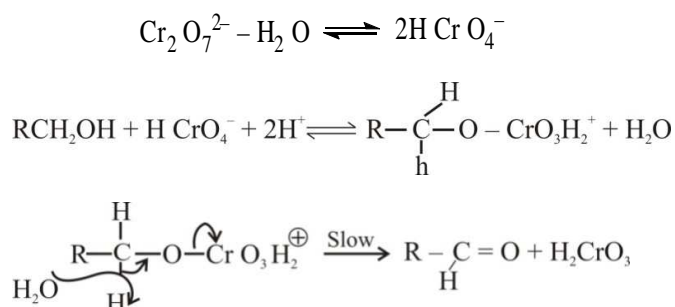
There are several reactions which can be used for the synthesis of aldehydes some of them are as follow:-

- Oxidation of alcohols:** Oxidation of Primary Alcohols under controlled condition gives aldehyde.



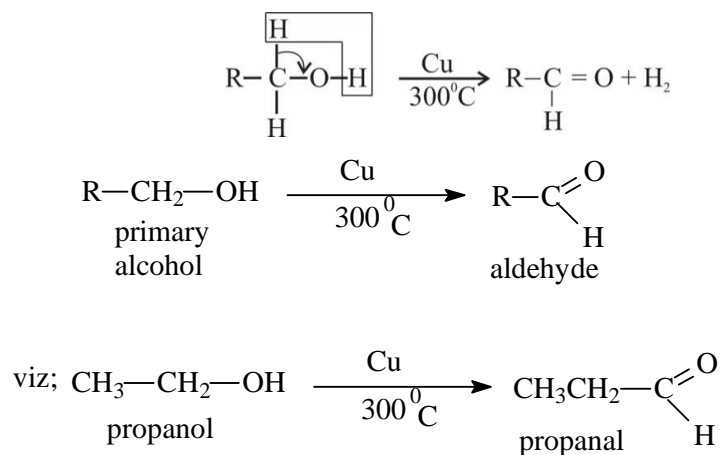
Oxidising agents used are acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  solution, alkaline  $\text{KMnO}_4$ , chromic acid  $\text{H}_2\text{Cr}_2\text{O}_7$ , pyridine chlorochromate (PCC)  $\text{C}_5\text{H}_6\text{N}(\text{CaO})_3\text{Cl}$  in (DCM solvent)  $\text{CH}_2\text{Cl}_2$ .

**Mechanism:** Mechanism of oxidation of alcohol by dichromate is following:

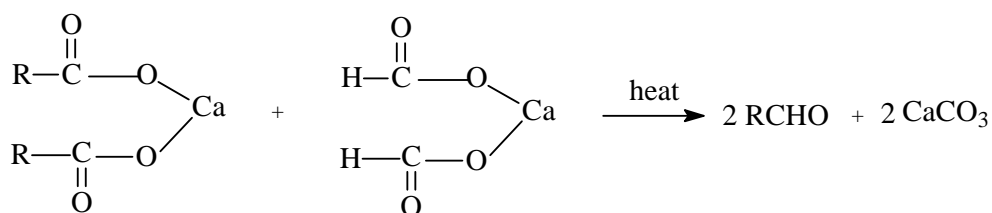


Similar ester intermediate is formed in oxidation with permanganate.

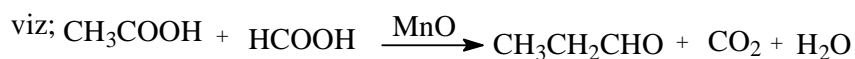
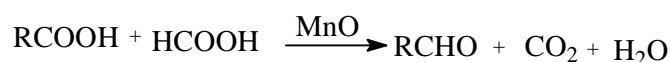
- Catalytic dehydrogenation of alcohols:** - Aldehydes may be prepared by dehydrogenation of primary alcohol by passing vapours over copper catalyst at about  $300^\circ\text{C}$  of alcohol.



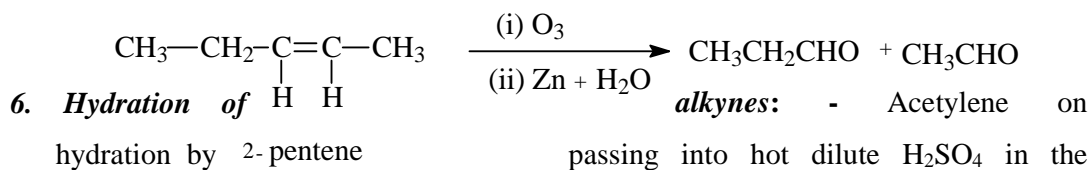
3. By heating a mixture of the calcium salts of formic acid and any one of its homologues



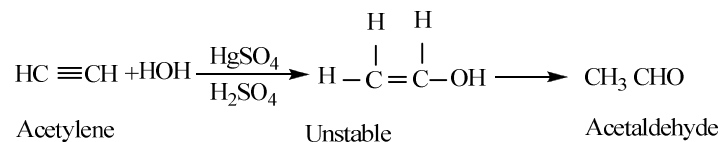
4. By passing a mixture of vapours of formic acid and any one of its homologues over manganous oxide a catalyst at 300°C.



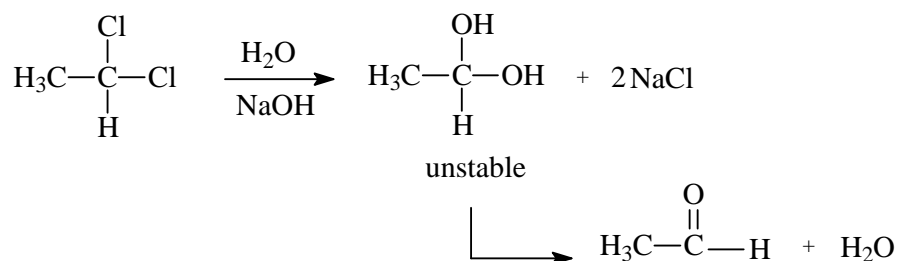
5. **Oxidation of alkenes (ozonolysis):-** Oxidation of alkene viz; 2-pentene with ozone gives ozonides which are often explosive in dry state and they are decomposed with  $\text{Zn} + \text{H}_2\text{O}$  to give carbonyl compounds.



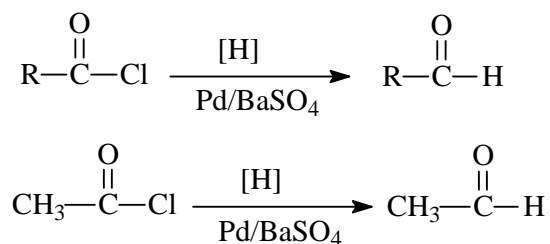
presence of  $\text{HgSO}_4$  as catalyst is converted into acetaldehyde.



**7. Alkaline hydrolysis of gem dihalides:** - The geminal dihalides (two halogens atoms are attached to the terminal carbon atom) gives Aldehyde

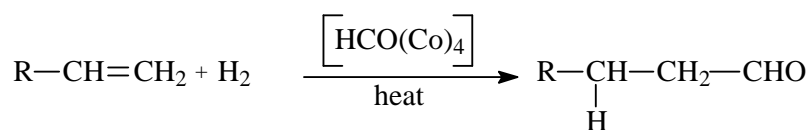


**8. Rosenmund's Reduction:** - This is one of the most common method for the synthesis of aldehydes. In this method reduction of an acid chloride with hydrogen in boiling xylene using a poisoned palladium catalyst supported on  $\text{BaSO}_4$  is used.

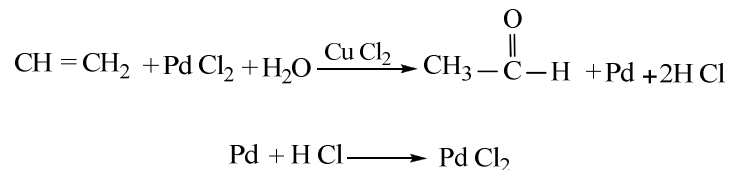


Here  $\text{BaSO}_4$  prevents further reduction of aldehyde to alcohol as it acts as a poison to Pd catalyst. So small amount of quinoline and sulphur is added to deactivate catalyst partially. Lithium tri-*t*.butoxy aluminum hydride (LTBA) can also be used as catalyst.

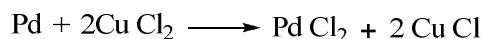
**9. Oxo process:** - It is an industrially important method to produce aldehydes. Here alkene is treated with carbon monoxide (CO) and hydrogen in the presence of cobalt carbonyl catalysts at high temperature and pressure.



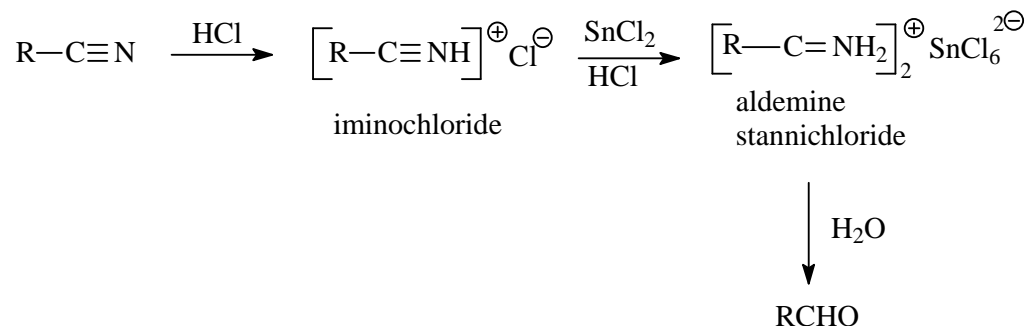
**10. Wacker process:** - In this process alkene is treated with an acidified aqueous solution of palladium chloride (PdCl<sub>2</sub>) and cupric chloride (CuCl<sub>2</sub>).



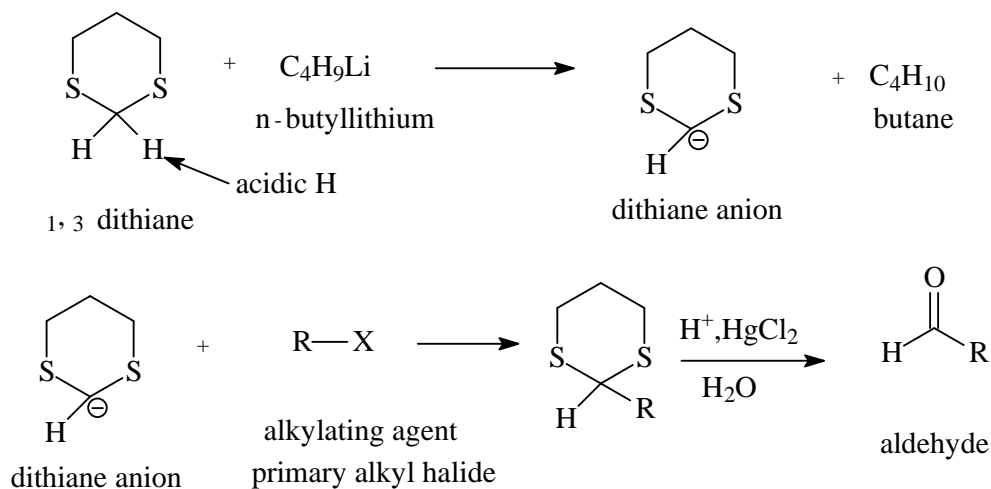
Cu Cl<sub>2</sub> promotes regeneration of Pd Cl<sub>2</sub> from Pd.



**11. Stephen's method:** - Here alkyl cyanide is dissolved in ether, or ethyl formate or ethyl acetate and reduced with stannous chloride and hydrochloride acid and then steam distilled.

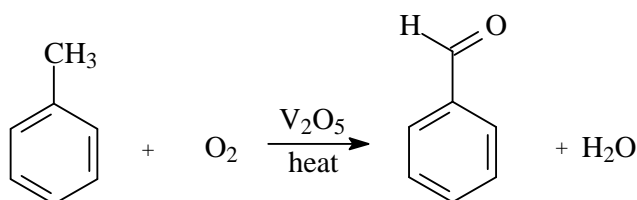


**12. Synthesis of aldehyde from 1,3-dithiane:** 1,3-dithiane has 2 weakly acidic protons that can be removed and alkylation of the carbon is possible. Once alkylated, the 1,3-dithiane becomes a "protected" carbonyl as it can be hydrolyzed to the corresponding carbonyl hydrolyzed to the corresponding carbonyl structure.

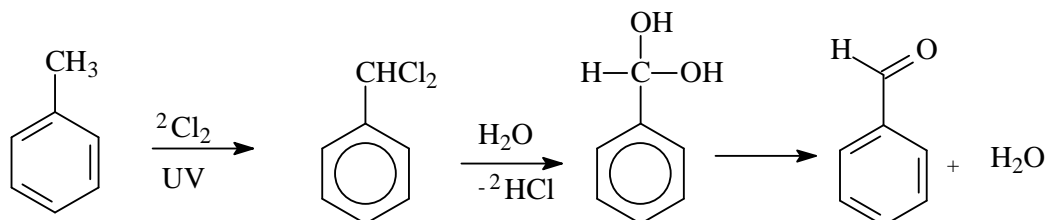


**13. Preparative methods of aromatic aldehydes:** Aromatic aldehydes are carbonyl compounds containing CHO functional group attached with phenyl ring /aromatic rings. Like aliphatic aldehydes there are several methods for the synthesis of aromatic aldehydes some of them are being discussed as follow.

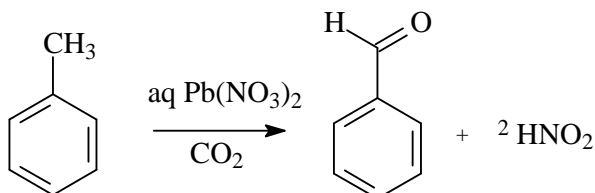
- i. Oxidation of Toluene with oxygen / air in the presence of vanadium pentoxide catalyst at  $350^\circ\text{C}$ .



- ii. By hydrolysis of benzylidene chloride with aqueous acid.

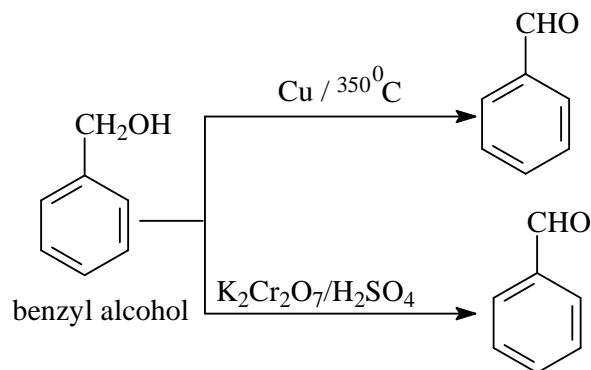


- iii. Boiling of benzyl chloride with aqueous copper or lead nitrate in a current of  $\text{CO}_2$  yields benzaldehyde.

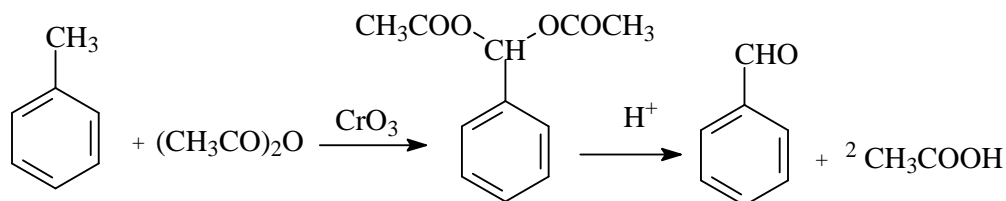




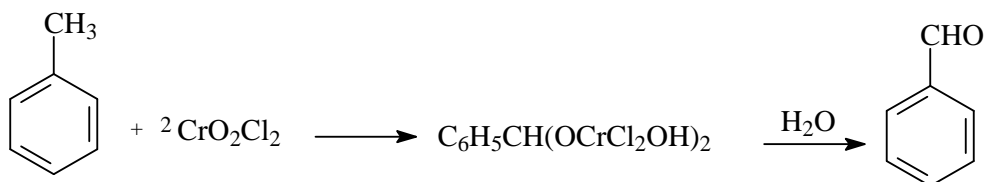
iv. Oxidation of benzylalcohol with acidic  $K_2Cr_2O_7$  or with copper catalyst at  $350^\circ C$ .



v. Oxidation of alkylbenzene by chromium trioxide in acetic anhydride yields benzylidene diacetate which on hydrolysis with dilute sulphuric acid or hydrochloric acid gives benzaldehyde.

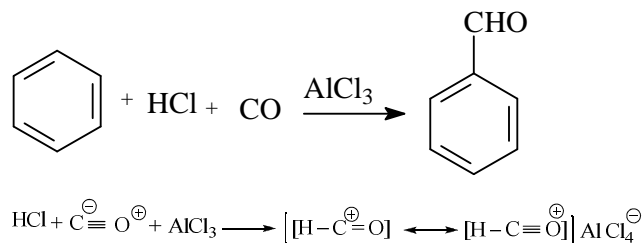


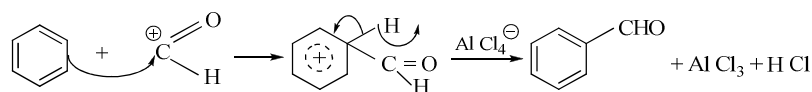
When Toluene is oxidized by chromyl chloride ( $CrO_2Cl_2$ ) in  $CCl_4$  solution yields complex, which on hydrolysis forms benzaldehyde.



This reaction is known as **Etard** reaction.

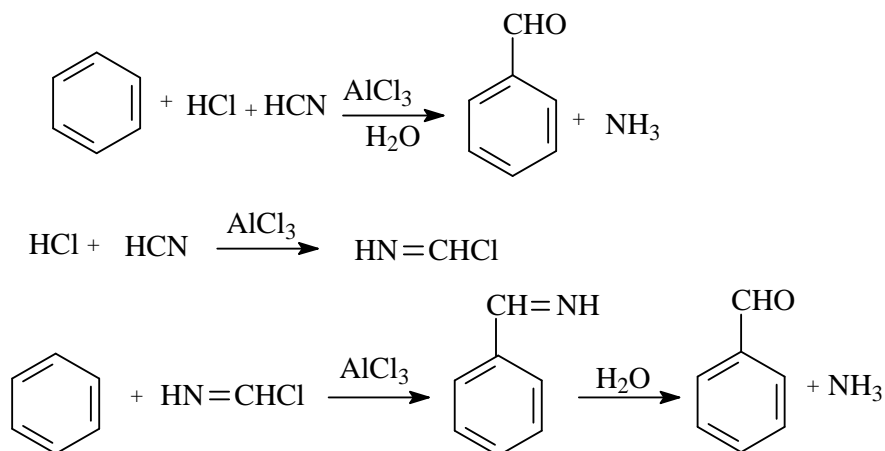
vi. **Gattermann Koch aldehyde synthesis:** Benzene is treated with mixture of carbon monoxide and hydrogen chloride in the presence of anhydrous  $AlCl_3$  and small amount of cuprous chloride.





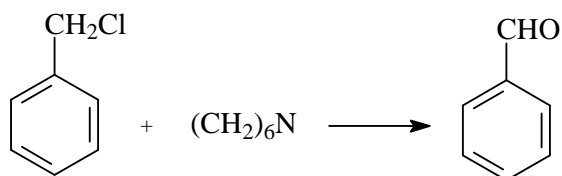
When methyl grp is present in benzene ring then CHO grp is introduced at para position. This synthesis is not applicable to phenols or deactivating grp having benzene.

vii. **Gattermann aldehyde synthesis:** - When Benzene is treated with a mixture of HCN and HCl in the presence of  $\text{AlCl}_3$ , it produces a complex and it is decomposed with water to produce benzaldehyde.

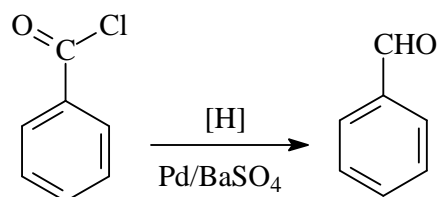


This reaction is applicable to phenols and phenolic ethers, but not to nitrobenzene.

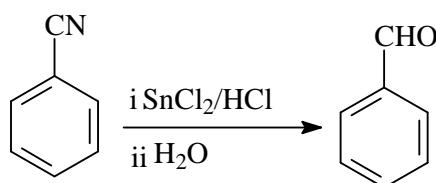
viii. **Sommelet's Reaction:** - Benzyl chloride is refluxed with hexamethylenetetramine in aqueous ethanolic solution, followed by acidification and steam distillation to yield Benzaldehyde.



ix. **Rosenmund Reduction :-** Catalytic reduction of benzoyl chloride in the presence of quinoline sulphur poison or  $\text{Pd}/\text{BaSO}_4$  yield benzaldehyde.

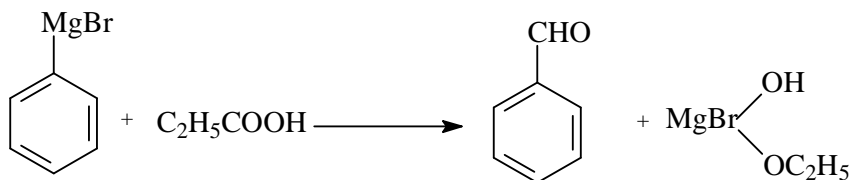


- x. **Stephen's method** :- When phenyl cyanide is reduced with stannous chloride and hydrochloric acid in ethereal solution it gives aldimine stannichloride complex which on hydrolysis with water forms benzaldehyde.

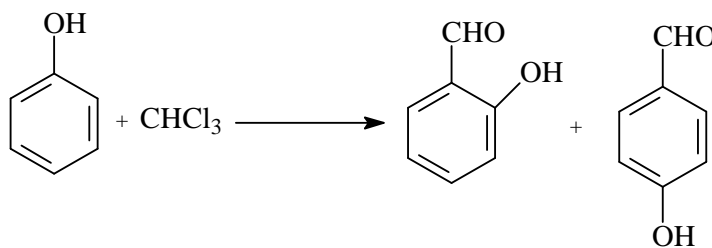


In ortho substituted cyanides case yield is negligible due to steric hinderance.

- xi. When Phenyl magnesium bromide is treated with ethyl formate or ethylorthoformate, it gives Benzaldehyde.



- xii. **Reimer Tiemann Reaction** :- When phenol is treated with CHCl<sub>3</sub> in the presence of alkali forms O-hydroxy formaldehyde.



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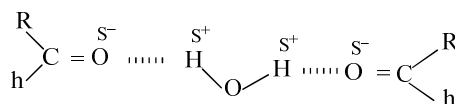
**4.5 PHYSICAL PROPERTIES OF ALDEHYDES**


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1. In aldehyde the first member HCHO is gaseous at room temperature. Acetaldehyde is liquid in nature with b.p. 20<sup>0</sup>C. Lower aldehydes are colourless liquids. Benzaldehyde is liquid with characteristic smell of bitter almonds.
2. Lower members of aldehydes possess unpleasant smell.
3. Carbonyl group compounds are polar in nature due to dipole - dipole interactions of partial negative charge of carbonyl oxygen of one molecule and partial positive charge on the carbonyl carbon of another molecule. So boiling points of aldehydes and ketones are higher than those of alkanes which have comparable molecular weights. However these dipole -dipole interactions are weaker than hydrogen bonding interactions, hence aldehydes and ketones due to lack of intermolecular hydrogen bonding have low boiling points as compared to alcohols of comparable molecular weights.

	$\text{CH}_3\text{CH}_3$	$\begin{array}{c} \text{O} \\    \\ \text{H}-\text{C}-\text{H} \end{array}$	$\text{CH}_3\text{OH}$
	ethane	methanal formaldehyde	methanol
Mol. wt.	30	30	32
b.p.	-89 <sup>0</sup> C	-21 <sup>0</sup> C	64.5 <sup>0</sup> C

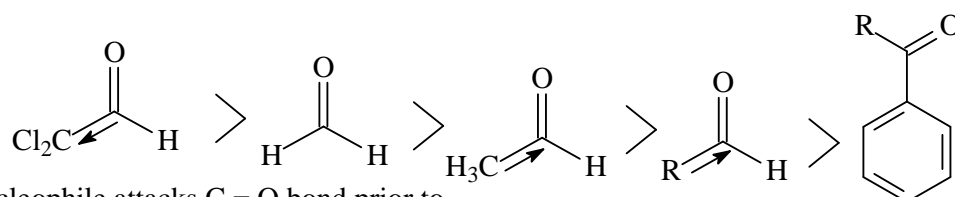
4. As aldehydes and ketones can form hydrogen bonds with water so lower aldehydes and ketones are soluble in water.



However solubility decreases as the hydrocarbon part of molecule increases. The lower aldehydes and ketones are soluble in organic solvents such as benzene, ether and CCl<sub>4</sub>. Carbonyl compound also form hydrates with water i.e. corresponding geminal diols.

### 4.5.1 RELATIVE REACTIVITY OF CARBONYL COMPOUNDS

The carbonyl group of aldehydes is reactive because of electromeric effect. However the electron withdrawing substituents make carbonyl group more electrophilic, as withdrawing groups generates extra positive charge at carbonyl carbon and electron donating alkyl groups reduce positive charge at carbonyl carbon. Increased positive charge at carbonyl carbon destabilize carbonyl compounds and favours attack of nucleophile at electron deficient carbonyl carbon which is followed by the addition of electrophile on negatively charged oxygen.



Nucleophile attacks C = O bond prior to

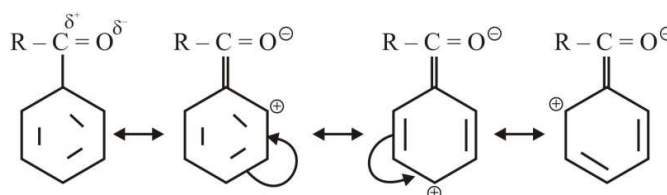
electrophile because the produced anion is more stable than the cation resulting due to electrophile attack.

The reactivity of nucleophilic addition is favoured by

- Electron withdrawing substituent at carbonyl carbon.
- Small size of substituent group to avoid steric hindrance for attacking reagent.

During nucleophilic addition reaction carbonyl carbon transforms from  $sp^2$  hybrid state to  $sp^3$  hybridized state and bond angle reduces from  $120^\circ$  approx. to  $109.5^\circ$  approx. So transition stage bears steric strain and this steric strain increases with increasing bulk of groups which are already present on carbonyl carbon.

Aromatic carbonyl compounds are less reactive than the corresponding aliphatic carbonyl compounds. Here partial positive charge present on carbonyl carbon is delocalized over benzene ring by resonance.



So electrophilic nature of carbonyl carbon which is desired for nucleophilic addition reaction is neutralized and nucleophilic addition reaction slows down. The acids and bases act as catalyst for a number of carbonyl addition reactions. Here acids catalysts make carbonyl group more electrophilic by protonating carbonyl groups lone pair and base catalysts make nucleophile more nucleophilic by deprotonating nucleophile.

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#### 4.5 CHEMICAL PROPERTIES OF ALDEHYDES

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The slightly positive carbon atom in the carbonyl group can be attacked by nucleophiles. A nucleophile is a negatively charged ion (for example, a cyanide ion, CN<sup>-</sup>), or a slightly negatively charged part of a molecule. Some of the important reactions of aldehydes are being given below

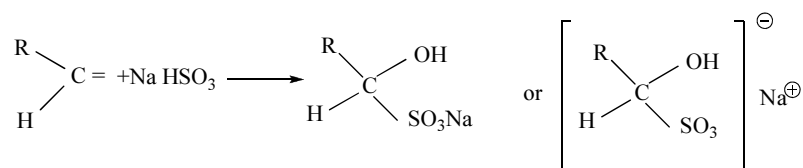
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##### 4.6.1 ADDITION REACTIONS

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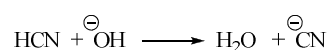
During the reaction, the carbon-oxygen double bond gets broken. The net effect of all this is that the carbonyl group undergoes addition reactions.

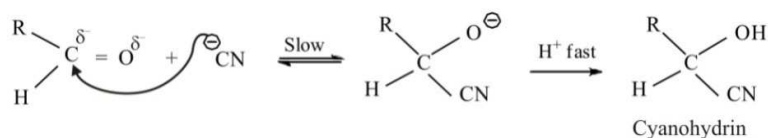
- (1) **Addition of Sodium Bisulphite** – Aldehydes add on sodium hydrogen sulphite to form bisulphite compounds.



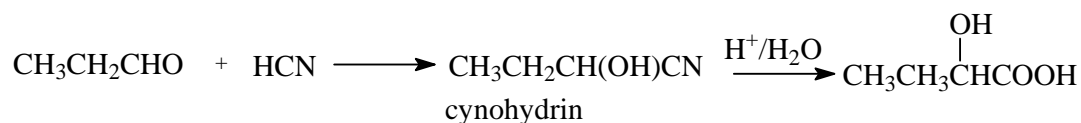
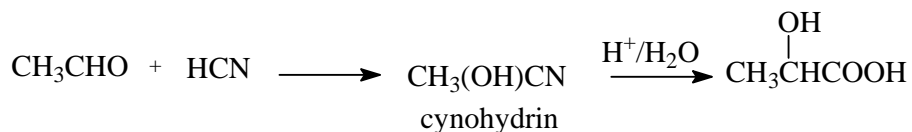
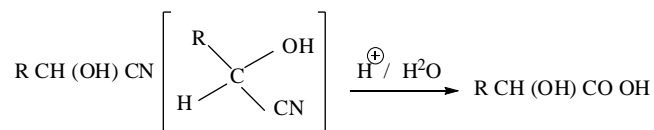
Thus the formed bisulphite compounds are hydroxysulphonic acid salts where sulphur atom is directly attached to the carbon atom. When bisulphite compounds are heated with dilute acid or Na<sub>2</sub>CO<sub>3</sub> solution then carbonyl compound is regenerated.

- (2) **Addition of hydrogen cyanide(HCN)** - All Aldehydes add HCN in the presence of base catalyst to form cyanohydrins.

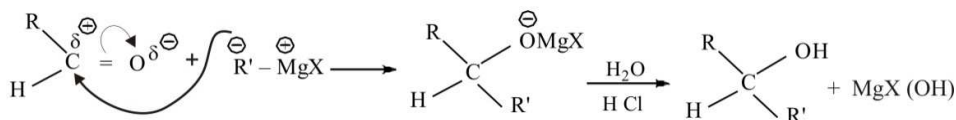




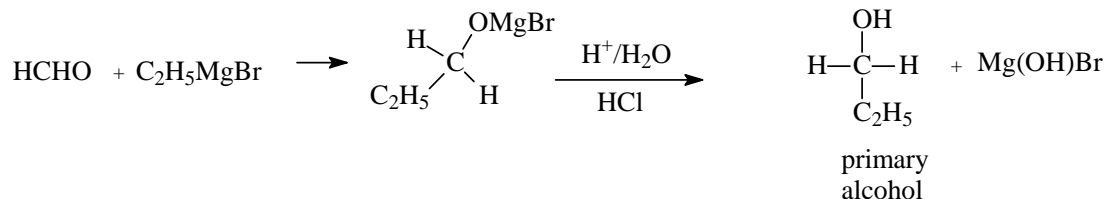
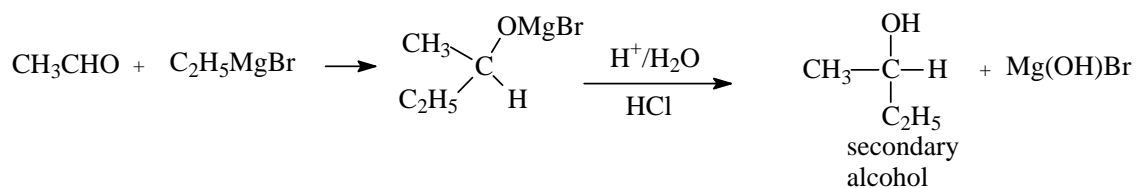
Cyanohydrins can be hydrolysed readily to  $\alpha$  hydroxy acids.



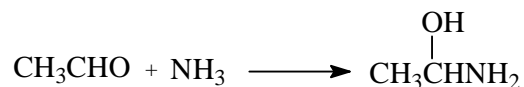
**(3) Addition of Grignard Reagents :** Aldehydes react with Grignard reagents to form a complex dilute acids gives alcohol.



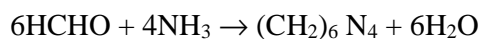
Formaldehyde gives primary alcohol. Other aldehyde gives secondary alcohols.



**(4) Addition of ammonia** – Aldehydes (except HCHO) react with ammonia in other to give aldehyde ammonia.

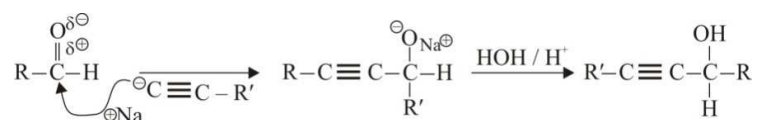


Formaldehyde on treatment with ammonia gives hexamethylenetetraamine.

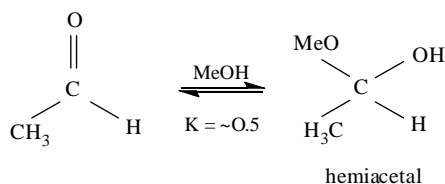


Addition Reactions followed by loss of water

**(5) Addition of terminal Alkynes** – Sodium salt of terminal alkynes reacts with aldehydes to give alkynol. This reaction is known as Ethinylation.

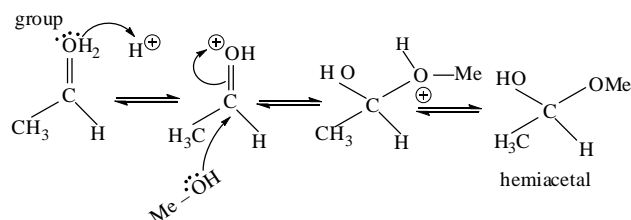


**(6) Addition of alcohols** – When acetaldehyde is dissolved in methanol it reacts to form hemiacetal which is unstable as compare to parent aldehyde.



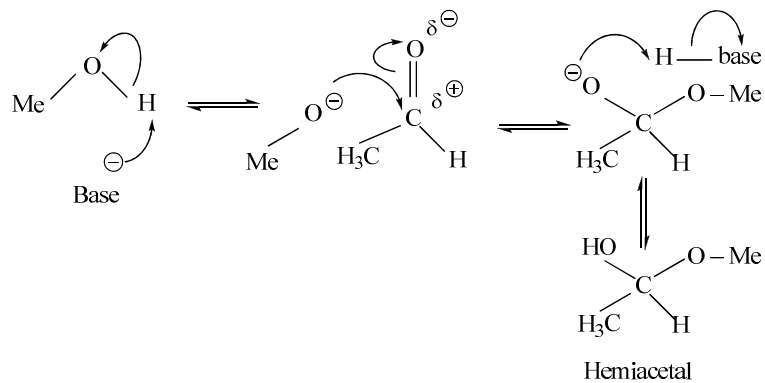
Rate of formation of hemiacetals is greatly increased either by acid or by base.

Acid catalysts increase electrophilicity of carbonyl.

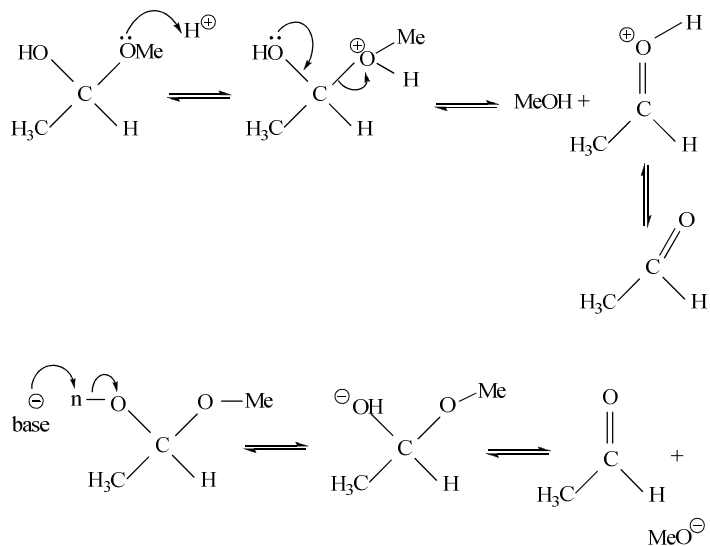


Base catalysts increase nucleophilicity of alcohol by removing the OH proton before it attacks the C = O group.

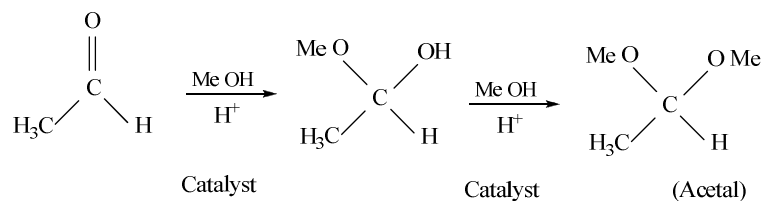


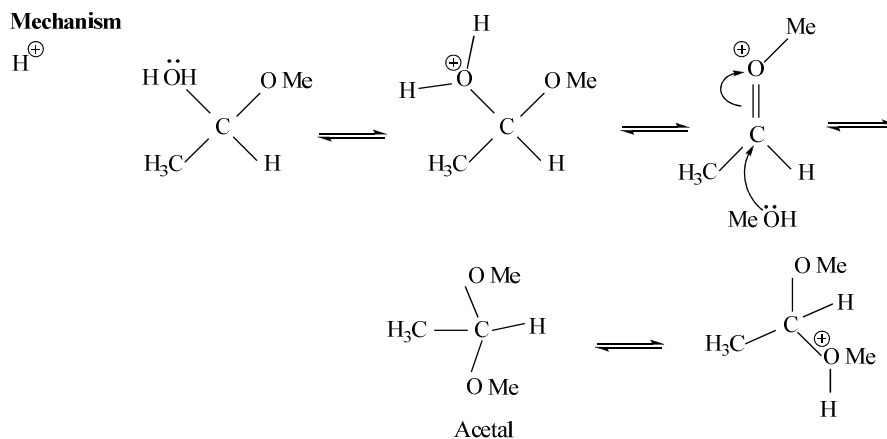


Hemiacetals are unstable. Here acid or base catalyse not only formation of hemiacetals but also decomposition them into aldehyde.

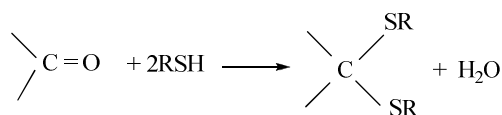


When catalytic acid is added to acetaldehyde-methanol mixture rate of reaction increases and two equivalents of alcohols are added to aldehyde to form new class of compound called acetal.





- (7) **Addition of mercaptans:** Aldehydes condense with thioalcohols (mercaptans) in the presence of HCl to form mercaptals.

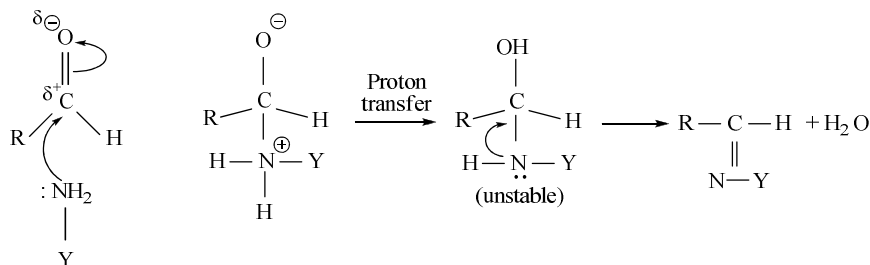


#### 4.6.2 ADDITION REACTIONS FOLLOWED BY ELIMINATION

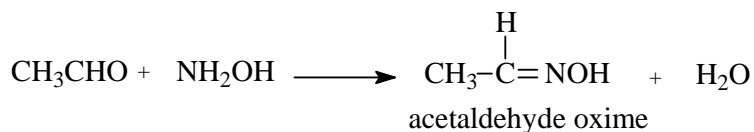
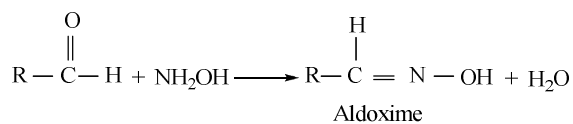
The addition reactions of aldehydes often followed by the loss of a water molecule. This gives a reaction known as addition-elimination or condensation. The important reactions in continuation to addition reactions as above (4.6.1) given by aldehydes are:

- (8) **Addition of ammonia Derivatives** – Aldehydes combines with various compounds of type Y — NH<sub>2</sub> (Y = NH<sub>2</sub>, OH, C<sub>6</sub>H<sub>5</sub>NH etc) to form carbon nitrogen double bonded compounds and a water molecule is eliminated.

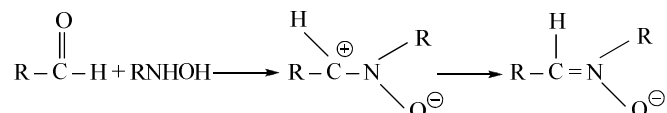
**Mechanism**



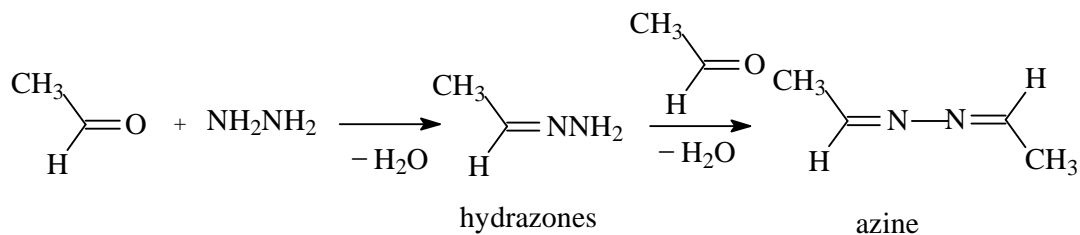
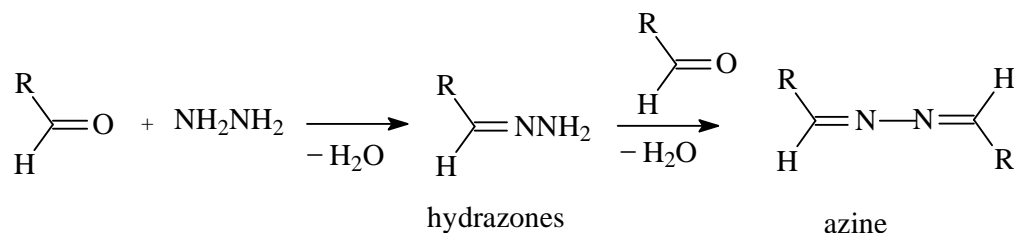
- (a) Hydroxylamine (NH<sub>2</sub>OH) form oximes with carbonyl compounds



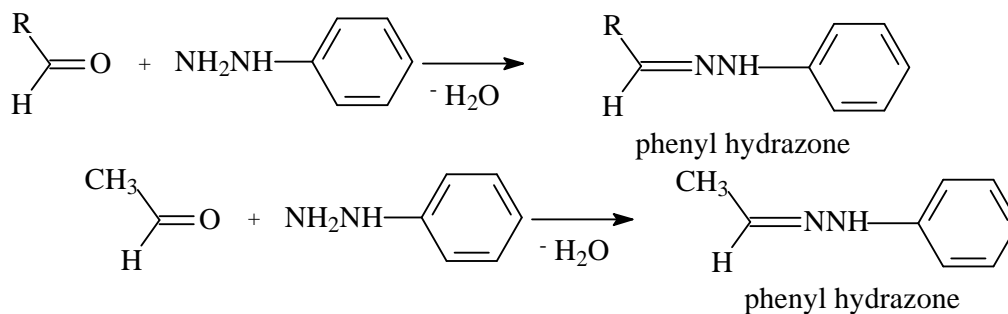
(b) N - substituted hydroxylamines form nitrones which show 1, 3 addition reactions.



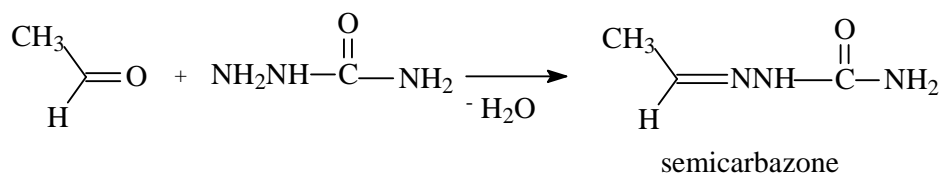
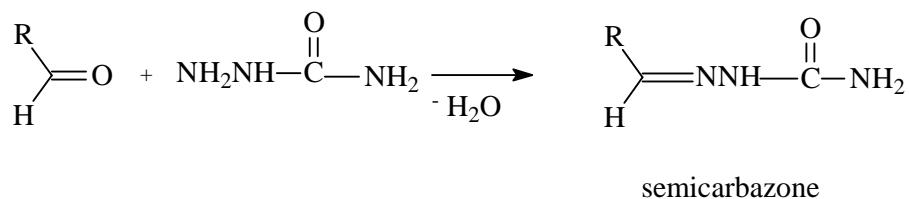
(c) Hydrazines (NH<sub>2</sub>NH<sub>2</sub>) react with carbonyl compound to give Hydrozones or azines.



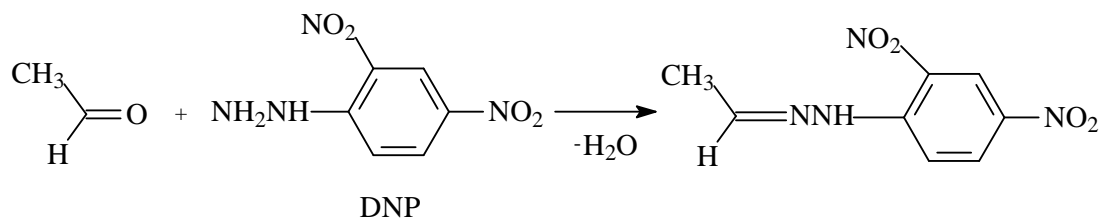
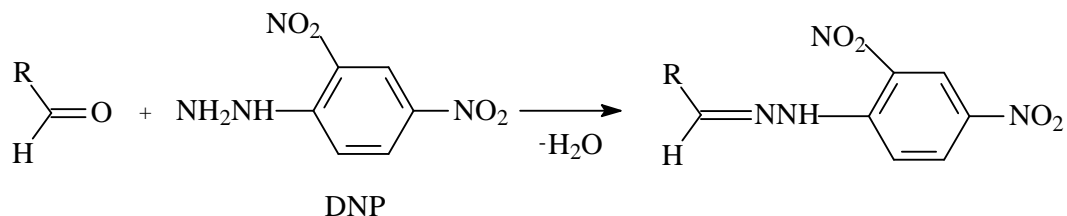
d) Phenyl hydrazine (NH<sub>2</sub>NHC<sub>6</sub>H<sub>5</sub>) forms phenyl hydrazones with carbonyl compounds.



- (e) Carbonyl compounds react with semicarbazides ( $\text{NH}_2\text{NHCONH}_2$ ) to form semicarbazones.

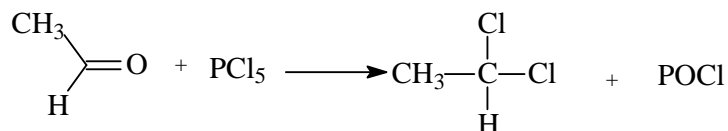
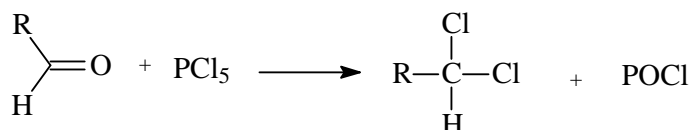


- (f) 2, 4 dinitrophenyl hydrazine (DNP) (Brady's reaction) react with carbonyl compounds to give 2, 4 dinitrophenyl hydrazones.

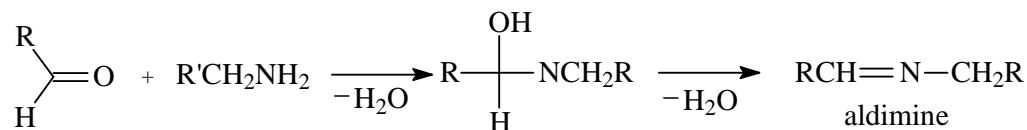


Oximes and hydrazones regenerate carbonyl compound when refluxed with dilute hydrochloric acid. Regeneration from phenylhydrazones is difficult.

- (9) Phosphorus pentachloride reacts with simple carbonyl compounds to form 1, 1, dichlorides.



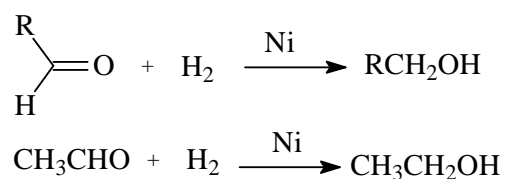
(10) Aldehydes react with aliphatic primary amines to form aldimines.



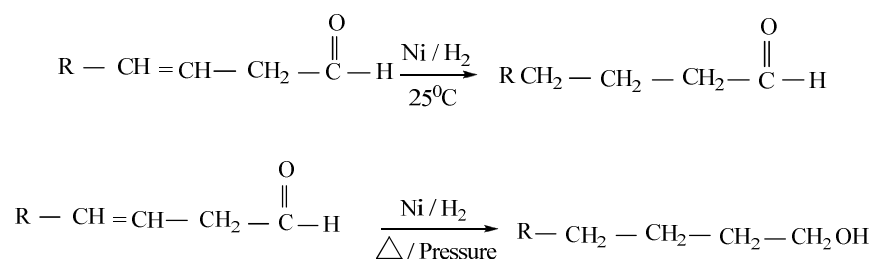
### 4.6.3 REDUCTION REACTIONS OF ALDEHYDES

Aldehydes can be reduced to alcohols. In continuation to other reactions as discussed above the reduction reactions are being discussed as follows.

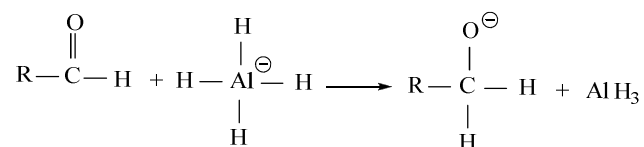
(11) Aldehydes can be reduced to alcohols by treatment with Hydrogen and Ni or Pt catalyst.



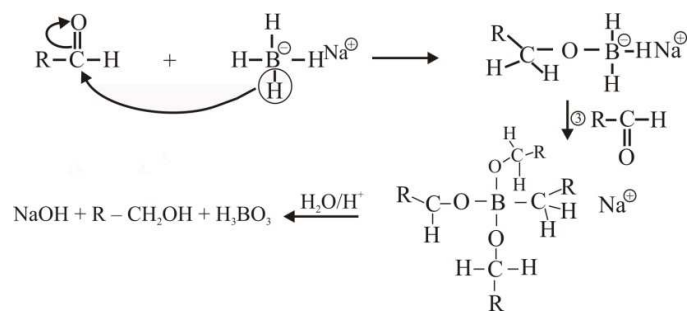
If both double bond and carbonyl groups are present then either both are hydrogenated or preferentially double bond is hydrogenated leaving carbonyl group intact.



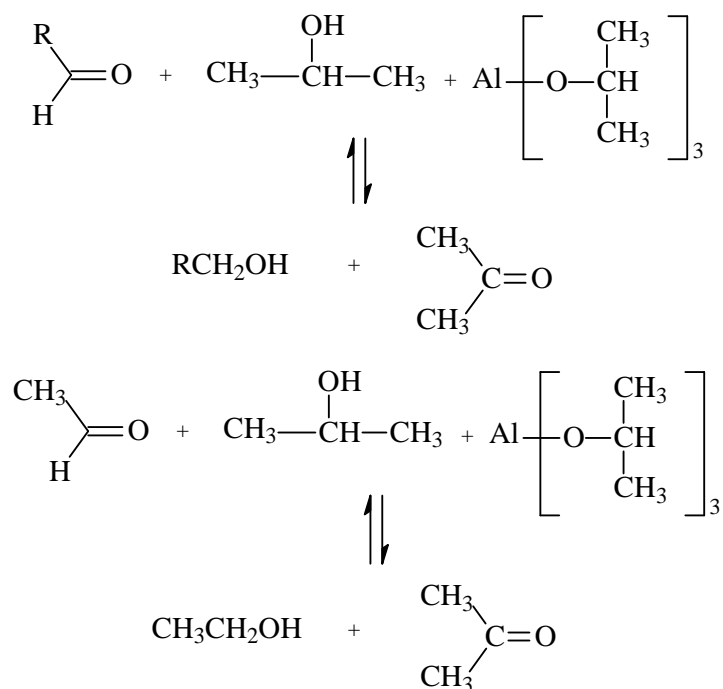
Some metal hydrides as LAH (lithium aluminium hydride) in anhydrous ether or THF solvent and NaBH<sub>4</sub> (sodium borohydride) in water or alcohol as solvent can be used as reducing agent.



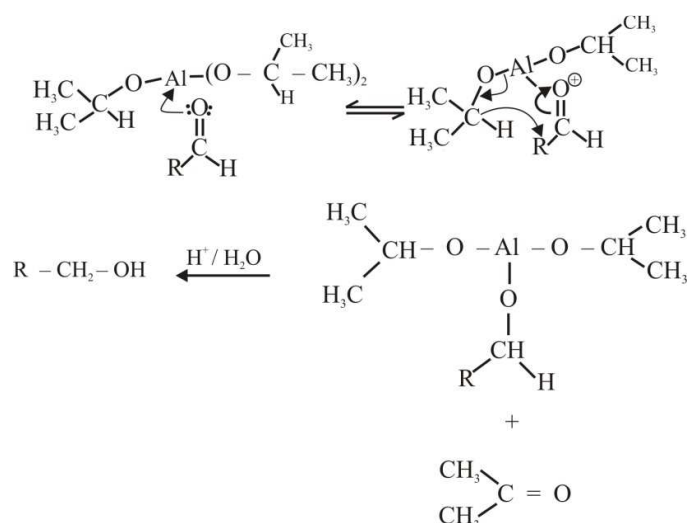
Each hydride ion can reduce one carbonyl group.



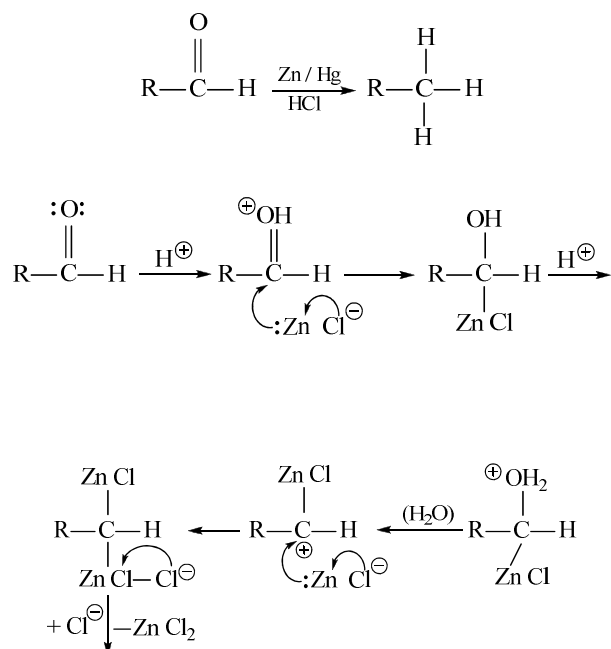
(12) Aldehydes can be reduced to corresponding alcohols by dissolving aldehydes in isopropyl alcohol containing aluminium isopropoxide. Here isopropyl alcohol is converted to acetone. This reaction is known as **Meerwein-Ponndorf-Verely (MPV) reduction**.

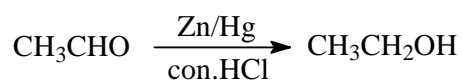
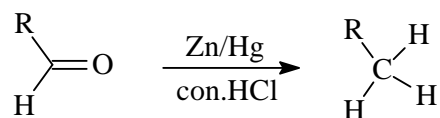
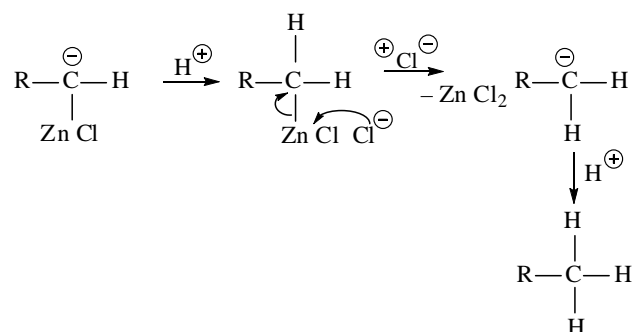


Mechanism:

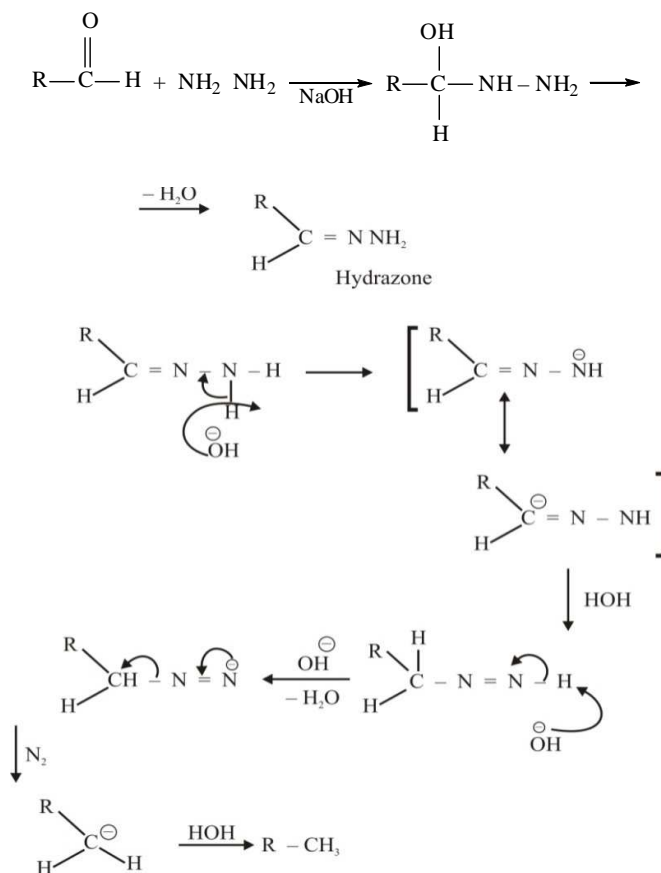


**(13) Reduction to hydrocarbon:** Carbonyl group of compound is reduced to methylene group by using zinc amalgam and hydrochloric acid. This reaction is called **Clemmensen reduction**. In this reaction carbonyl group is reduced to  $-\text{CH}_2-$  group. Ketones are more effective than aldehydes in this reduction. The mercury alloyed with the Zn does not participate in the reaction; it serves only to provide a clean active metal surface. Some times alcohols may be used as the solvent in **Clemmensen reduction**





(14) **Wolff-Kishner reduction:** Hydrazones are heated with Sodium ethoxide at 180°C, Nitrogen is eliminated and carbonyl group is converted to methylene group i.e. hydrocarbon.





Reaction can be carried out at room temperature in the presence of polar solvents like DMSO. Use of Potassium t-butoxide gives better yield.

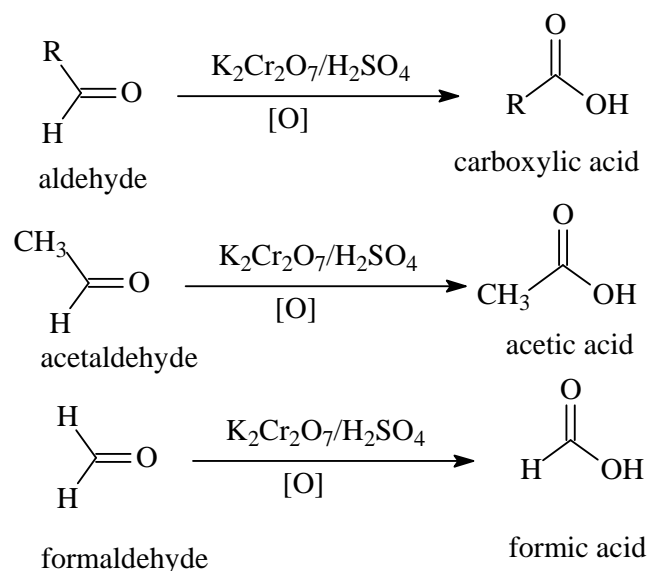
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#### 4.6.4 OXIDATION REACTIONS OF ALDEHYDES

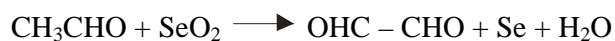
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The aldehydes in presence of oxidizing agent can be oxidized to corresponding carboxylic acids in continuation the reactions are being described as follow.

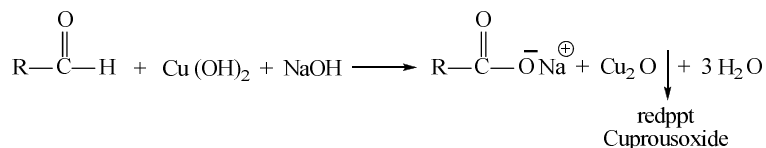
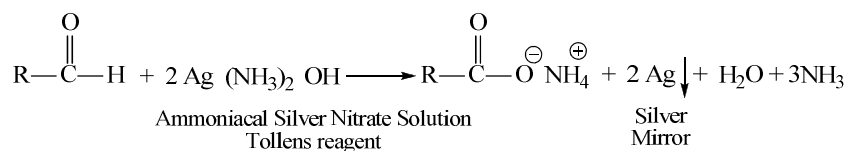
(15) (i) Aldehydes are easily oxidized with  $K_2Cr_2O_7$  in Sulphuric acid, or  $KMnO_4$ .



(ii) Aldehydes with methyl or methylene group adjacent to carbonyl group are oxidised to dicarbonyl compounds by Selenium oxide.



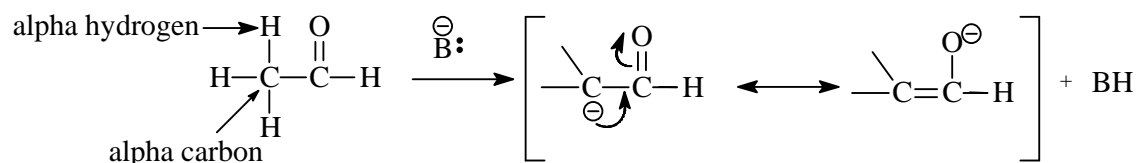
(iii) Mild oxidizing agents like tollen's reagent  $[Ag(NH_3)_2OH]$ , Fehling's solution i.e. alkaline solution of cupric ion or Benedict's solution i.e. alkaline solution of Cupric ion complexed with citrate ion; oxidize aldehydes.



Benzaldehyde gives positive test with Tollen's reagent but not with Fehling's and Benedict's solution because of + Resonance effect of Benzene ring which makes C-H bond stronger and weak oxidizing agents like Fehling and Benedict solutions could not oxidize aromatic aldehydes.

#### 4.6.5 OTHER REACTIONS

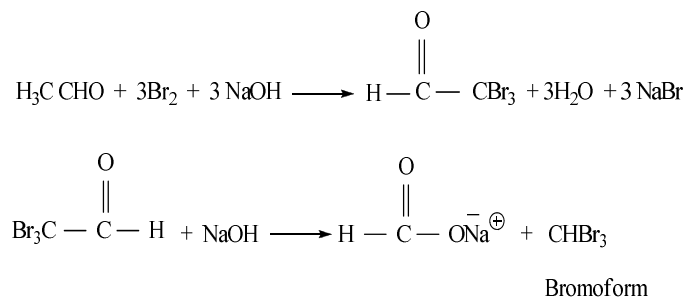
The carbonyl groups are polar and this polarity increases acidity of hydrogens of  $\alpha$ -carbon. These  $\alpha$ -hydrogens may lead to form enolate ions. These enolate ions are good nucleophile and can attack on electrophiles like protons. The pKa value of aldehyde is lower than that of ethane or acetylene but it is comparable to those of alcohols. So  $\alpha$  halogens of aldehydes are removable by strong bases.



Enolate ion is ambident anion. Here partial negative charge is located on both  $\alpha$  carbon and oxygen i.e. two different sites of one molecule are having -ve charges. So this nucleophile can attack electrophiles at either of two sites.

If electrophile like alkyl group attacks at carbon then it is called alkylation or **C-alkylation**, or if it attacks at oxygen it is **O-alkylation**, O alkylation is uncommon and oxygen site is common for protonation. Protonation leads to unsaturated alcohol called alkenol or enol which are unstable and rapidly isomerizes back to carbonyl compound. Some of the reactions under this had in continuation are being given follow:

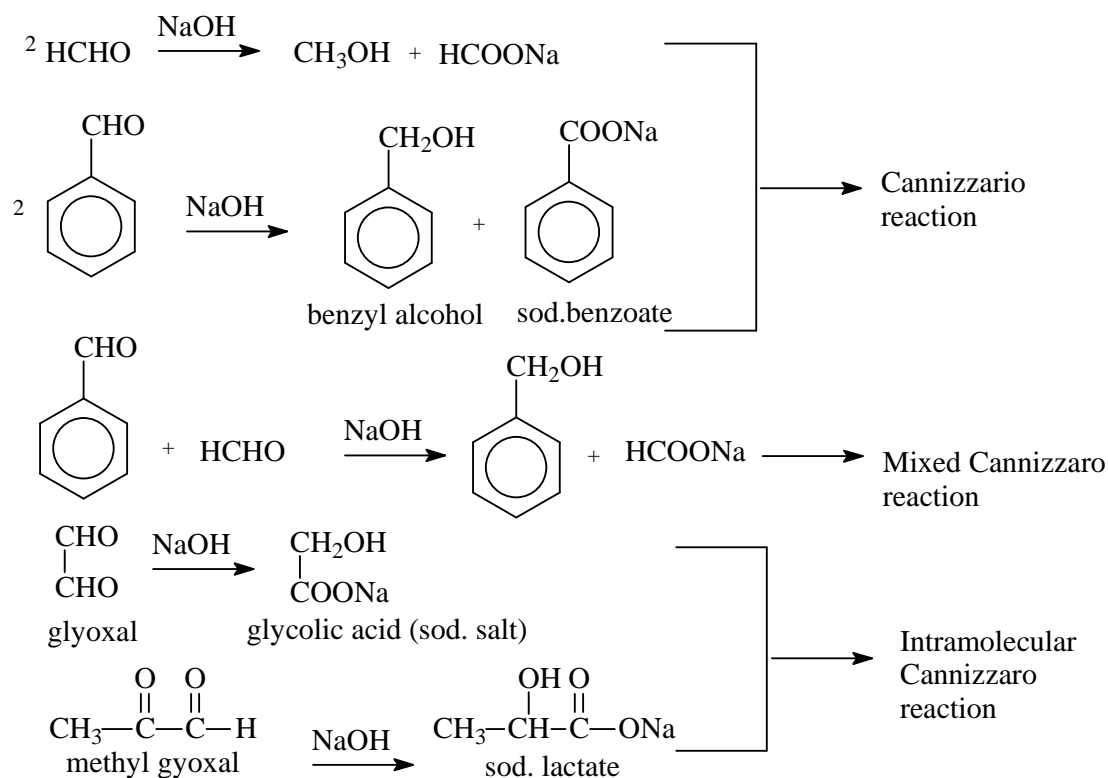
(16) **Haloform reaction:** Acetaldehyde reacts rapidly with halogen (Cl<sub>2</sub>, Br<sub>2</sub>, or I<sub>2</sub>) in the presence of alkali to form haloform.



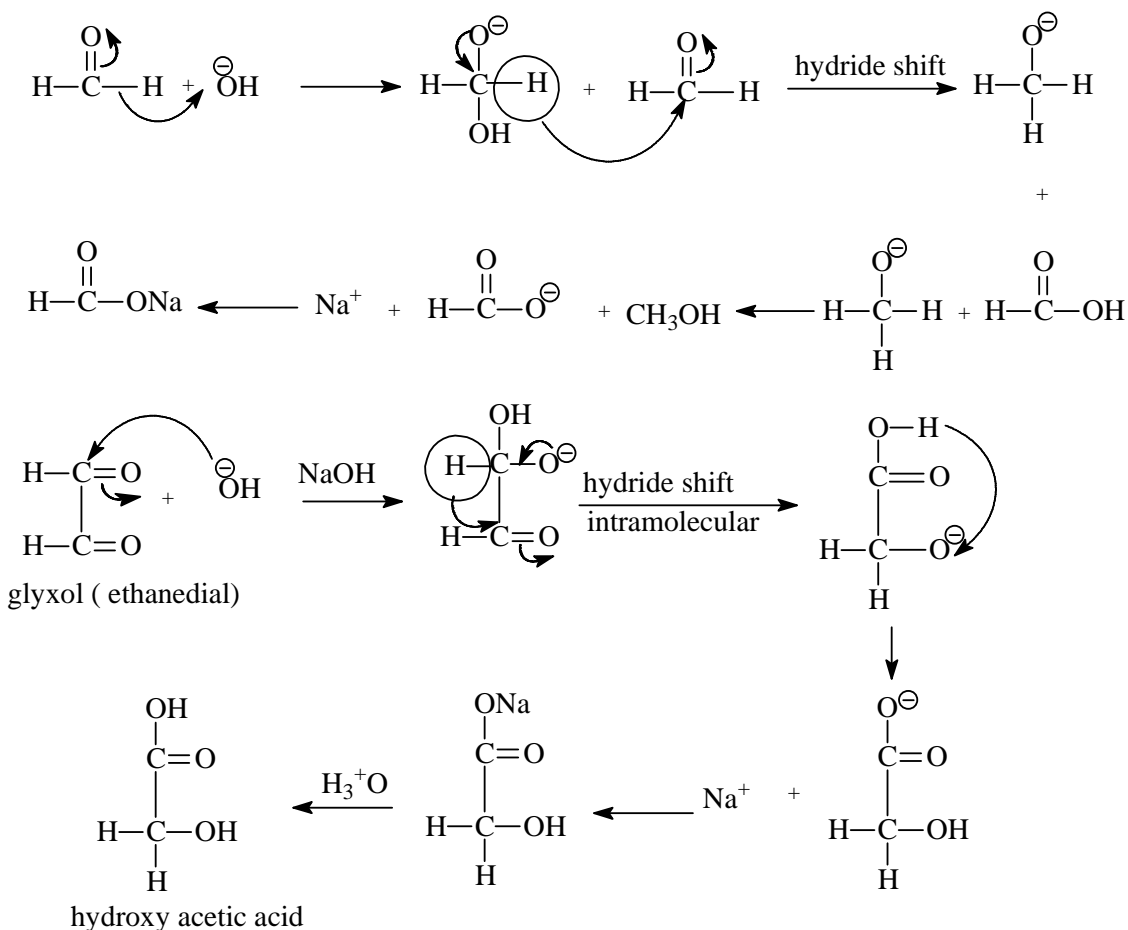
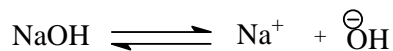
Haloform reaction is useful in identifying the presence of -COCH<sub>3</sub> group.

If instead of Bromine, Iodine is used as solution of iodine in aqueous alkali then CH<sub>3</sub>I yellow precipitate of Iodoform is obtained and reaction is called Iodoform reaction. Ethyl alcohol and secondary alcohols also give this test positive.

**17. Cannizzaro reaction:** Aldehydes that have no α hydrogen atoms undergo disproportionation reaction. Here when aldehydes (with no α hydrogen) are treated with concentrate NaOH, one molecule is converted to alcohol and one molecule to acid.

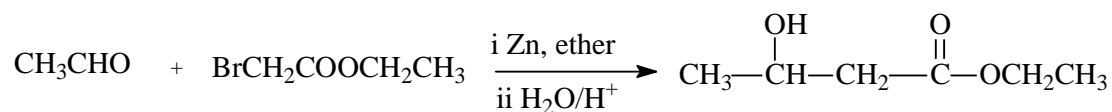


**Mechanism :** Attack of  $\text{OH}^{(-)}$  group on the carbonyl group followed by hydride transfer. The sequential mechanism is as follow both for inter and intramolecular Cannizzaro reaction



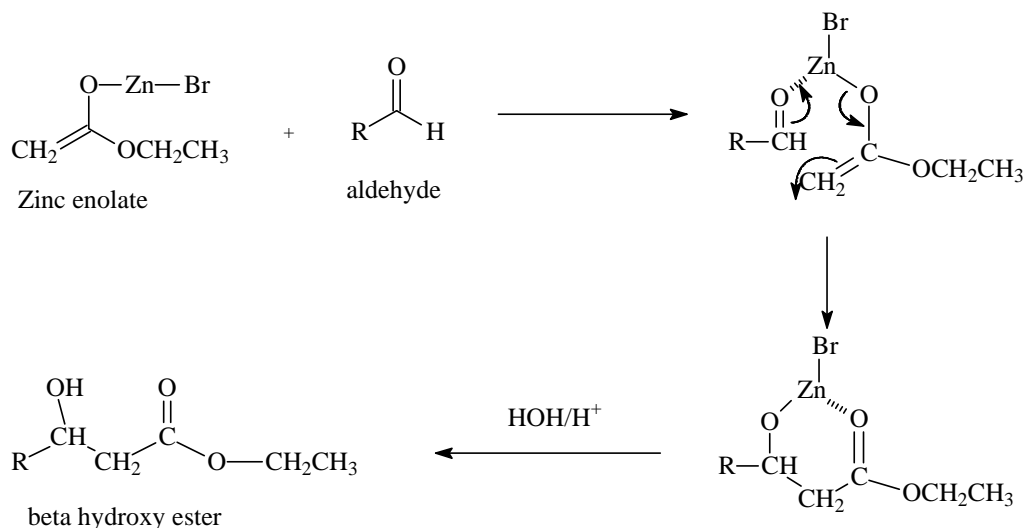
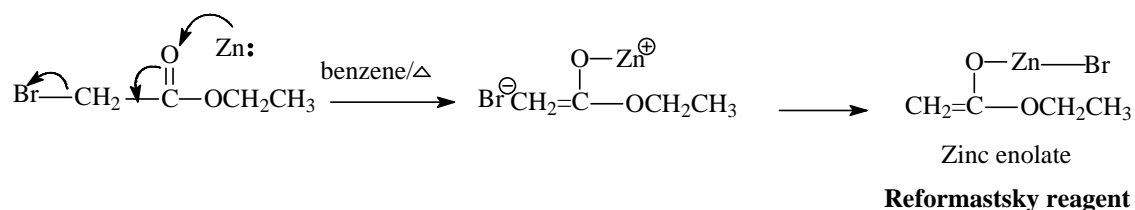
In mixed Cannizzaro reaction it is the formaldehyde that is oxidized to formate ion and other aldehyde viz; benzaldehyde is reduced to alcohol because CHO group of HCHO is the most electrophilic among all the substituted aldehydes and require the least activation energy to react with nucleophile reagent like  $\text{OH}^-$  ion.

**18. Reformatsky reaction:** Carbonyl compounds on treatment with  $\alpha$ - bromoester in the presence of zinc, followed by acid hydrolysis yields  $\beta$  hydroxyl ester.



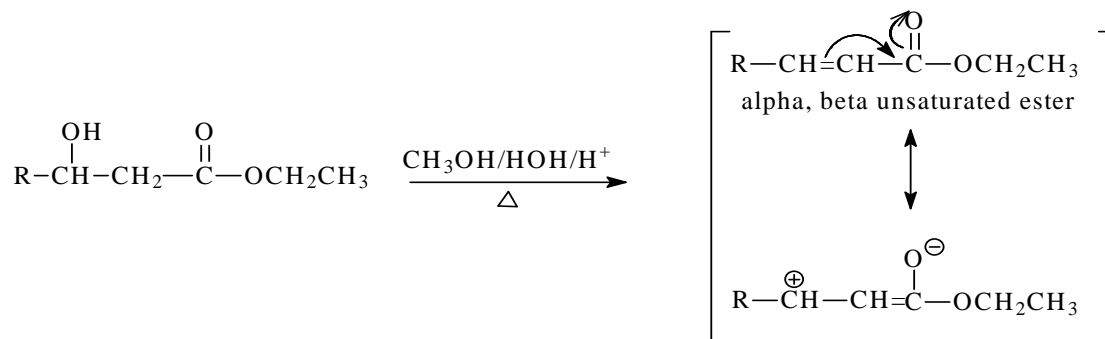
**Mechanism:**

Zn reacts with  $\alpha$ - halo ester to form Zn-enolate reactive intermediate, which is also known as Reformatsky reagent. This enolate react with aldehyde/ketones to give another intermediate which upon hydrolysis gives  $\beta$ -hydroxy ester as follow.

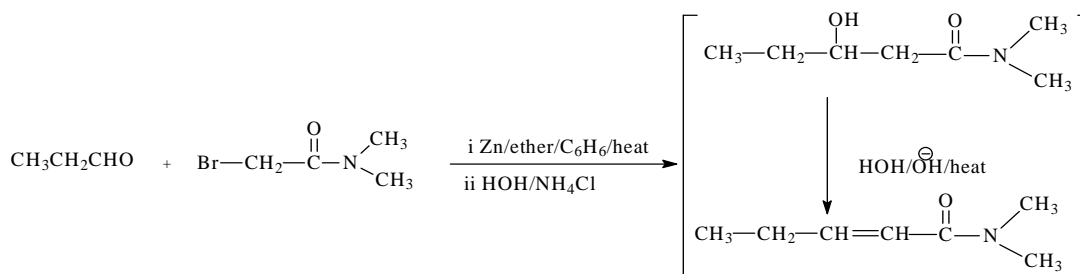
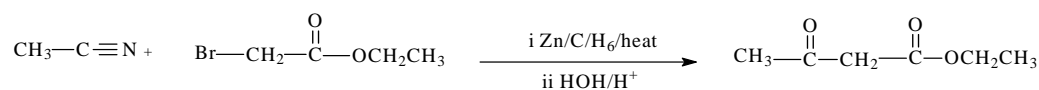
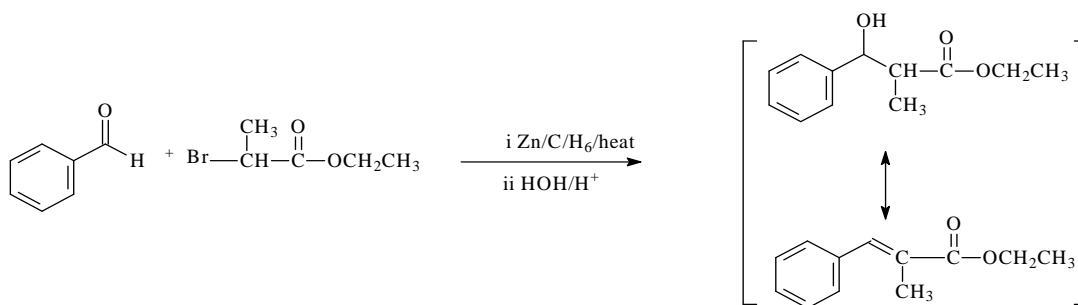
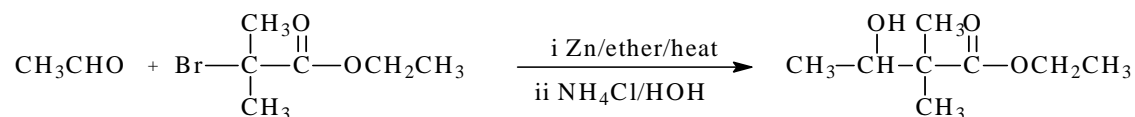
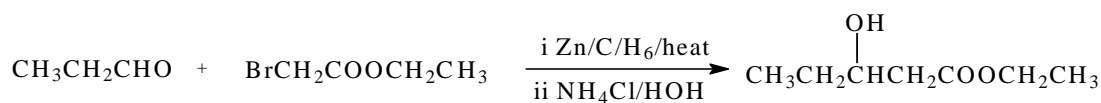


Zinc enolate do not react with ester, hence there is no chance of ester-ester self condensation. Zn also does not form Zn-enolate from a  $\alpha$ - bromo ketone or aldehyde. Thus there is no self condensation between aldehyde or ketone.

The  $\beta$ -hydroxy ester produced in this reaction can easily be dehydrated to  $\alpha, \beta$  - unsaturated ester because dehydration gives a resonance stabilized conjugated system

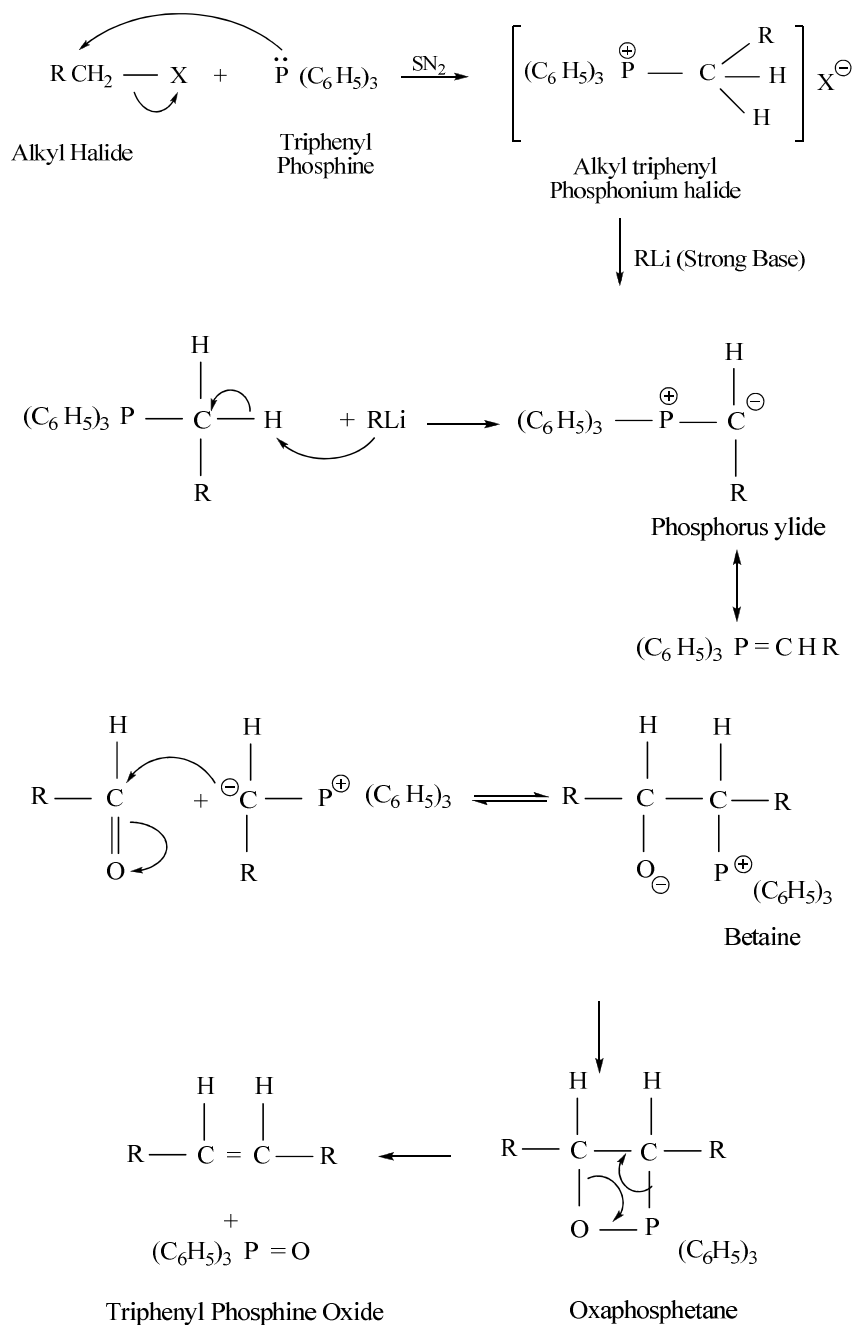


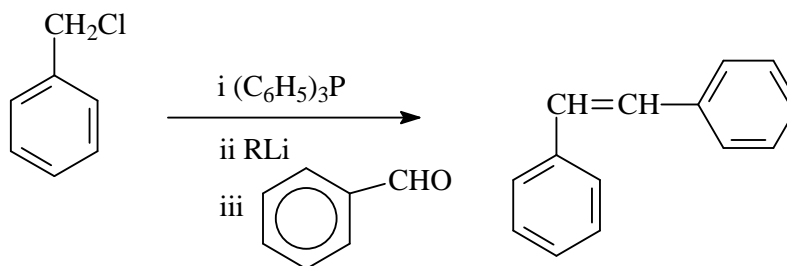
Examples of Reformatsky reaction:



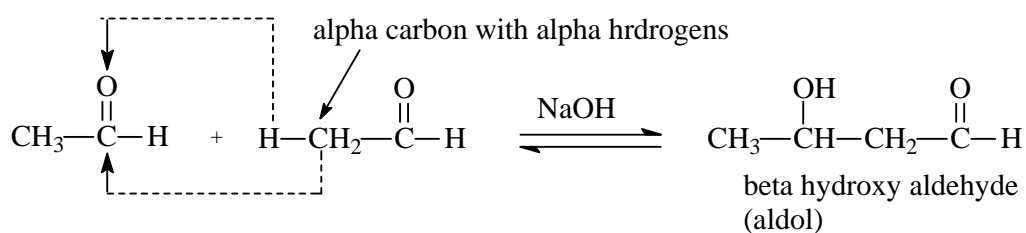
**19. Wittig reaction :** Carbonyl compounds react with alkylidene phosphoranes (ylids which is nucleophile) leads to formation of alkene and triphenyl phosphine oxide.

Phosphorus ylids are formed when triphenyl phosphine and primary or secondary alkyl halide react in the presence of strong base as NaH, NaNH<sub>2</sub> etc.

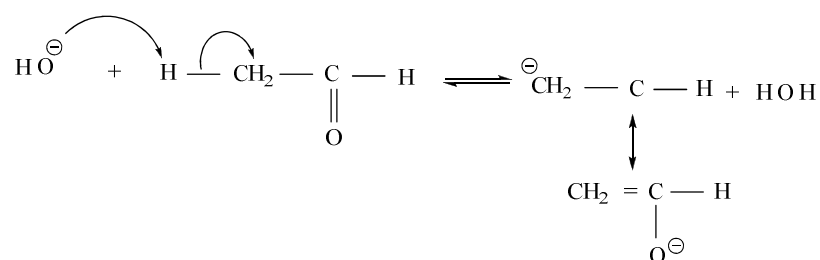




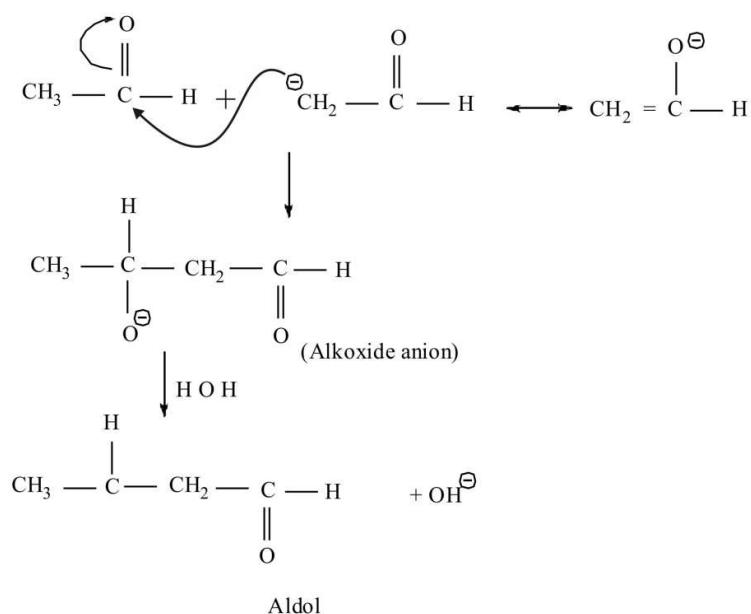
**20. Aldol condensation:** Carbonyl compounds aldehydes containing  $\alpha$ - hydrogens condense in the presence of dilute base form addition product  $\beta$ -hydroxy aldehyde also known as aldols.



**Mechanism:** Base generates enolate ion from carbonyl compounds having at least one  $\alpha$  hydrogen (acidic  $\alpha$  hydrogen). Enolate ion is good nucleophile, attacks carbonyl carbon of other unionized carbonyl compound form alkoxide anion which accepts proton from water to give aldol.

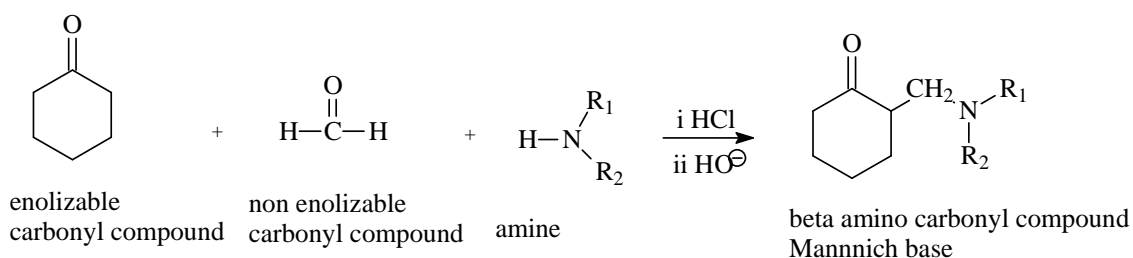






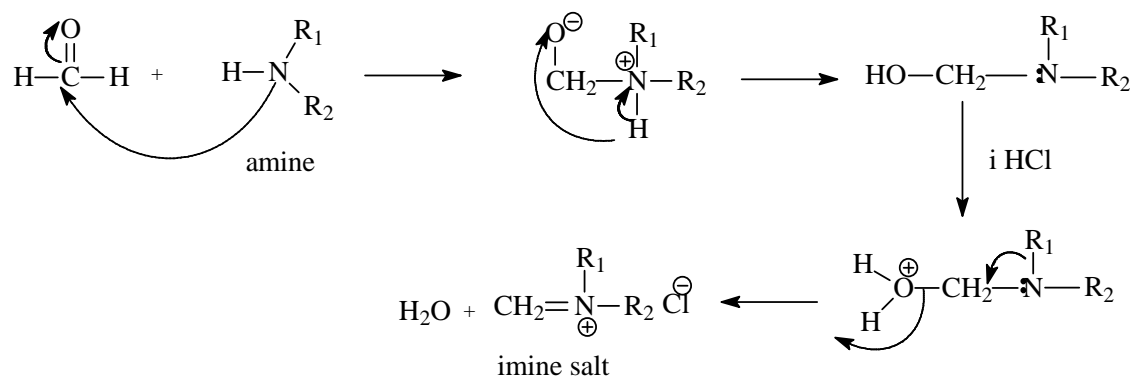
Benzaldehyde, formaldehydes type compound (which donot have  $\alpha$  hydrogens) donot show aldol condensation.

**21. Mannich reaction:** A Mannich Reaction is a formation of a  $\beta$  - amino carbonyl compound. The Mannich base is an endproduct in the Mannich reaction, which is formed through nucleophilic addition reaction of a non-enolizable aldehyde (formaldehyde) and any primary or secondary amine to produce resonance stabilized imine salt. Finally the addition of a carbanion from compound (any enolizable carbonyl compound, amide, carbamate etc.) to the imine gives the Mannich base.

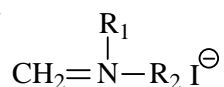


**Mechanism:**

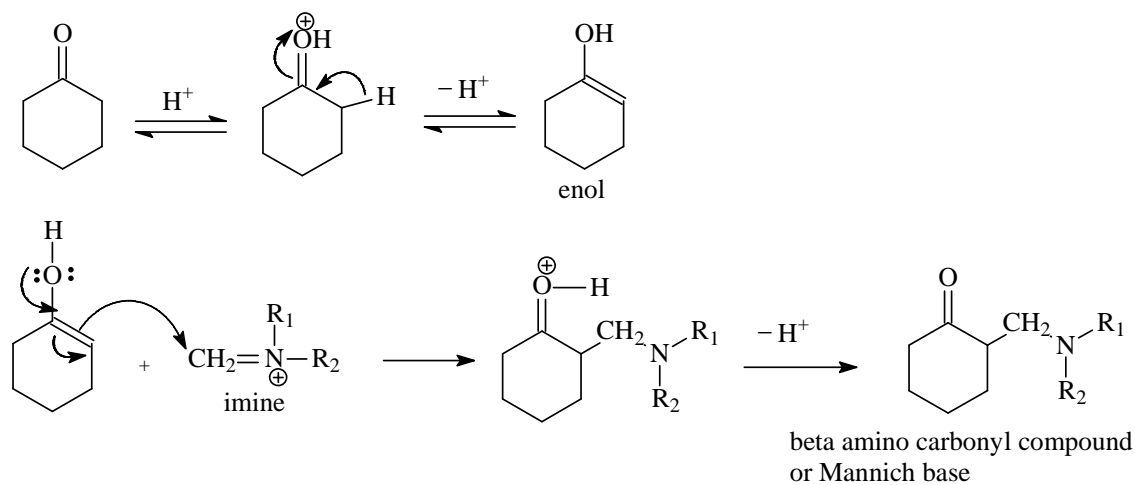
The mechanism involve the formation of imine salt first from formaldehyde and amine. In this reaction being nucleophilic nature of amine it attacks the carbonyl group of formaldehyde. No acid is required for that, however the acid-catalysed dehydration of the addition product reveals the imine salt as follow.



The imine salt is a just intermediate but quite stable. The iodide salt is solid in nature and known as **Ecchenmoser salt**.

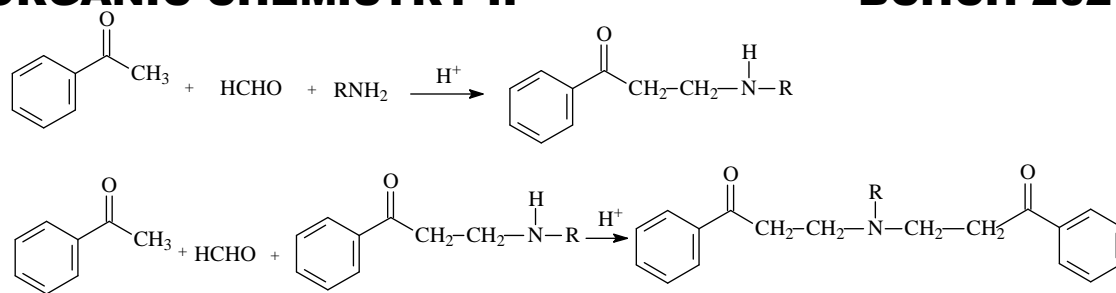


The electrophile imine salt now add to the enol form of carbonyl compound to give the product of the reaction,  $\beta$ - amino carbonyl compound or Mannich base

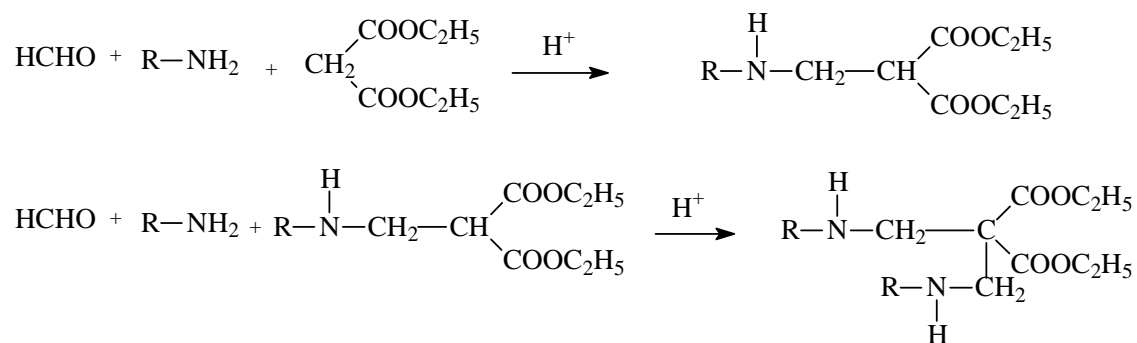


The reaction can further react by three different way provided that:

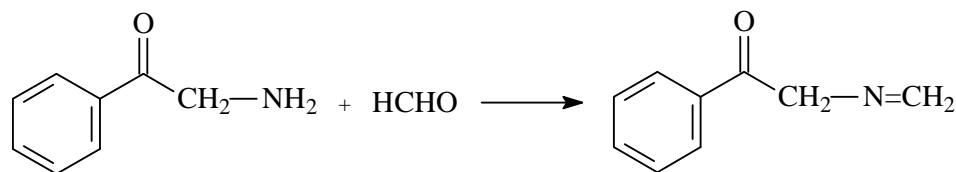
1 The Mannich base is  $1^0$  or  $2^0$  amine, in such cases it condenses further with two or one additional  $\text{HCHO}$  and enolizable carbonyl compound.



2. The enolizable carbonyl compound has active methylene group, stepwise condensation of two or more molecules of HCHO and amine with one molecule of the compound with active methylene group will take place.

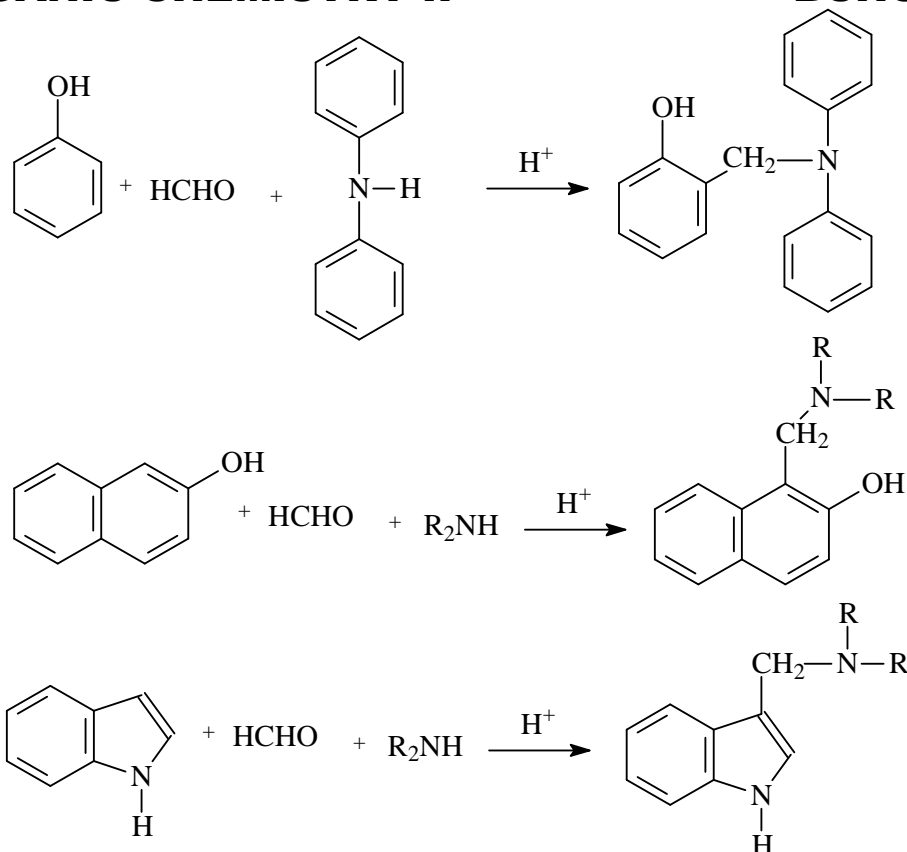


1. The Mannich base obtained may condense with excess HCHO

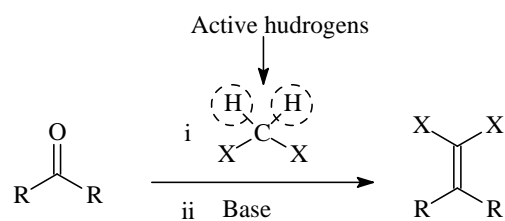


Mannich reaction is very important reaction for the synthesis of reaction intermediate imine salt. The mannich product can be converted to enones which can be used in Mannich addition.

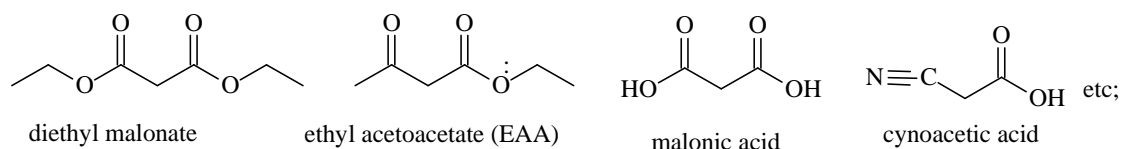
Phenols, furan, pyrrole, indole also give this reaction because intermediate of the reaction is iminium salt which is a strong electrophile and these compounds give aromatic electrophilic substitution (ArSE) reaction.

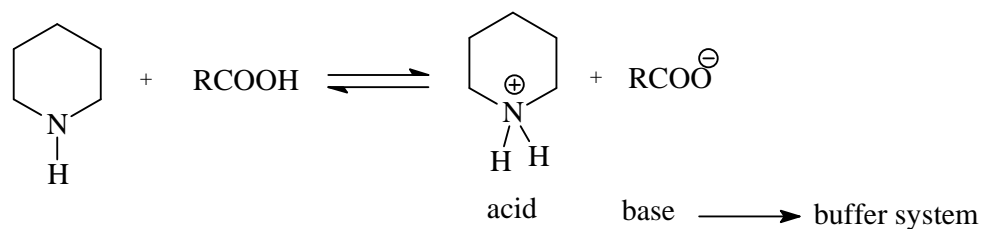


**22. Knoevenagel reaction:** It is a modified aldol condensation. It is simply a nucleophilic addition of active hydrogen to the carbonyl group which finally undergoes dehydration with the formation of  $\alpha, \beta$ -unsaturated product. This reaction is catalysed by amines generally piperidine/buffer system containing an amine and acid. A base is required to generate carbanion while acid is for activation carbonyl group.



X = electron withdrawing group, XCH<sub>2</sub>X may be

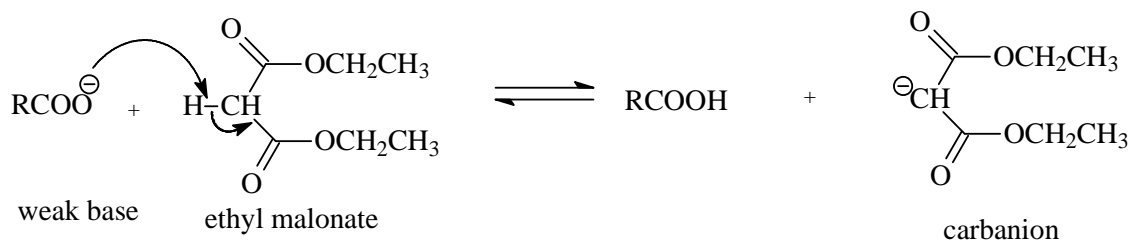




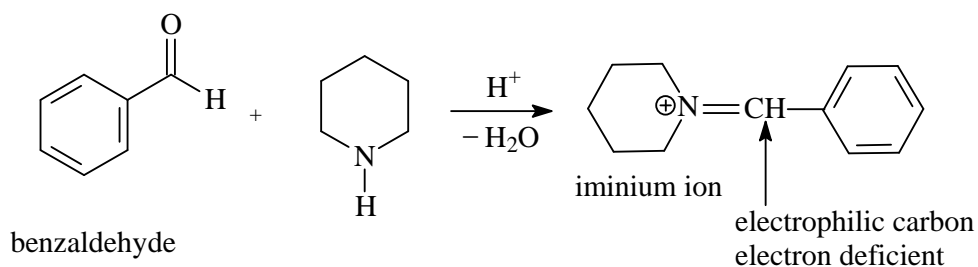
Mechanism of the reaction:

The sequencewise mechanism of Knoevenagel reaction is as follow:-

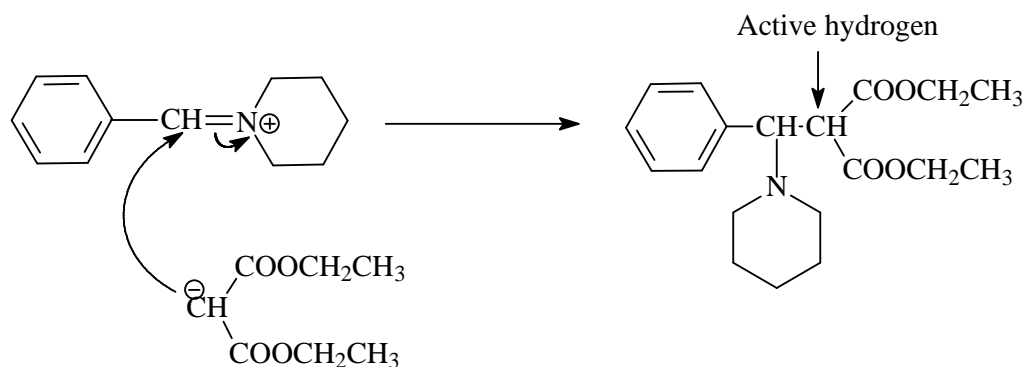
**Step-I** The weak base  $\text{RCOO}^-$  abstract the hydrogen from active methylene group and provide a resonance stabilized enolate/ carbanion



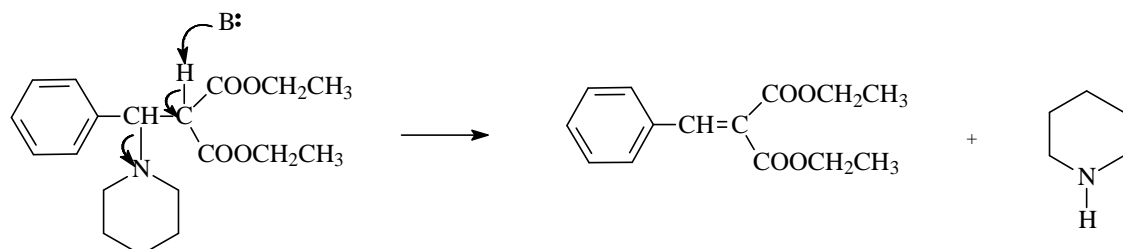
**Step II.** This step involves the formation of a reactive electrophile from pyridine by reaction with an aldehyde, viz; benzaldehyde to form an iminium ion. This intermediate is more reactive than a carbonyl group.



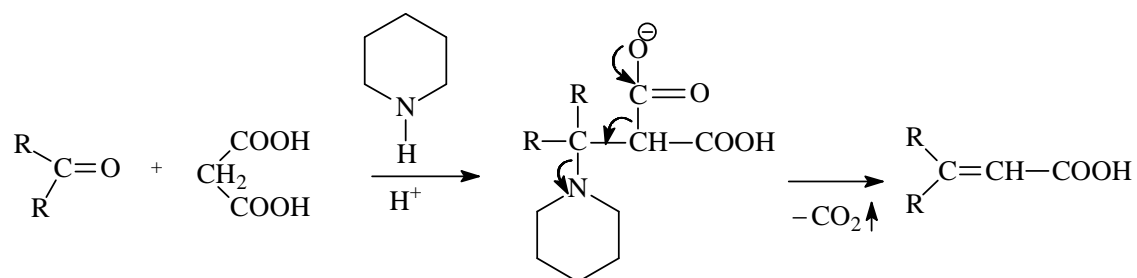
**Step III** In this step the electron-deficient carbon of the iminium ion is attacked by the carbanion.



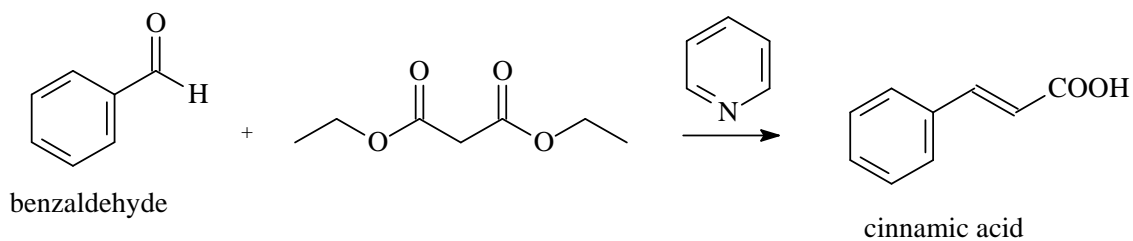
**Step IV** The weak base deprotonates acidic hydrogen followed by elimination of NR<sub>2</sub> group to give α, β-unsaturated derivative of the adduct



With malonic acid or cyanoacetic acid as reactant, the products usually undergo decarboxylation, which occurs as a concerted decomposition.

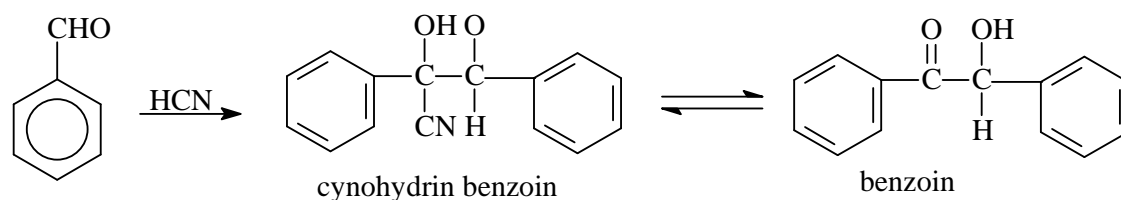
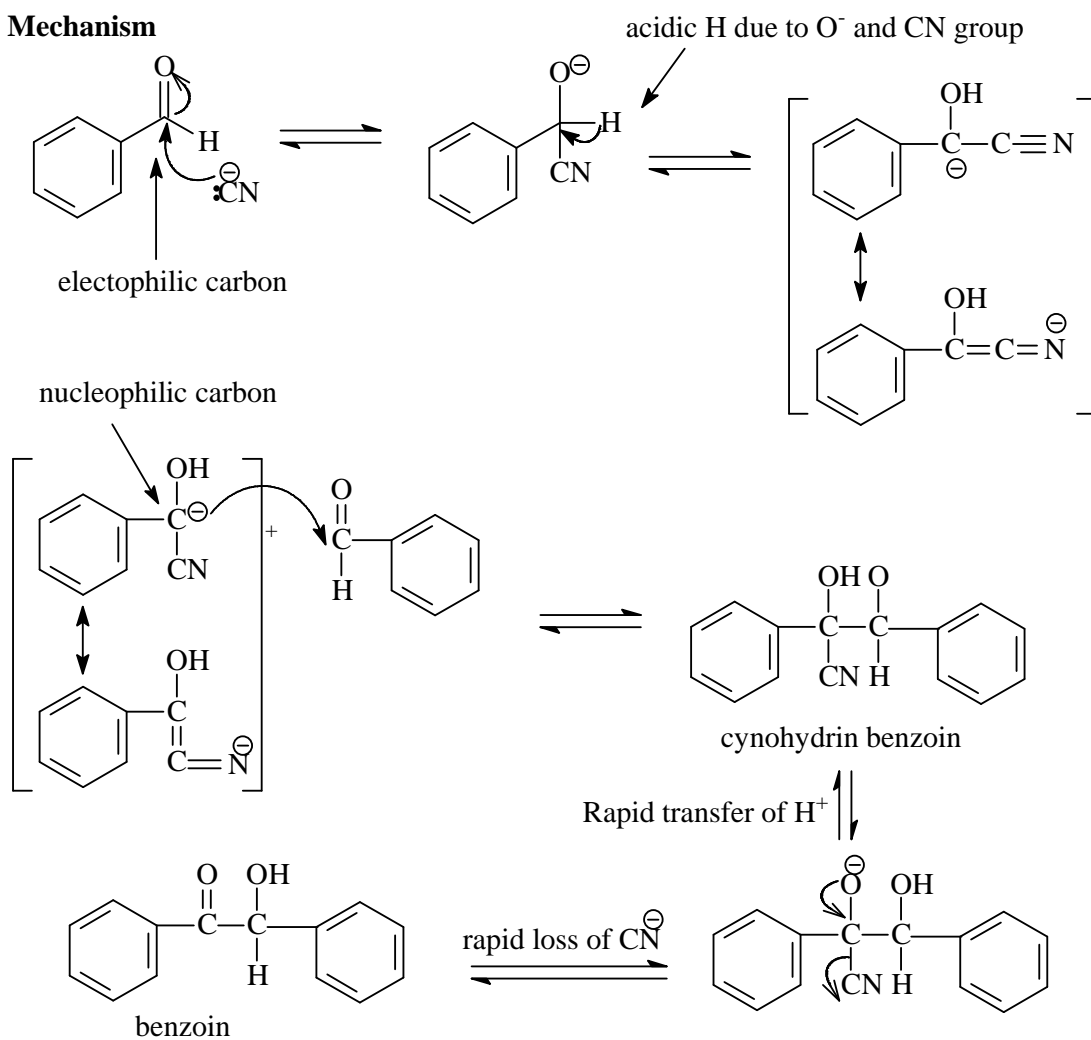


Decarboxylation is also carried out in presence of pyridine.



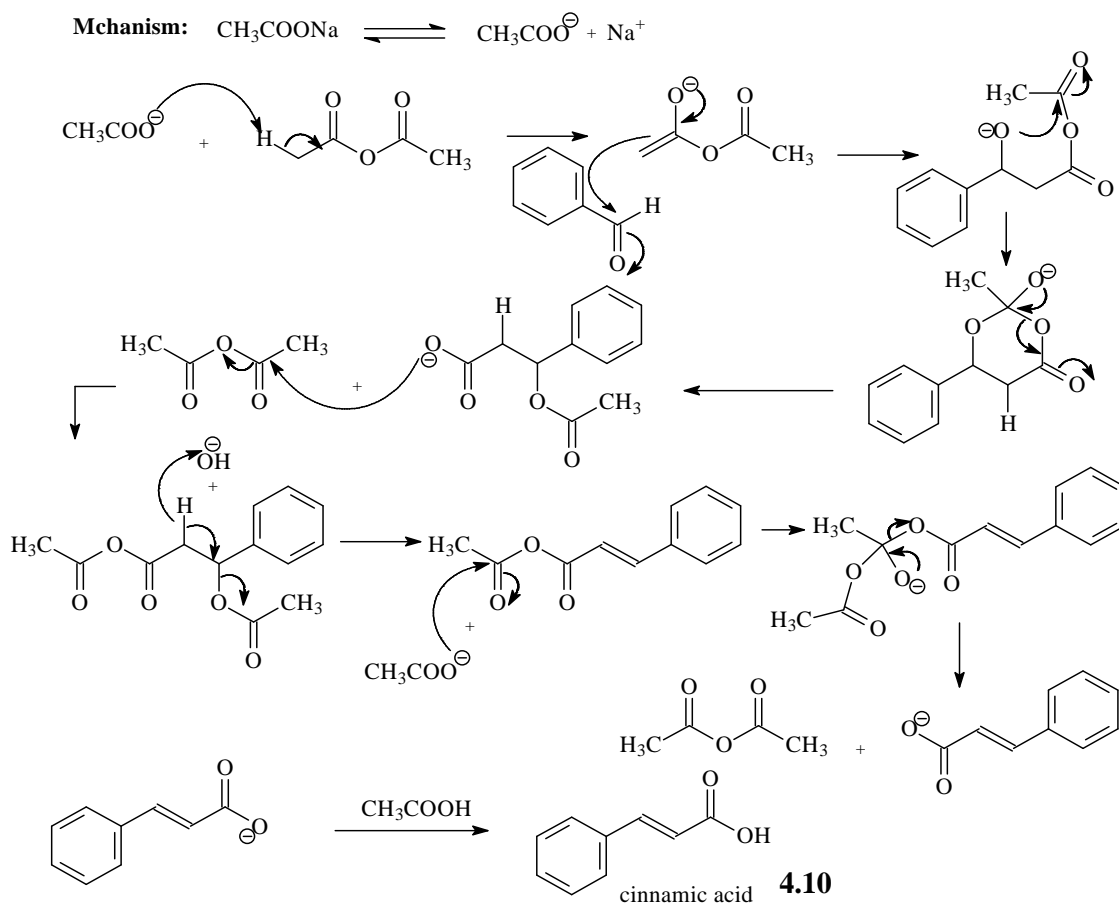
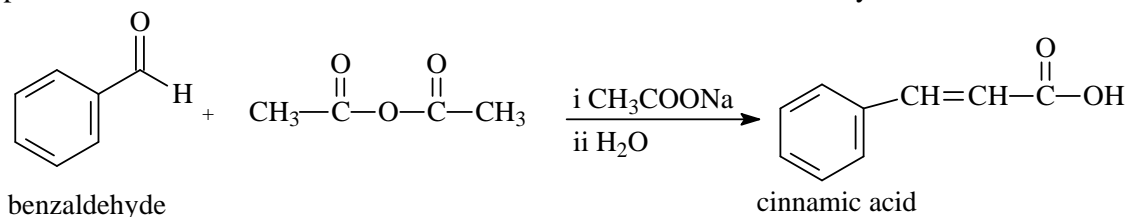
**23. Benzoin condensation reaction:** The benzoin condensation is a reaction (often called a condensation reaction, for historical reasons) between two aromatic aldehydes, particularly benzaldehyde. The reaction is catalyzed by a nucleophile such as the

cyanide anion or an N-heterocyclic carbene. The reaction product is a benzoin. In this umpolung reaction  $\text{CN}^-$  play key role as catalyst the well known example:

**Mechanism**

In this reaction  $\text{CN}^-$  act as catalyst which is due to its good nucleophilicity, stabilizing nature to carbanion and good leaving group.

**24. Perkin reaction:** The Perkin was developed by English chemist William Henry Perkin to synthesize cinnamic acids in which an  $\alpha,\beta$ -unsaturated aromatic acid is formed by the aldol condensation of an aromatic aldehyde and an acid anhydride, in the presence of an alkali salt of the acid. The alkali salt acts as a base catalyst.





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### 4.7 SUMMARY

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**Aldehydes** are compounds having general formula  $C_nH_{2n}O$  and contain Oxo (Carbonyl) group  $>C=O$ . Here functional group  $-CHO$  occurs at the end of a chain. Primary alcohols are oxidized to aldehydes only by Collins reagent ( $CrO_3 \cdot 2C_5H_5N$ ) and Corey's reagent ( $CrO_3 \cdot C_5H_5N$ , PCC). Aldehydes undergo nucleophilic addition reactions due to polarity of carbonyl group. Reactivity of aldehydes towards nucleophilic addition reactions decreases as steric hindrance and +I effect of attached alkyl group increases. Aldehydes are easily oxidized, so they work as powerful reducing agents (reduce Fehling solution and Tollen's reagent). Aldehydes give a series of condensation reactions and alpha hydrogen substitution reactions as per their structural constitution. Aldehydes can be used as starting materials for the synthesis of other synthetically important compounds.

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### 4.8 SELF ASSESSMENT

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#### 4.8.1 FILL IN THE BLANKS :

(1) The carbon of carbonyl carbon is \_\_\_\_\_ hybridised.

- (a)  $sp^3$             (b)  $sp^2$             (c)  $sp$             (d)  $sp^3d$

Ans. :- (b)

(2) Boiling points of primary alcohols are \_\_\_\_\_ than the boiling points of corresponding aldehydes.

- (a) higher            (b) lower

Ans :- (a)

(3) Aldehydes are prepared by the oxidation of \_\_\_\_\_

- (a) Primary alcohol    (b) Secondary alcohol    (c) Tertiary alcohol

Ans :- (a)

(4) Melting points of aldehydes tend to \_\_\_\_\_ with increasing molecular weight.

- (a) decrease      (b) increase      (c) remain unchanged

Ans :- (b)

(5) Aldehydes have \_\_\_\_\_ boiling points compared with those of alcohols.

- (a) low              (b) high

Ans. :- (a) low

(6) Catalytic hydrogenation readily converts aldehydes to \_\_\_\_\_ alcohols.

- (a) Primary      (b) Secondary      (c) Tertiary

Ans. :- (a)

(7) Aldehydes having  $\alpha$ -hydrogen atoms usually do not undergo \_\_\_\_\_ reaction under its reaction condition.

- (a) Cannizaro      (b) Aldol      (c) Haloform

Ans. :- (a)

(8) Appearance of silver mirror in Tollen's test indicates the presence of

- (a) Alcohol      (b) Aldehyde      (c) Alkene      (d) alkane

Ans. :- (b)

(9) Acetaldehyde on treatment with Fehling solution gives a precipitate of -

- (a) Cu              (b) Cu<sub>2</sub>O              (c) CuO              (d) CuCl<sub>2</sub>

Ans :- (b)

(10) Acetaldehyde on boiling with chlorine gas gives –

- (a)  $\text{CH}_3 - \underset{\text{O}}{\parallel}{\text{C}} - \text{Cl}$       (b)  $\text{C Cl}_3 - \underset{\text{O}}{\parallel}{\text{C}} - \text{H}$       (c)  $\text{CH}_3 \text{CH Cl}_2$       (d)  $\text{CHCl}_3$

Ans. :- (b)

---

**4.8.2 TRUE/FALSE**

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1. Both carbon and oxygen of .....group is  $sp^2$  hybridised.
2. IUPAC names of aldehydes are obtained by replacing the ending  $-e$  of the corresponding alkane with  $-al$ .
3. Controlled oxidation of secondary alcohols using an acidified solution of  $K_2Cr_2O_7$  produces aldehydes.
4. Hydration of acetylene yields acetaldehyde.
5. Density of aldehydes is less than water.
6. Lower aldehydes are insoluble in water.
7. As hydrocarbon part of aldehyde "compound increases solubility also increases.
8. Carbon atom next to carbonyl group is called  $\alpha$ -carbon.
9. Wolf kishner reduction of aldehydes involves use of basic solution of Hydrazine as reducing agent.
10. Aldehydes react with  $PCl_5$  to form gem – dihalides.

Ans. :- 1. T, 2. T, 3. F, 4. T, 5. T, 6. F, 7. F, 8. T, 9. T, 10. T

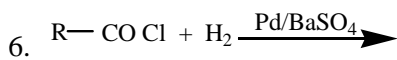
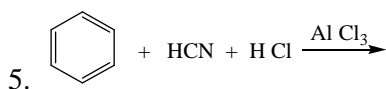
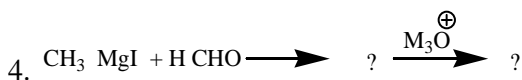
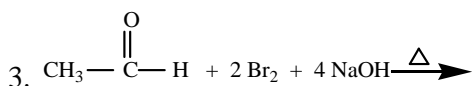
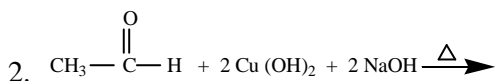
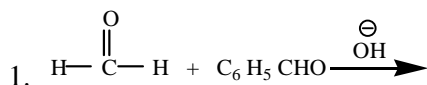
**4.8.3 SHORT ANSWER QUESTIONS**

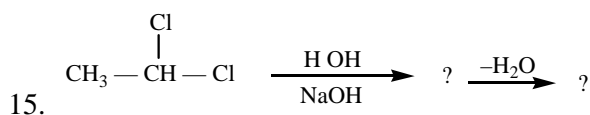
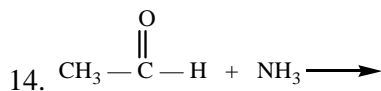
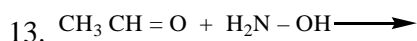
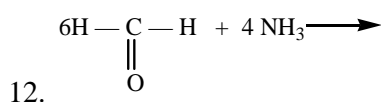
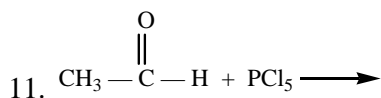
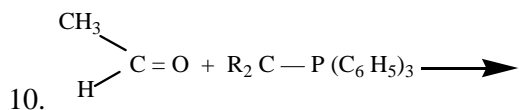
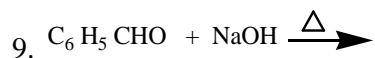
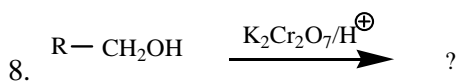
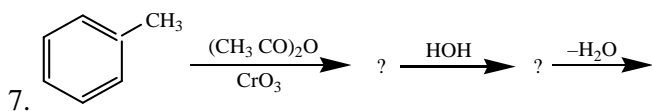
1. Writing the structures arrange the following compounds in increasing order of their reactivity in nucleophilic addition reaction.  
(a) Benzaldehyde, p-Tolualdehyde, p-Nitrobenzaldehyde  
Ans :- p tolualdehyde < Benzaldehyde < p-Nitrobenzaldehyde
2. What is the structure of carbonyl group? How does it react with (i) HCN (ii)  $NaHSO_3$
3. What happens when formaldehyde is treated with NaOH ?
4. Explain the reaction mechanism when acetaldehyde is treated with NaOH ?

5. Carbonyl compounds undergo nucleophilic addition reactions, why?
6. Write note on :-
  - (a) Wittig reaction
  - (b) Reformatsky reaction
  - (d) MPV reaction
  - (e) Perkin reaction
7. What happens when Aldehydes combine with alcohols in the presence of dry HCl ?
8. Aldehydes are powerful reducing agents. Explain.
9.  $\alpha$  hydrogen of aldehydes is acidic. Discuss.
10. Different reagents give different products on reduction of carbonyl compounds. Elaborate it.

**4.8.4 QUESTIONS RELATED TO IMPORTANT REACTIONS**

Complete the following reaction with mechanism wherever applicable :-






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### 4.9 REFERENCES

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**UNIT -5 KETONS**

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**CONTENTS:**

- 5.1 Objectives
- 5.2 Introduction
- 5.3 Nomenclature
- 5.4 Synthesis of ketones
- 5.5 Preparative methods of aromatic ketones
- 5.6 Physical properties
- 5.7 Chemical properties
  - 5.7.1 Addition reactions
  - 5.7.2 Addition reactions followed by elimination
  - 5.7.3 Reduction reaction
  - 5.7.4 Oxidation reaction
  - 5.7.5 Other reactions
  - 5.7.6 Some reactions of aromatic ketones
- 5.8 Summary
- 5.9 Terminal Question
- 5.10 References

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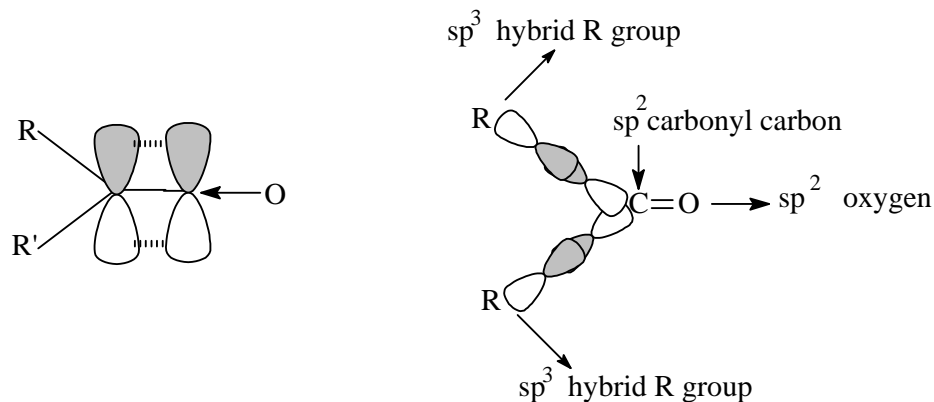
***5.1 OBJECTIVES***

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The objectives of this unit are to study about functional group carbonyl, Molecular orbital structure of functional group, reactivity of carbonyl group, nucleophilicity of carbonyl group. To study types of reactions carbonyl group undergo, mechanism of name reactions, effect of conjugation on carbonyl group reactivity. Although we already have discussed above factors in aldehydes unit. Now we will discuss the changes because of replacement of group H by an alkyl group.

## 5.2 INTRODUCTION:

In chemistry, a ketones (alkanone) are an organic compound with the structure  $RC(=O)R'$ , where R and R' can be a variety of carbon-containing substituents. Structurally the ketone carbon is often described as " $sp^2$  hybridized", a description that includes both their electronic and molecular structure. Ketones are trigonal planar around the ketonic carbon, with C–C–O and C–C–C bond angles of approximately  $120^\circ$

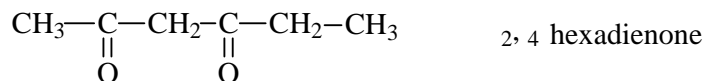
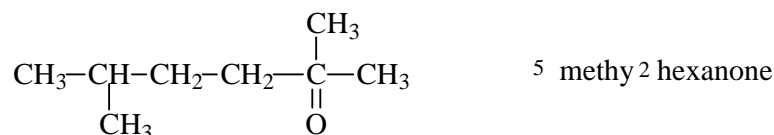
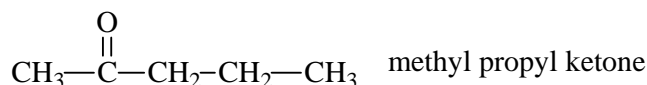
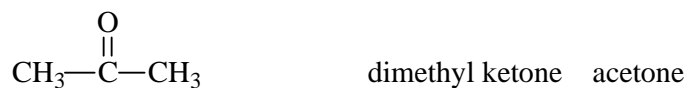


Basic skeletal structure of carbonyl group in ketone is same (Planer) as in aldehydes.

## 5.3 NOMENCLATURE

Common names of ketones are named on the basis of the alkyl group attached to the carbonyl group. In IUPAC nomenclature ketones are designated by suffix – one. Prefix is the name of hydrocarbon (Alkanones). Here longest hydrocarbon chain containing carbonyl carbon is selected and named it by substituting 'e' of Alkane with 'one'. While numbering the chain lowest number is given to carbonyl carbon. Other substituents are numbered named and placed as prefixes in alphabetic order. If there are two carbonyl groups in a molecule, it is named as Alkanedione.





Polarised C = O bond (electronegativity C - 2.5, O - 3.5) makes carbon partially positively charged which attracts negatively charged nucleophiles (Here electrons from HOMO of nucleophile move to LUMO of electrophile i.e. C of C = O group).

Newly formed sigma bond converts trigonal  $sp^2$  hybridized carbon atom of carbonyl group to tetrahedral  $sp^3$  hybridized state attack of nucleophile is at approx.  $107^\circ$  to the C = O bond. And any part of molecule that causes steric hindrance to this will reduce rate of addition (nucleophilic addition). Acid and Base catalysis of carbonyl carbon in Nucleophilic addition reactions has been discussed in aldehyde unit.

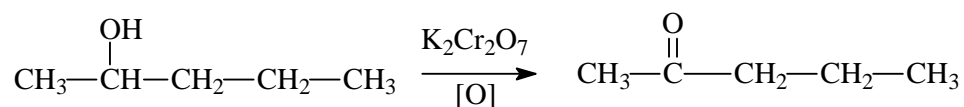
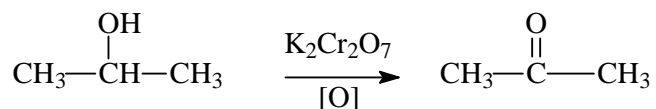
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## 5.4 SYNTHESIS OF KETONES:

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Like aldehydes ketones are prepared/synthesized by number of methods some are being discussed as follow.

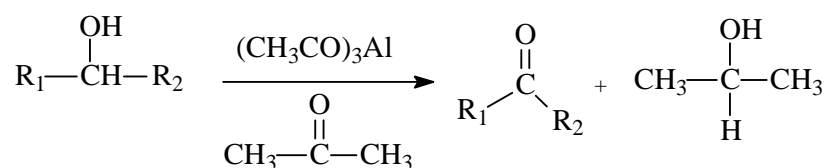
**1. Oxidation of secondary alcohols:** - Oxidation of secondary alcohols with  $K_2Cr_2O_7$ ,  $MnO_2$ , or chromic anhydride in acidic medium yield ketones. Firstly sec. alcohol gives ketone with same number of carbon atoms as the original alcohol. However, prolonged treatment with oxidizing agents produce a mixture of acids, containing fewer number of carbon atoms than the original alcohol.



Tertiary alcohols are resistant to oxidation in neutral or alkaline medium but they are oxidized in acidic medium resulting in formation of mixture of acid and ketone and each contains fewer number of carbon atoms than the original alcohol.

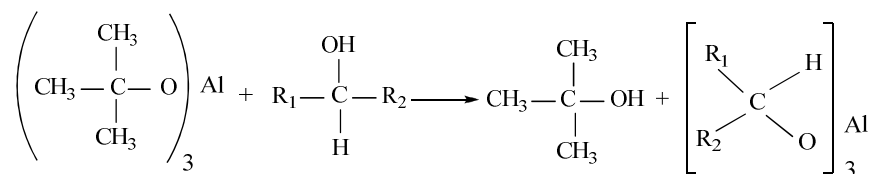
Alkaline  $KMnO_4$  is also oxidizing agents.

**2. By Oppenauer oxidation:** - It involves a special reagent aluminium-t-butoxide  $[(CH_3)_3CO]_3Al$ , which is refluxed with secondary alcohol and acetone cyclohexanone is used as solvent. Here  $[(CH_3)_3CO]_3Al$  acts as oxidizing agent and acetone accepts hydrogen as hydride ion from sec. alcohol.



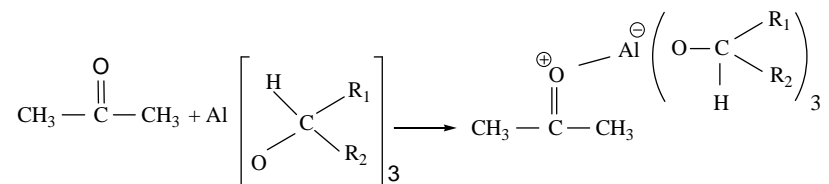
**Mechanism: -**

**Step-I**



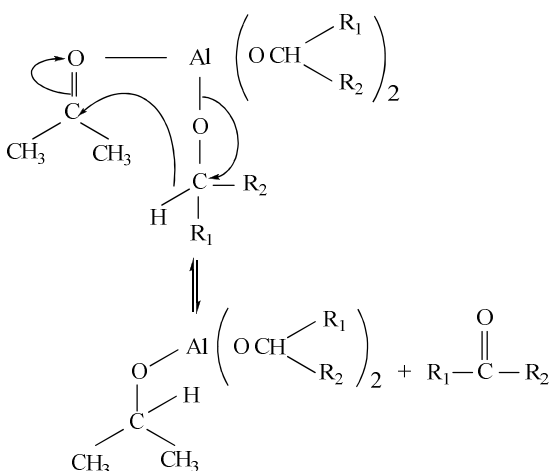
Here exchange reaction takes place

**Step-II**

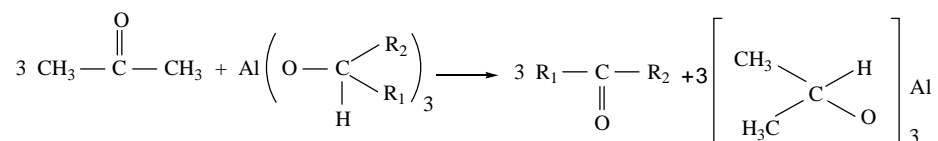


New complex is formed.

**Step-III**



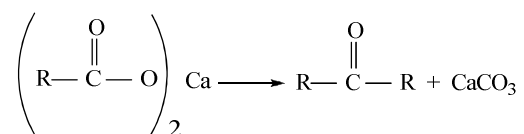
Similarly two more moles of acetone will react with above (one mole) formed complex and give two more moles of ketone product.



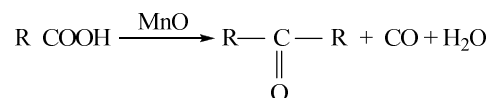
This reaction is useful as for oxidation of polyfunctional compounds as this reaction conditions are mild. For e.g. in unsaturated alcohols as it (reagent) does not affect double bond.

Primary alcohols can also be oxidized by  $[(\text{CH}_3)_3\text{CO}]_3\text{Al}$  if in acetone is replaced by p benzoquinone as it is better hydrogen acceptor than acetone.

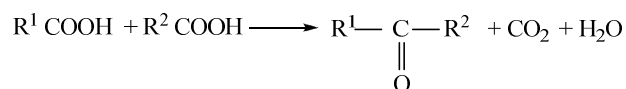
3. By heating calcium salt of any monocarboxylic acid other than formic acid, ketones are obtained.



4. When vapours of any monocarboxylic acid except formic acid are passed over Manganous oxide at  $300^\circ\text{C}$  then ketone is obtained.



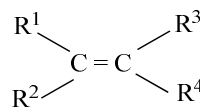
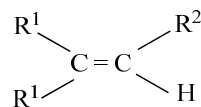
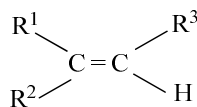
Mixture of monocarboxylic acids yield mixed ketones

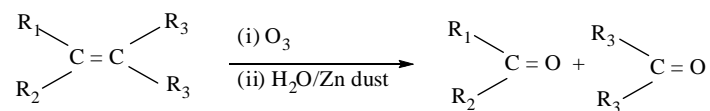


Besides this  $\text{R}'\text{COR}'$  and  $\text{R}^2\text{COR}^2$  are also obtained.

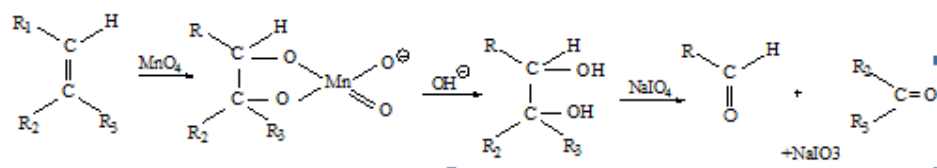
5. **From Alkenes:** Ketones can be prepared from alkenes as follow.

(a) **Ozonolysis:** - Alkenes of following types when treated with ozone, yield ozonides and this on subsequent treatment with  $\text{H}_2\text{O}$  and zinc dust yield ketones



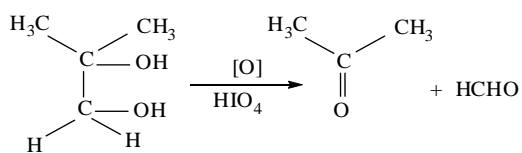
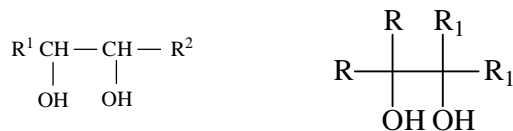


**(b) Lemieux Reagent:** - An aqueous solution of  $NaIO_4$  and trace of  $KMnO_4$ , lemieux reagent cleaves alkene to is diol and then to aldehydes or ketones.

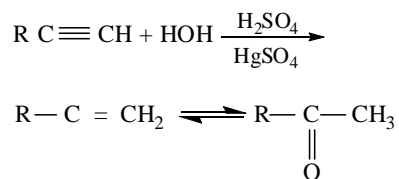


In place of  $KMnO_4$ , trace of  $OsO_4$  can also be used and it prevents further oxidation to acids.

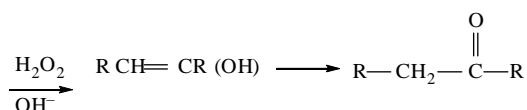
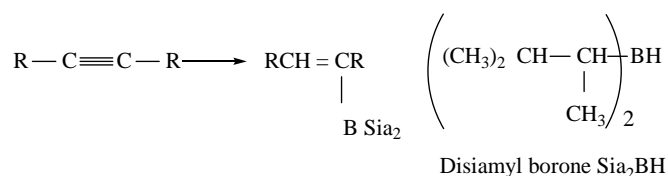
**6. Oxidation of 1, 2 glycols:** - The following types 1, 2 glycols are oxidised (by lead tetracetate  $(CH_3COO)_4Pb$  or periodic acid  $HIO_4$  or  $H_5IO_6$ ) and form aldehydes and ketones respectively according to structure of glycols



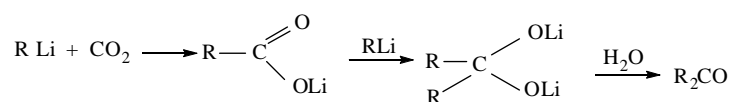
**7. Alkynes:** - Proper alkyl substituted on treatment with water in the presence of dil  $H_2SO_4$  and  $HgSO_4$  gives ketones



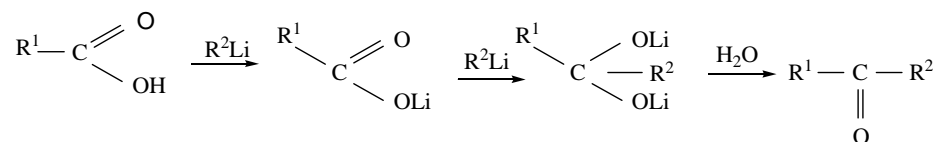
Similarly other homologues of acetylene on treatment with disiamyl borane followed by oxidation with H<sub>2</sub>O<sub>2</sub> give ketones



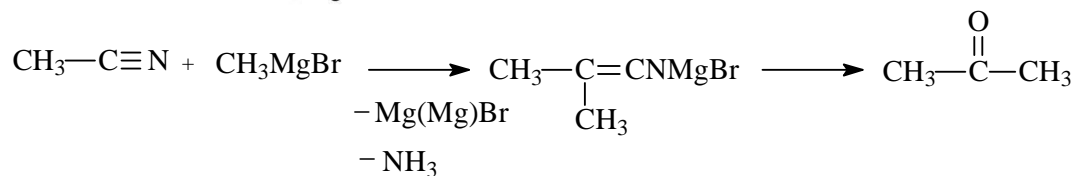
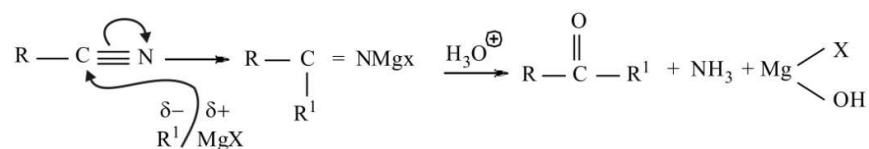
**8. Lithium alkyls on treatment with CO<sub>2</sub> give good yield of ketone.**



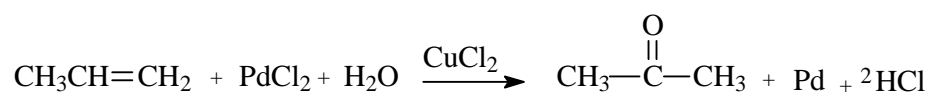
Similarly with acids also we get ketone



**9. Addition of Grignard reagent to nitrile:** - Reaction of Grignard reagents with nitriles forms ketones.



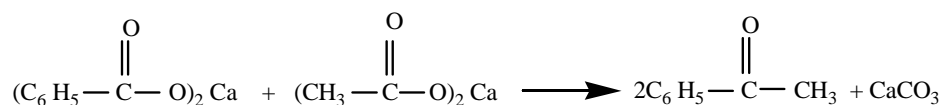
**10. Wacker's Process:** - Alkenes on treatment with PdCl<sub>2</sub> and Cu Cl<sub>2</sub> give ketone



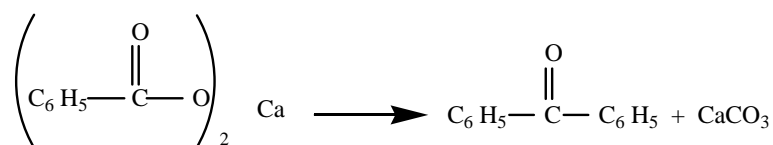
### 5.5 PREPARATIVE METHODS OF AROMATIC KETONES

The aromatic ketones are those compounds having a carbonyl appendage on the aromatic structure to the other side of which one finds an alkyl or aryl group. Like aliphatic ketones aromatic ketones can be prepared by various methods

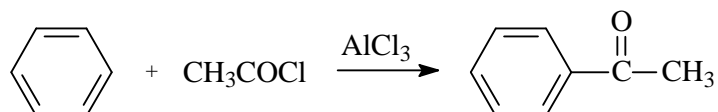
(1) Distillation of mixture of calcium benzoate and acetate yields acetophenone



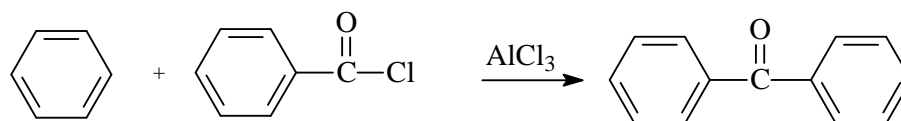
Heating of Calcium benzoate yields Benzophenone



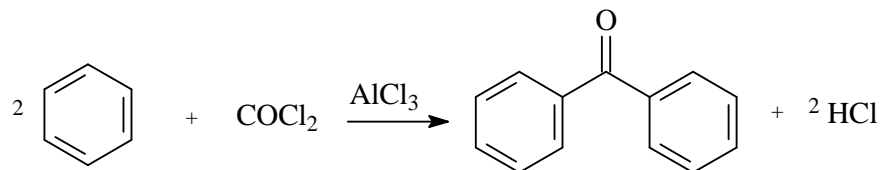
(2) **Friedel Crafts acylation:** - Treatment of benzene with acetyl chloride or acetic anhydride in the presence of  $\text{AlCl}_3$  yields acetophenone



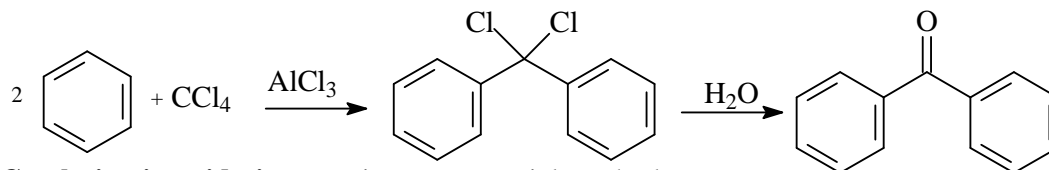
Use of benzoyl chloride gives benzophenone



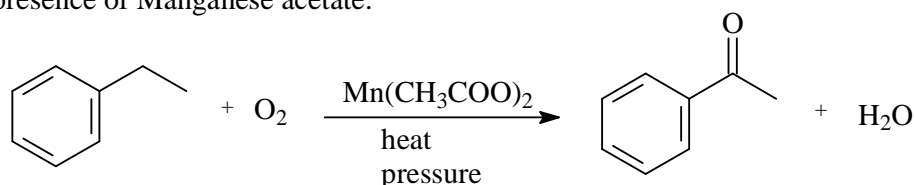
3) Benzene with carbonyl chloride in the presence of  $\text{AlCl}_3$  gives benzophenone.



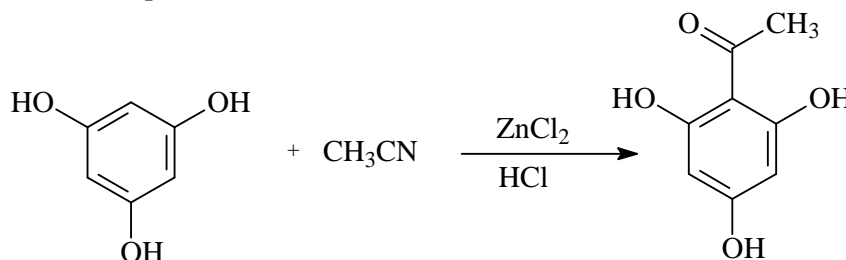
(4) Benzene with  $\text{CCl}_4$  in the presence of  $\text{AlCl}_3$  yields dichloro compound, which on further steam distillation gives Benzophenone



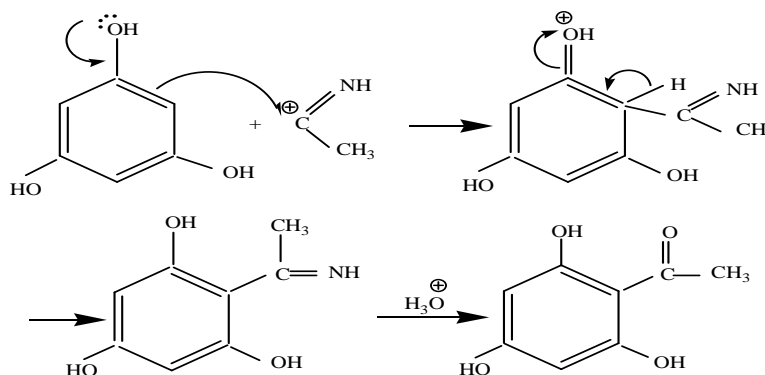
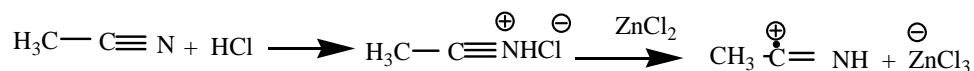
(5) **Catalytic air oxidation** – It is a commercial method to prepare acetophenone where ethyl benzene is treated with oxygen at  $126^\circ\text{C}$  under pressure in the presence of Manganese acetate.



(6) **Houben Hoesch reaction:** - This reaction involves condensation reaction of cyanides with polyhydric phenols in the presence of  $\text{ZnCl}_2$  and  $\text{HCl}$  resulting in formation of phenolic ketones.

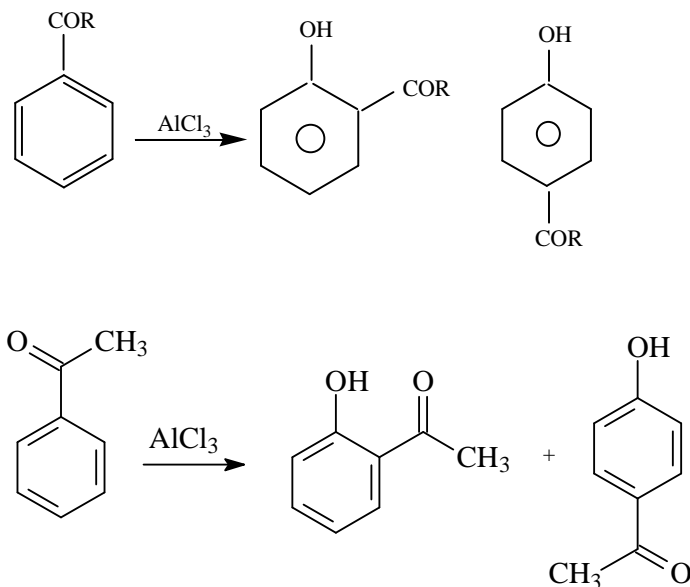


Mechanism: This reaction is extension of Gattermann's synthesis and follows the following sequential mechanism.

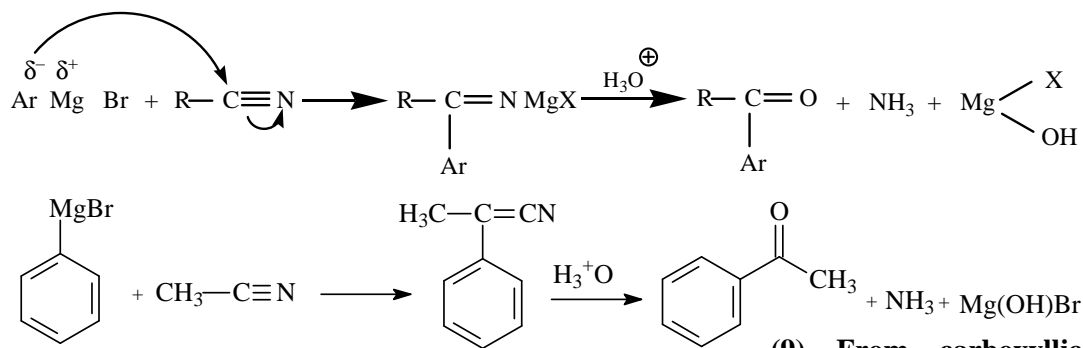




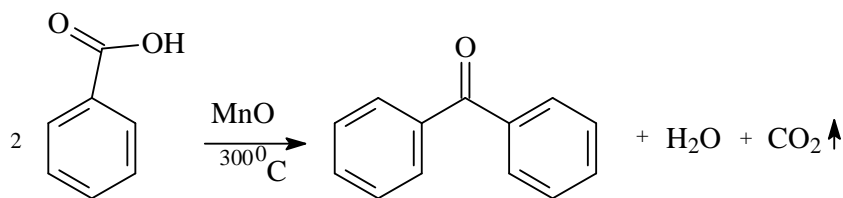
(7) **Fries rearrangement** – When aryl esters are treated with anhydrous  $\text{AlCl}_3$  at  $0\text{C}$ , results in the formation of o-and p- acyl derivative of phenols.



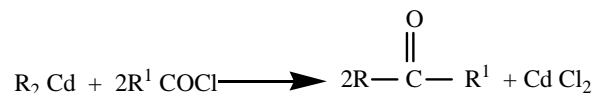
(8) **From Grignard Reagent :-** Aryl magnesium bromide with alkyl cyanides undergo nucleophilic addition reaction at carbon of cyanide, which on further hydrolysis with  $\text{H}_3\text{O}^+$  gives aromatic ketone.



(9) **From carboxylic acids:** - By passing vapours of any carboxylic acid except formic acid over  $\text{MnO}$ , We get a ketone.



(10) Organo Cadmium compounds on reaction with acid chloride form ketones.



Reaction of cadmium chloride with Grignard reagent gives Organo Cadmium compounds.



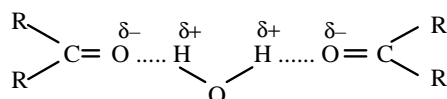
Here R is primary alkyl group or aryl group.

### ***5.6 PHYSIICAL PROPERTIES***

1. Lower ketones are colourless liquids.
2. Lower ketones possess pleasant, sweet odours.
3. Density of ketones is less than water.
4. As discussed in aldehyde unit ketones have higher boiling points than corresponding alkanes but lower boiling points compared with those of alcohols of comparable molecular weights.

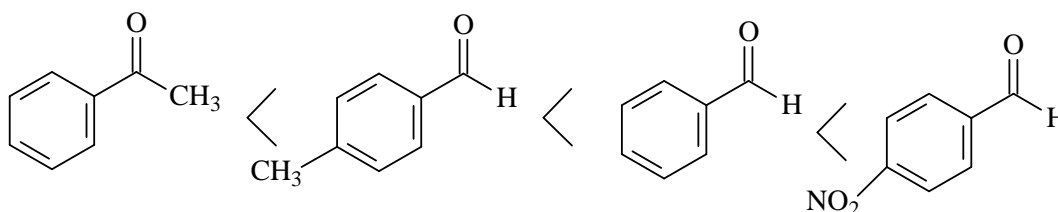
$\begin{array}{c} CH_3 \\   \\ CH_3 - CH - CH_3 \end{array}$	$\begin{array}{c} O \\    \\ CH_3 - C - CH_3 \end{array}$	$\begin{array}{c} OH \\   \\ CH_3 - CH - CH_3 \end{array}$
mol. wt. 58	58	60
boiling Point $-12^0C$	$56^0C$	$82.5^0C$
isobutane	acetone	isopropyl alcohol

5. Lower ketones are soluble in water as they form hydrogen bonding with water. As alkyl chain of molecule increases, solubility in water decreases..



In infrared spectrum strong C = O Stretching band is observed in  $1700 - 1740 \text{ cm}^{-1}$  region.

**Relative Reactivity:** As discussed in detail in aldehyde unit it is to be noted that relative reactivity of ketones is less than aldehydes towards nucleophilic addition reaction. Here electron releasing alkyl group reduce positive charge of carbonyl carbon and thereby decrease reactivity of carbonyl group. Moreover as compare to H atom alkyl group increases steric hindrance for attacking reagent (nucleophile) to reach at carbonyl carbon. Secondly after attack  $sp^2$  hybridised carbonyl carbon becomes  $sp^3$  hybridised in resultant adduct. Here bond angles are reduced from appr.  $120^\circ$  to around  $109^\circ$ . This adducts also gets steric strain due to increase of bulky groups. This strain is higher in ketones as compared to aldehydes.



Acetophenone is ketone while other three are aldehyde. So, acetophenone is least reactive. *p*-tolaldehyde has electron donating methyl group at para position of benzene ring whereas *p*-nitrobenzaldehyde has an electron withdrawing nitro group at the para position and we know that reactivity of carbonyl group is inversely proportional to electron density at carbonyl carbon so *p*-tolaldehyde is less reactive than benzaldehyde while *p*-nitrobenzaldehyde is more reactive than benzaldehyde.  $\alpha$ -hydrogen of ketones are acidic and removable by strong bases.

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## 5.7 CHEMICAL PROPERTIES

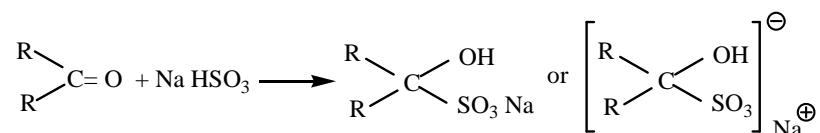
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Ketones are reactive organic compounds and undergo many reactions like aldehydes.

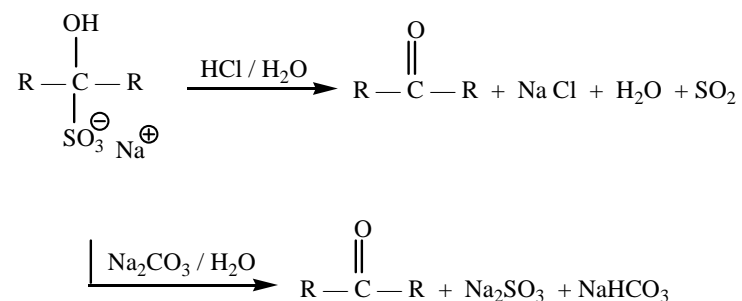
### 5.7.1 ADDITION REACTIONS:

Like aldehydes the reactive carbonyl group of ketones gives addition reactions.

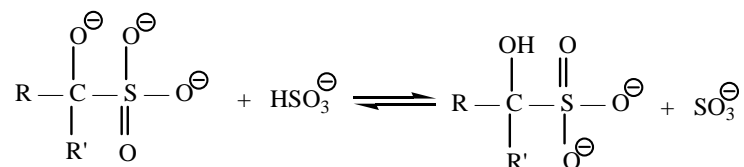
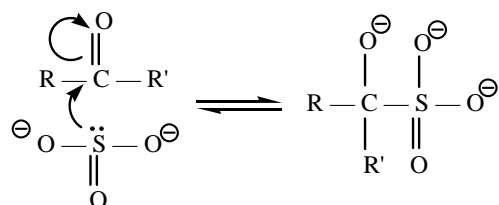
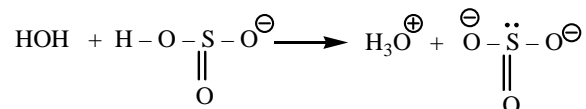
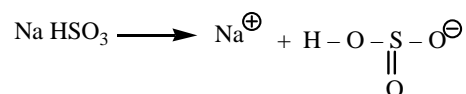
**(1) Addition of sodium bisulphate ( $\text{NaHSO}_3$ ) :-** Ketones add on sodium hydrogen sulphite and form adducts called bisulphite addition compounds which are water soluble salts.



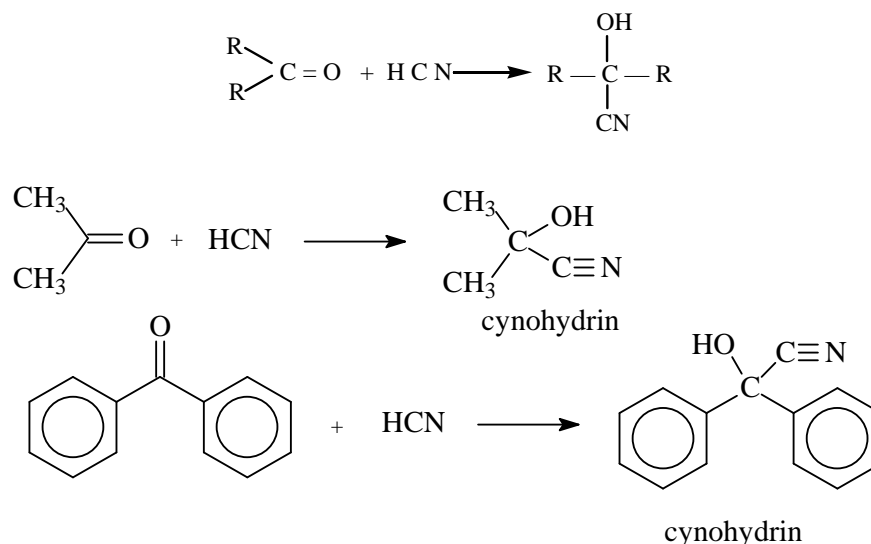
Thus formed adduct when treated with acid, base gives corresponding carbonyl compound.



**Mechanism:** - In this reaction  $\text{Na}_2\text{SO}_3$  acts as nucleophile through sulphur and attacks at carbonyl carbon which is followed by protonation of carbonyl anionic oxygen by bisulphite ion.

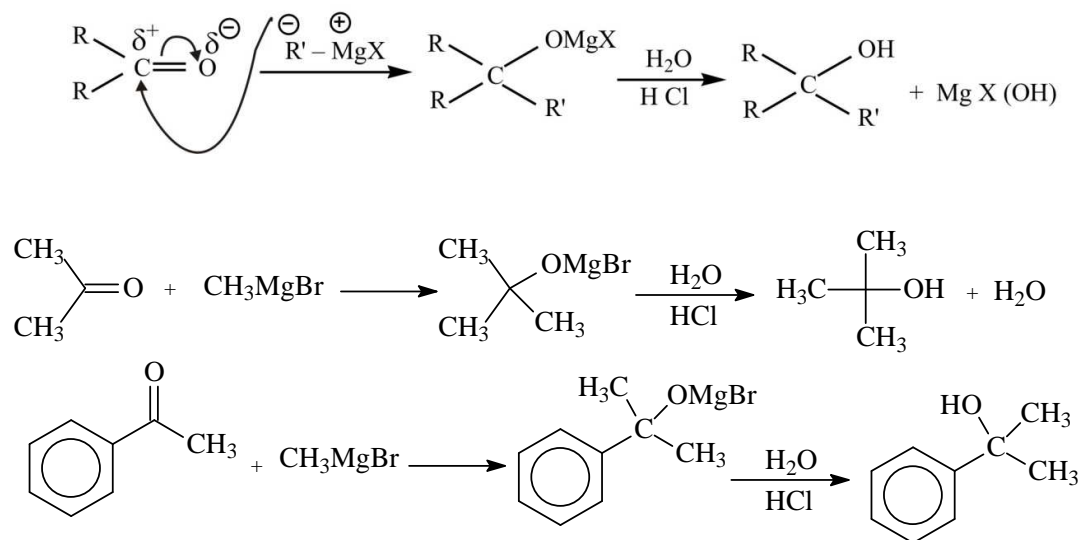


(2) **Addition of hydrogen cyanide (HCN) :-** Ketones add HCN in the presence of base catalyst to form cyanohydrins, which can further be hydrolysed to –COOH group

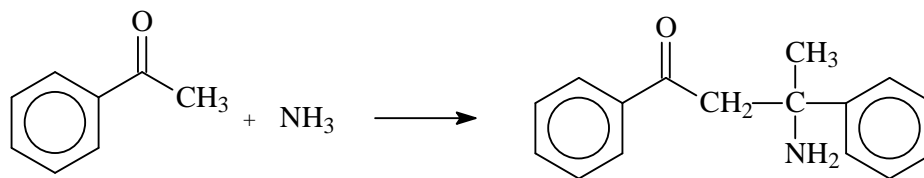
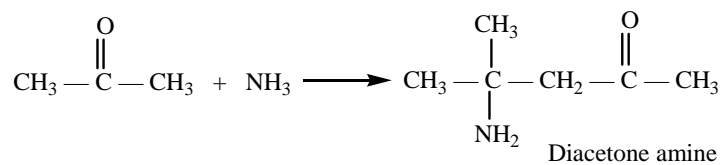


The mechanism of formation of cynohydrin is similar as discussed in aldehyde unit, hence can be persued from aldehyde unit.

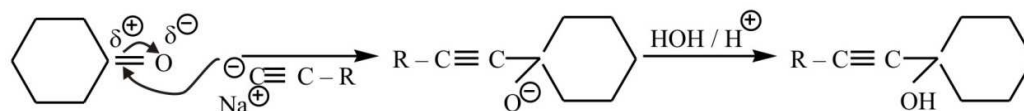
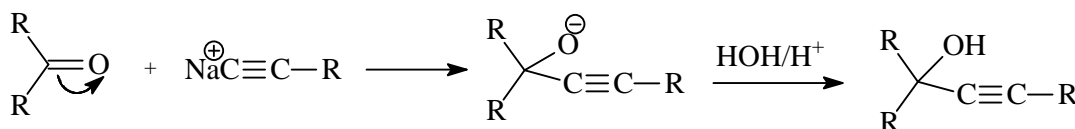
(3) **Addition of Grignard reagents (RMgX):** - ketones react with Grignard reagent to form complex which on hydrolysis with dilute acids gives tertiary alcohol.



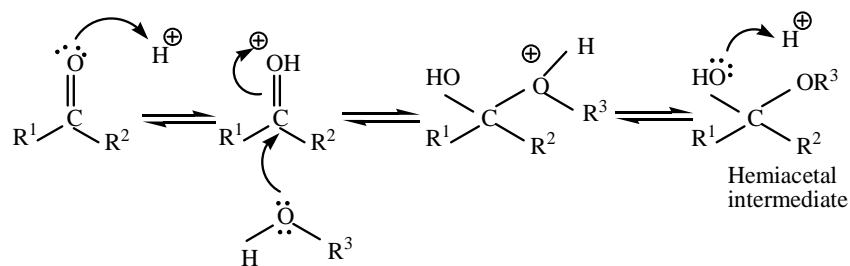
(4) **Addition of ammonia (NH<sub>3</sub>):**- Ketones react with NH<sub>3</sub> and form complex condensation products.

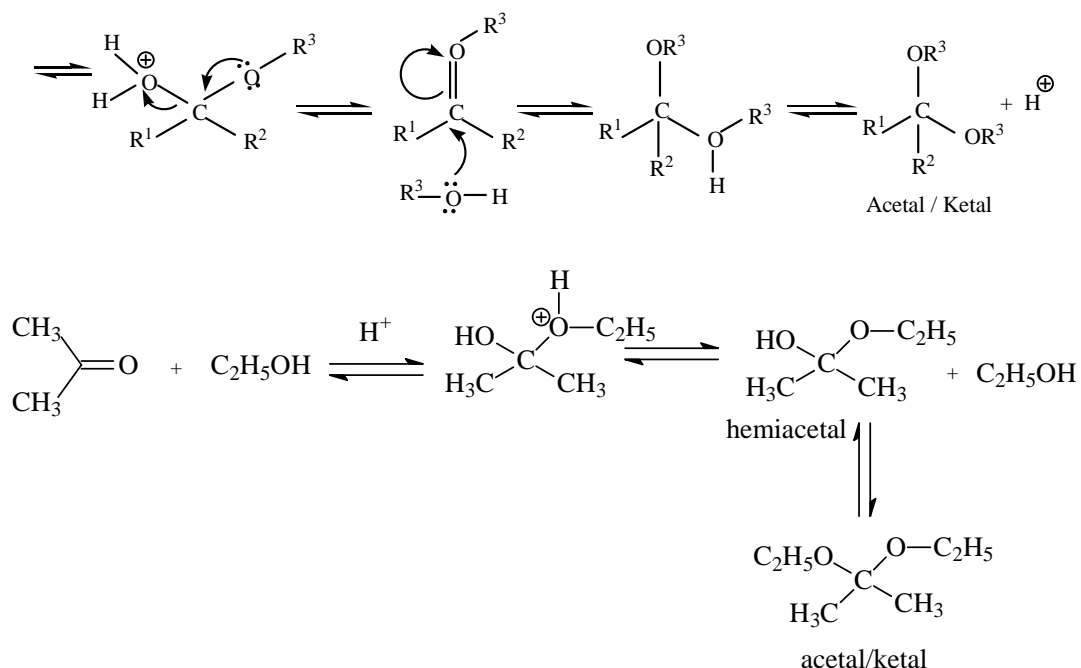


**(5) Addition of terminal alkynes:** - Ketones react with sodium salt of terminal alkynes to give alkynol.

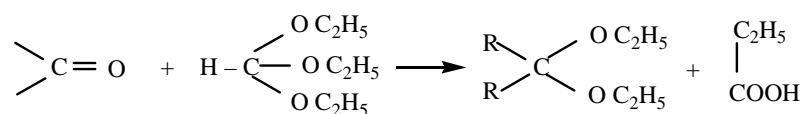


**(6) Addition of alcohols (ROH):** - Ketones react with alcohol in the presence of acids or base catalyst form hemiketals. Hemiketals are less stable than hemiacetals.

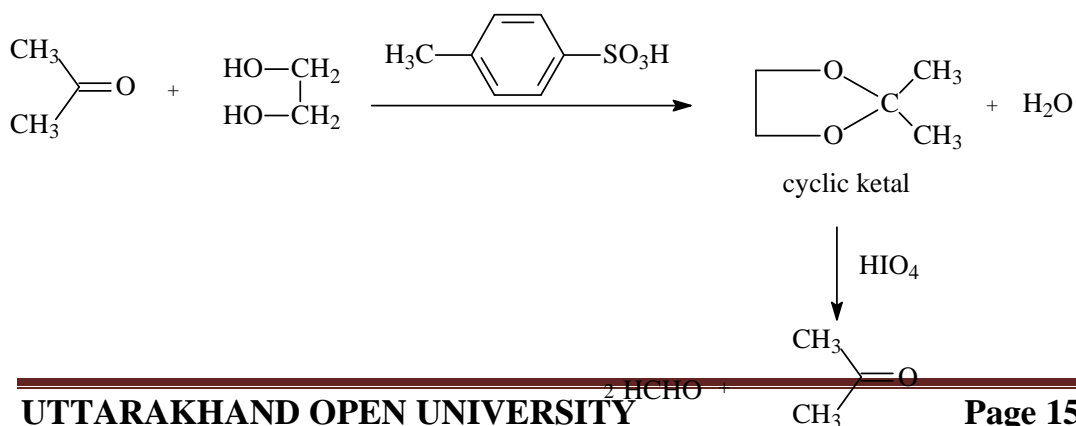




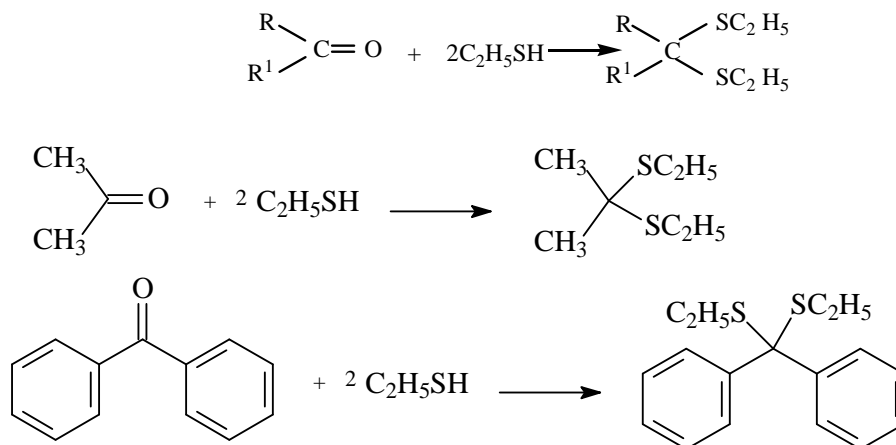
Hemiacetals of ketones are sometimes called hemiketals. In the above reaction excess of alcohol and removal of water leads reaction forward and excess of water favours backward reaction. Ketones don't form ketals readily as formed by aqueous dioxin. Solution of dioxolan on treatment with periodic acid regenerates ketone. Aldehydes, ketals may however be prepared by treating the ketone with ethyl orthoformate.



Ketones readily react with 1, 2 glycols to form dioxolans/cyclic ketal



(7) **Addition of mercaptans:** - Thiols react more rapidly than alcohols to more rapidly to give thioketals.

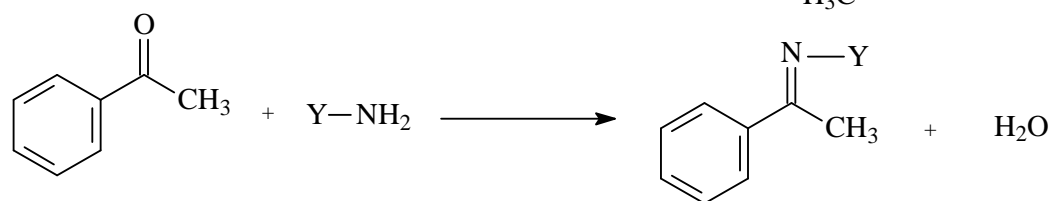
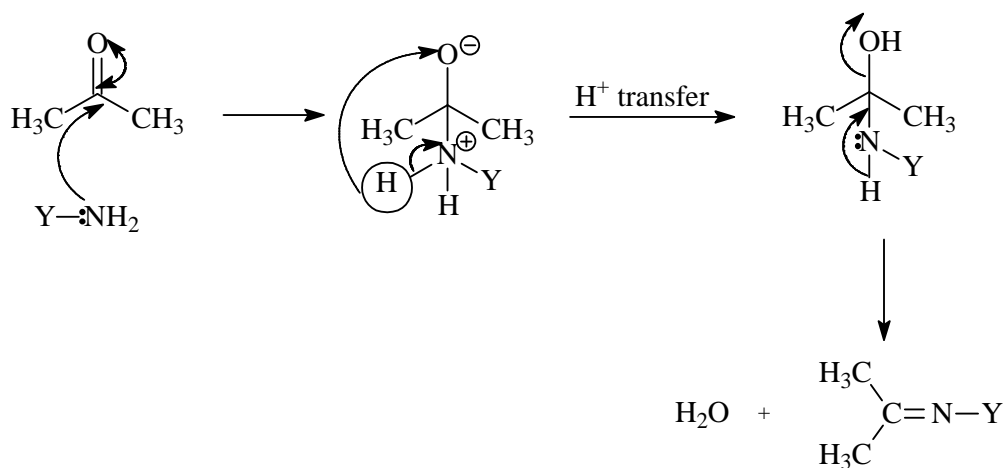
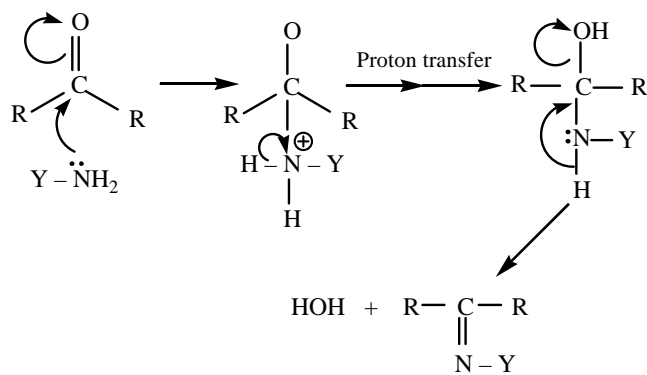


### 5.7.2 ADDITION REACTIONS FOLLOWED BY ELIMINATION:

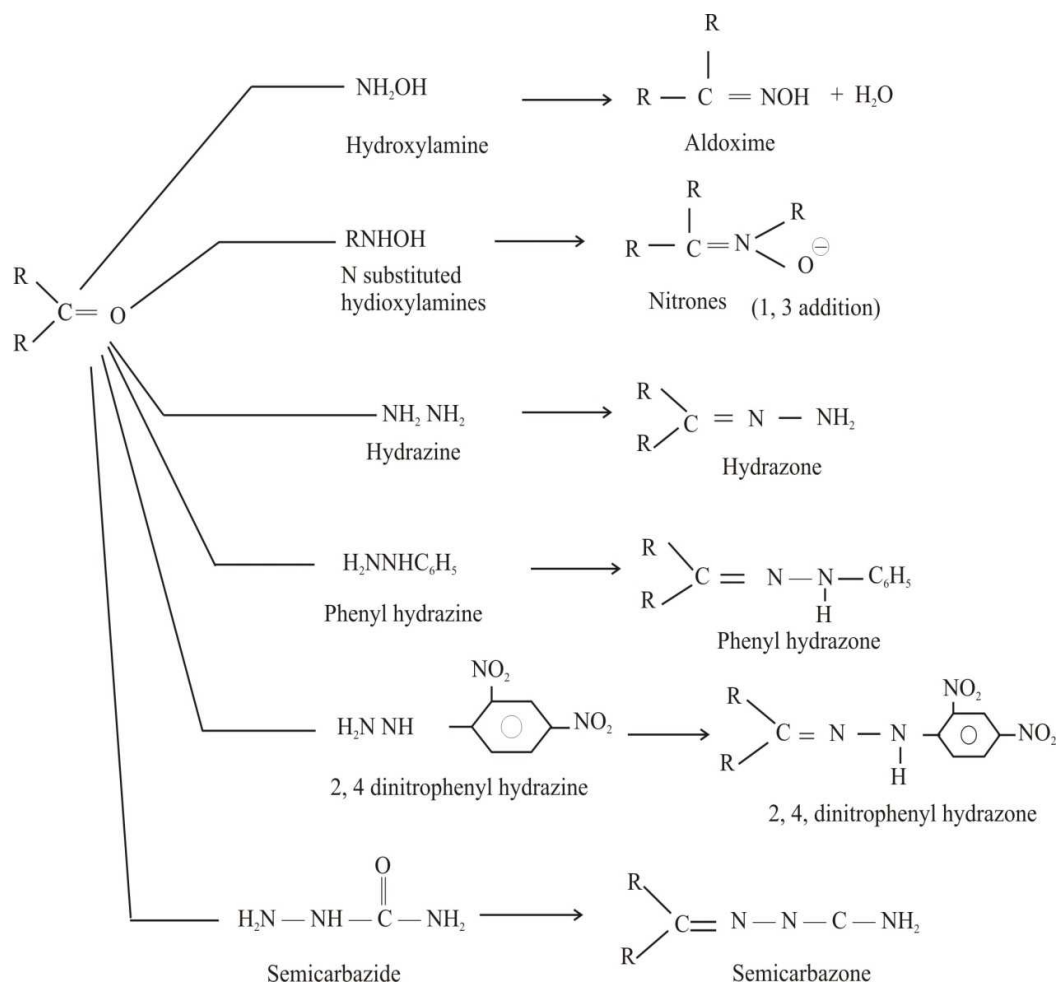
Ketones like aldehydes combine with nucleophile and eliminate neutral molecule like  $\text{H}_2\text{O}$ . The addition reaction of ketones followed by eliminations are being described as follow.

(8) **Addition of ammonia derivatives:** - Nucleophiles of type  $\text{Y} - \text{NH}_2$  ( $\text{Y} = \text{NH}_2$ ,  $\text{OH}$ ,  $\text{C}_6\text{H}_5\text{NH}$ , etc) combine with ketones and form carbon nitrogen double bonds, followed by elimination of water molecule.

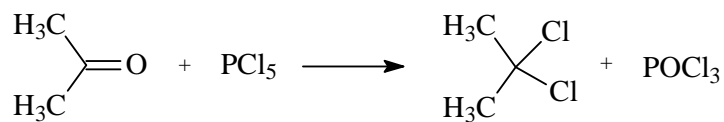




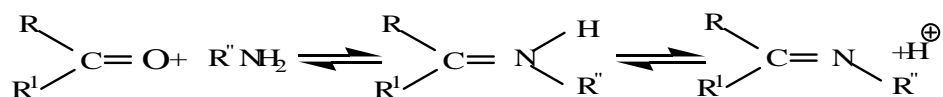
Above reaction is acid catalysed.



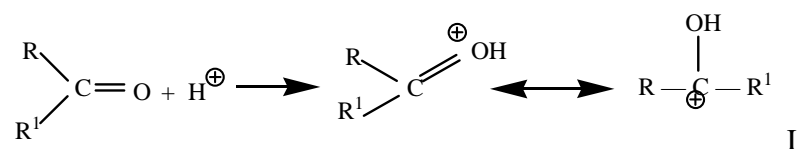
(9) Phosphorus pentachloride reacts with carbonyl compounds (simple).



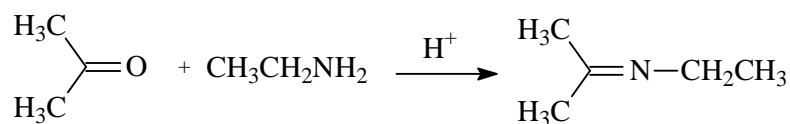
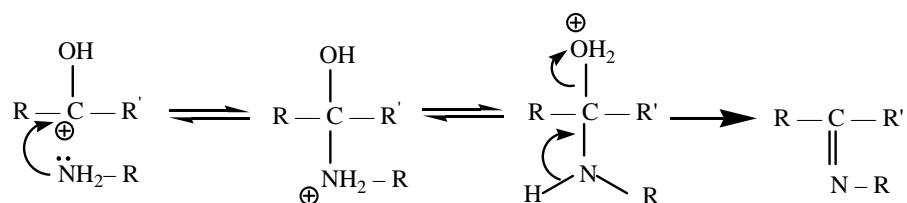
(10) Ketones react with aliphatic primary amines to form ketimines.



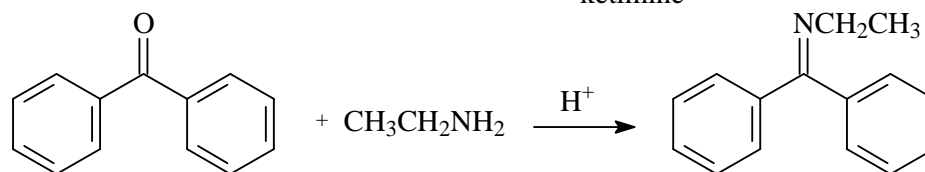
Mechanism :



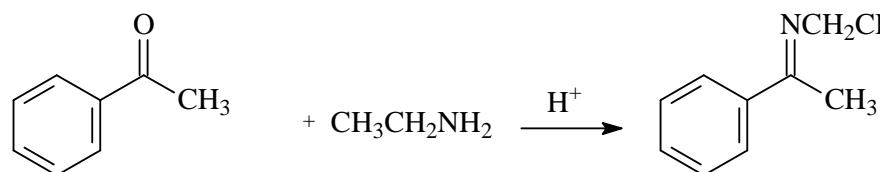
Acid catalyses above reaction and makes carbonyl carbon more electrophilic.



ketimine

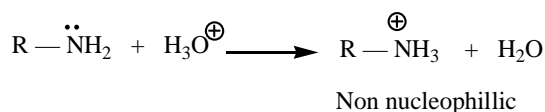


ketimine



ketimine

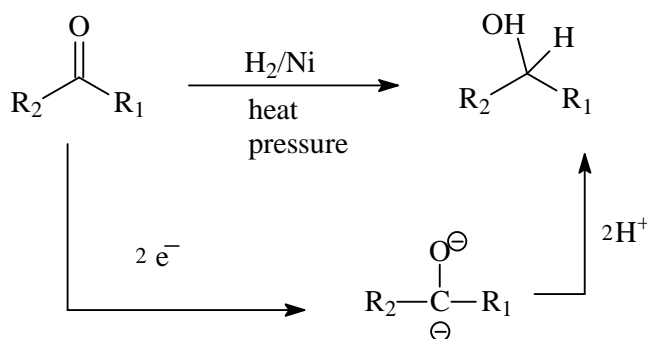
At pH<sub>7</sub> formation of I is fast and as acidity increases dehydration also increases. However if acidity increases further then I<sup>st</sup> step addition of nucleophilic nitrogen of RNH<sub>2</sub> group decreases as acidity forms non nucleophilic nitrogen conjugate acid.



### 5.7.3 REDUCTION REACTIONS:

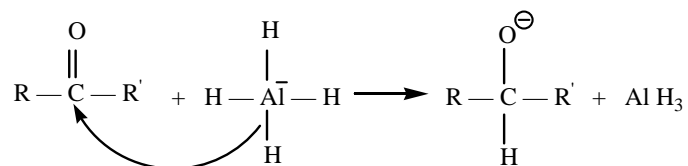
The carbonyl group of ketones can be reduced to  $-\text{CH}_2-$  or  $-\text{CH}$  by using reducing reagents. In continuation to other reactions the reductions are as follow.

(11) Ketones are reduced to secondary alcohol, when treated with  $\text{H}_2$  and Ni,  $\text{H}_2$  and Pt,  $\text{LiAlH}_4$  (lithium aluminium hydride) in THF (tetrahydro furan),  $\text{NaBH}_4$  (sodium borohydride) in water or alcohol.

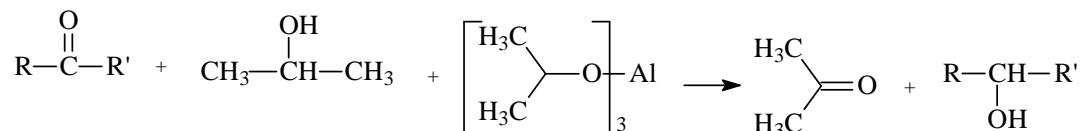


When reduction of unsaturated ketone with Ni and  $\text{H}_2$  is carried out then preferentially double bond is hydrogenated or both double bond and carbonyl group are hydrogenated. But here only carbonyl group cannot be hydrogenated.  $\text{LiAlH}_4$  and  $\text{NaBH}_4$  type metal hydrides reduce carbonyl group but not isolated carbon-carbon double bond.  $\text{C}=\text{C}$  in conjugation with carbonyl group is sometimes reduced.  $\text{NaBH}_4$  is milder reducing agent than  $\text{LiAlH}_4$ . So  $\text{NaBH}_4$  is selective for carbonyl group if carbonyl and ester groups are present in same molecule.

Metal hydrides ( $\text{LiAlH}_4$  and  $\text{NaBH}_4$ ) transfer hydride ion to positive carbon of carbonyl group and then treatment with water or aqueous acid sets free alcohol from its salt.



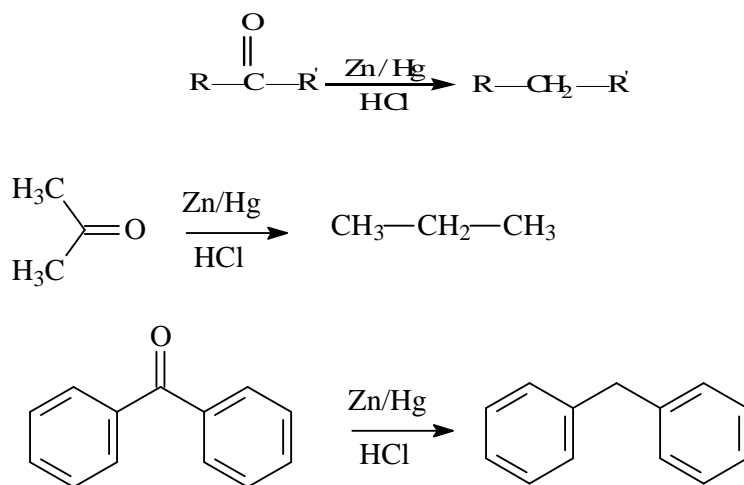
(12) **Meerwein-Ponndorf-Verely reduction:** - As discussed in aldehyde unit, ketones are also reduced to corresponding alcohol when ketones are dissolved in solution of isopropyl alcohol containing aluminium isopropoxide.



If aldehydes or ketones are unsaturated then it attacks only carbonyl group. Mechanism of MPV reduction of ketones is same as of aldehydes (discussed in aldehyde unit).

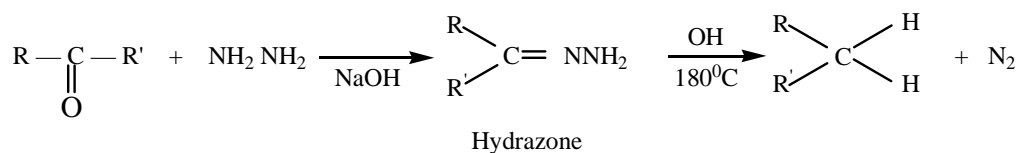
(13) Reduction to hydrocarbon: Ketones are reduced to  $-\text{CH}_2-$  groups:

(a) **Clemmensen reduction:** - Carbonyl group of ketones is reduced to methylene group by using zinc amalgam and hydrochloric acid.

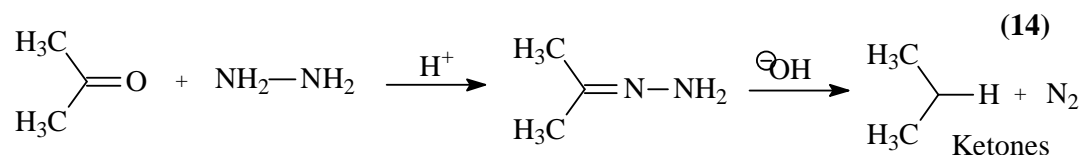


Mechanism of clemmensen reduction is already discussed in aldehyde unit.

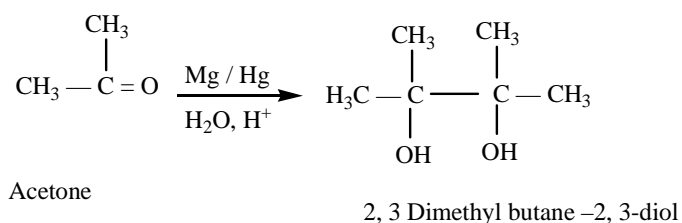
(b) **Wolf Kishner Reduction :-** It involves conversion of carbonyl group to methylene group by heating ketones in the presence of excess hydrazine and a strong base (sodium ethoxide) at  $180^\circ\text{C}$ .



Reaction can be carried out room temperature in the presence of polar solvents like DMSO. In  $\alpha$ ,  $\beta$ - unsaturated carbonyl compounds, the Wolf Kishner reduction lead to double bond migration.

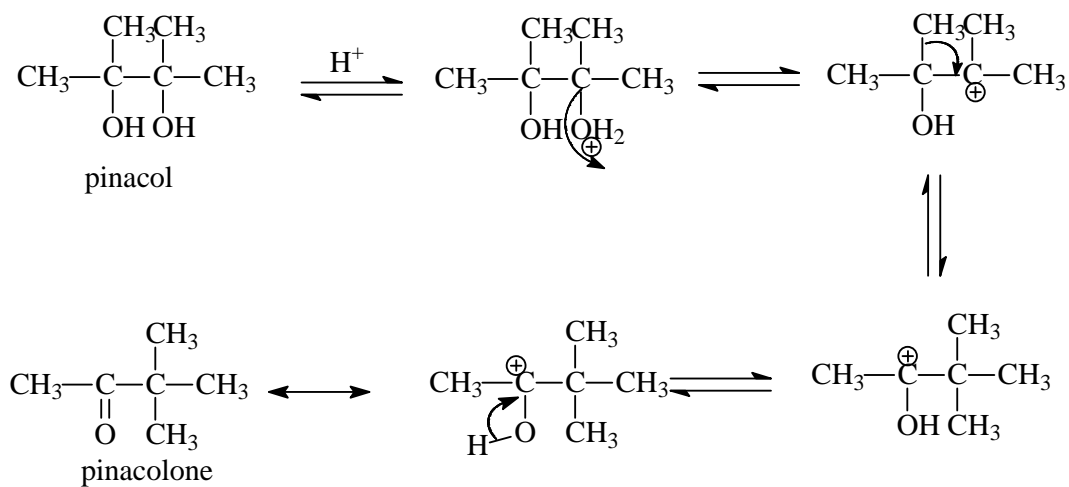


when reduced by metals eg. magnesium in neutral or acidic medium forms pinacols (1, 2 glycols)



Pinacol under acidic condition undergo rearrangement to form pinacolone. This rearrangement is known as Pinacole-Pinacolone rearrangement.

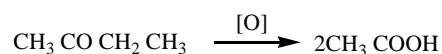
This reaction is given by only ketones (not aldehydes).



## 5.7.4 OXIDATION REACTIONS:

Ketones like aldehydes are oxidized to carboxylic acids. The oxid. Reactions of ketones in continuation are as under.

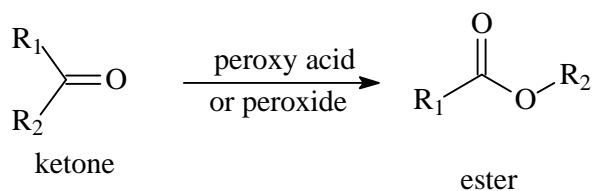
(15) Ketones can be oxidized by strong oxidizing agents such as alkaline  $\text{KMnO}_4$  or hot concentrated  $\text{HNO}_3$  etc. Here carbon atoms adjacent to carbonyl group are attacked and carbon atom joined to the smaller number of hydrogen atoms is oxidized preferably.



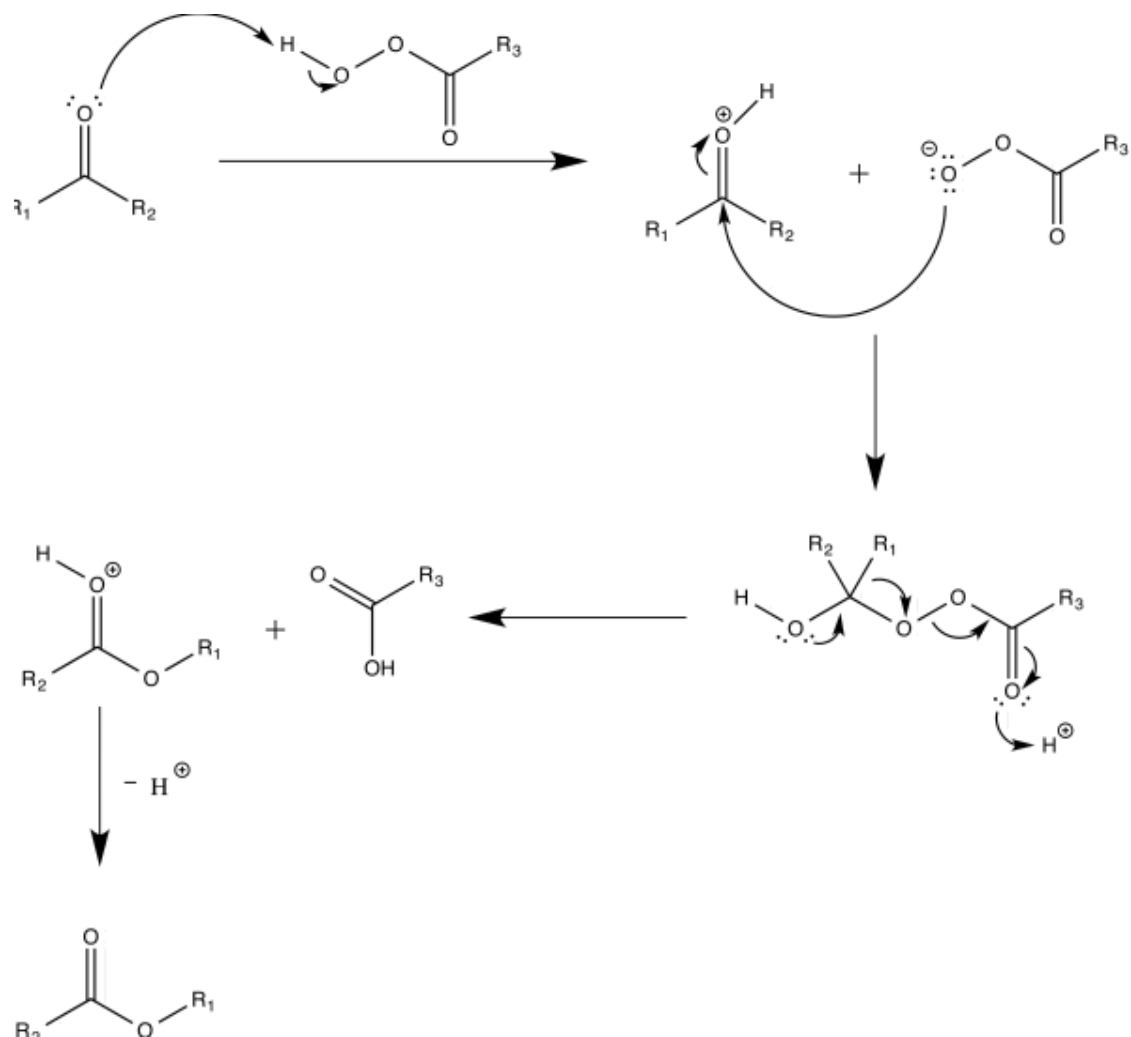
If adjacent carbon atoms have same number of hydrogen atoms, then smaller alkyl group retains carbonyl group.

Ketones do not reduce Fehling's solution, Benedict's solution or ammoniacal silver nitrate.

(a) **Baeyer Villiger Oxidation:** - Aliphatic ketones on treatment with perbenzoic, peracetic, and monoperothalic acid or permonosulphuric acid  $\text{H}_2\text{SO}_5$  forms esters called Baeyer Villiger Oxidation.

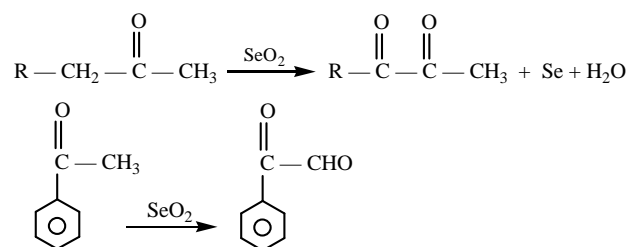


**Mechanism:** The sequential mechanism of Baeyer-Villiger reaction is as follows



This rearrangement is intramolecular and migratory aptitude of an alkyl group is  $3^{\circ} > 2^{\circ} > 1^{\circ}$ .

**(b) Oxidation with SeO<sub>2</sub>:**- SeO<sub>2</sub> oxidises methylene group adjacent to the carbonyl group of aldehydes and ketones.

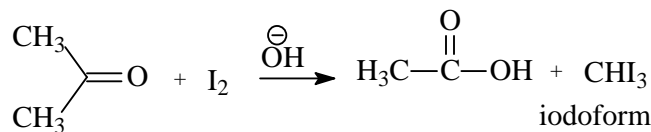
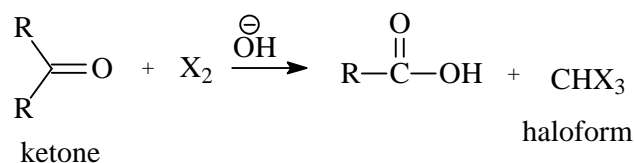
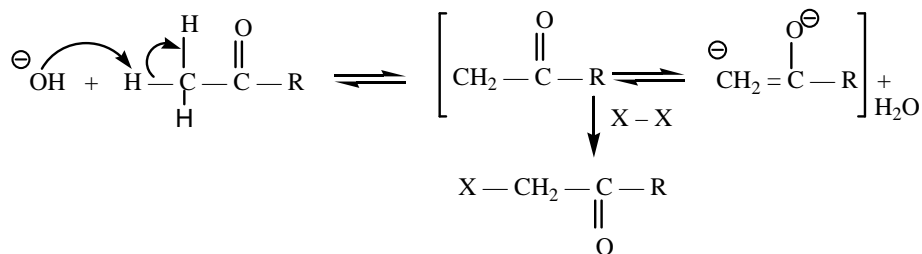




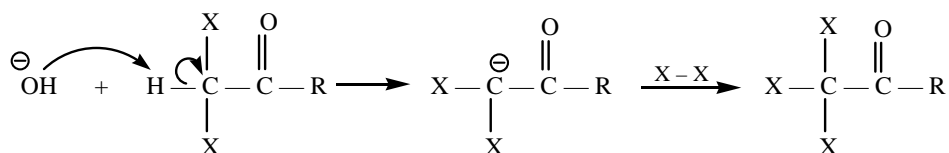
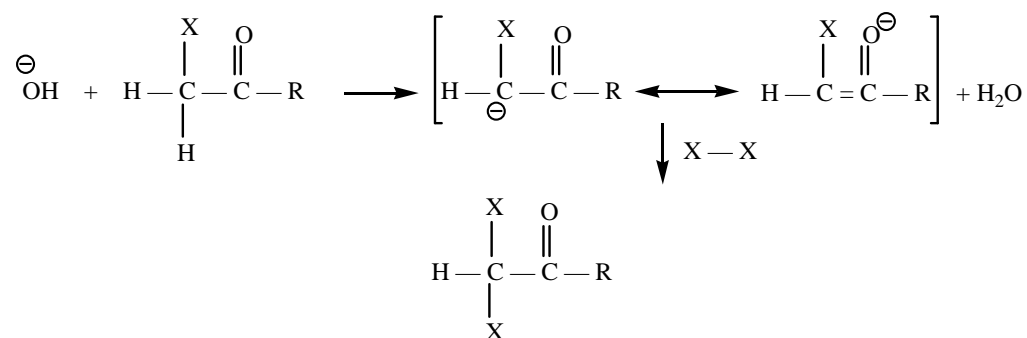
## 5.7.5 OTHER REACTIONS:

Earlier it has been discussed the acidity of  $\alpha$ - hydrogens in carbonyl compounds which leads to different types of reactions in ketones eg. halogenation, condensation etc. In continuity some of the reactions of ketones are being discussed as follow

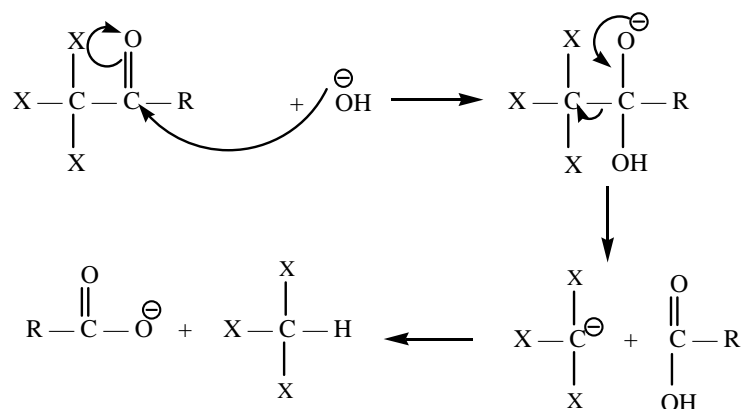
**(16) Haloform Reaction:** - Methyl ketones react rapidly with halogens ( $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{I}_2$ ) in the presence of alkali to form mono, di and tri haloderivatives.

**Mechanism**

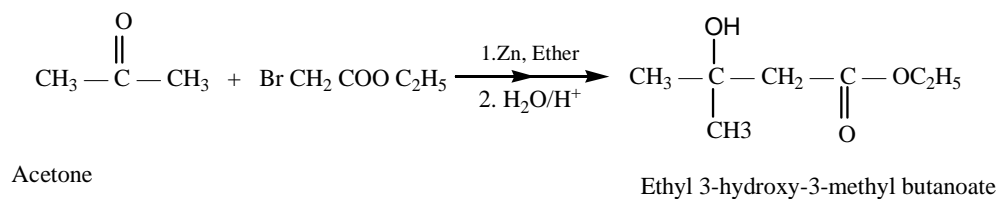
It involves abstraction of hydrogen by alkali and then resonance stabilization of conjugate base. Then carbanion displaces a halide from a halogen molecule. Introduction of halogen to methyl ketone enhances electronegativity of remaining  $\alpha$ - hydrogens and they again undergo above process repeatedly forming trichalogenated ketones.



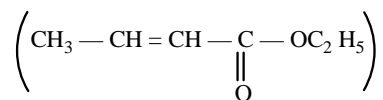
The trihalogenated ketones are unstable to base.



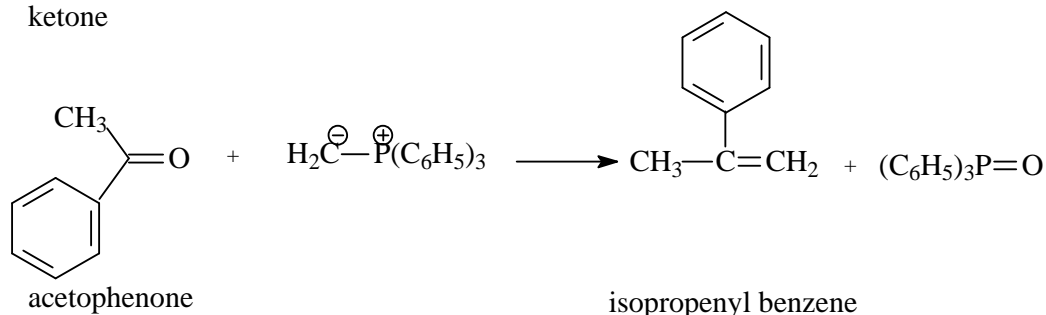
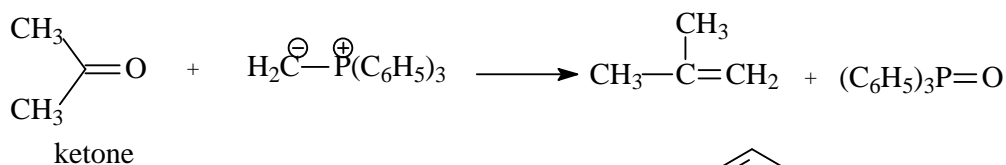
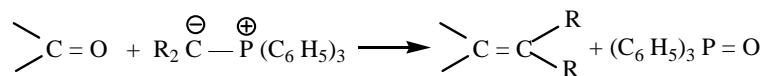
(17) **Reformatsky Reaction:** - Like aldehydes ketones also react with  $\alpha$  bromoester in the presence of Zinc which subsequently on acid hydrolysis result in  $\alpha$ -hydroxy ester.



$\beta$ - hydroxyl ester dehydrate to give unsaturated ester.

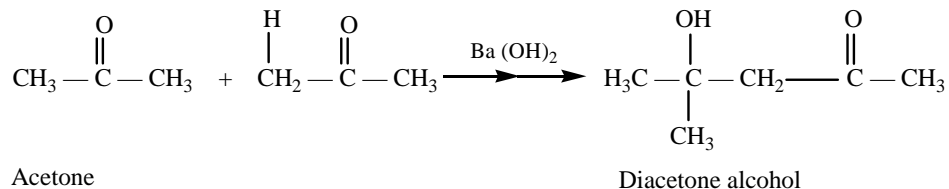


**18) Wittig reaction:** - Ketones react with alkylidene-phosphoranes (phosphorus ylides) in an atmosphere of nitrogen leads to alkene synthesis.

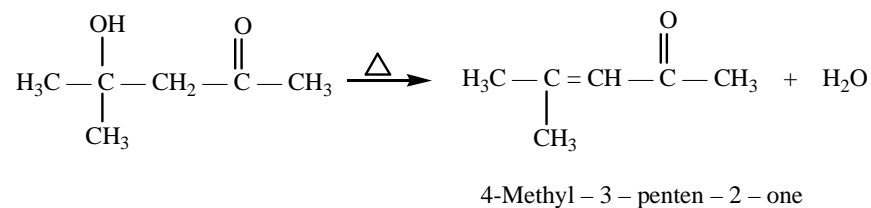


Mechanism of formation of phosphorus ylides and Wittig reaction has been discussed in the previous unit pertaining to aldehydes. Reaction of ylides with ketones is slow as compared to aldehydes.

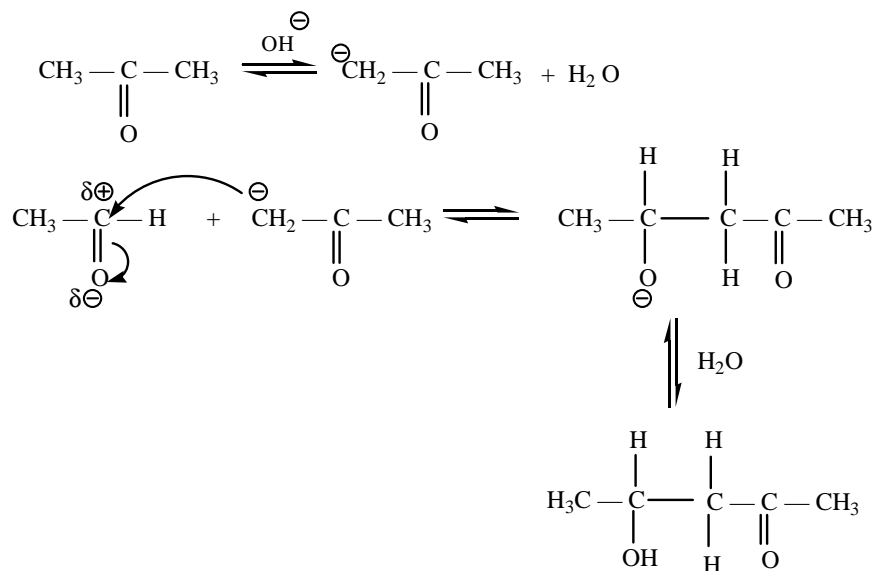
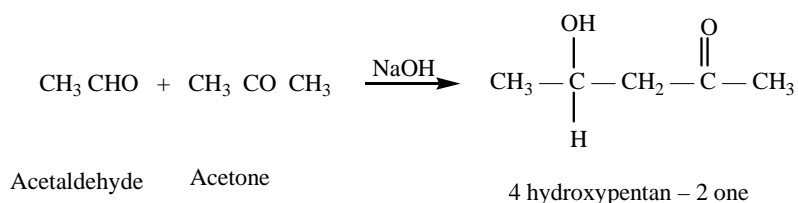
**(19) Aldol condensation:** - Analogues to aldehydes, ketones having a hydrogen undergo self condensation in the presence of  $\text{Ba}(\text{OH})_2$  to form ketols.



Ketols are easily dehydrated by heating or by dilute acids to form unsaturated ketones.

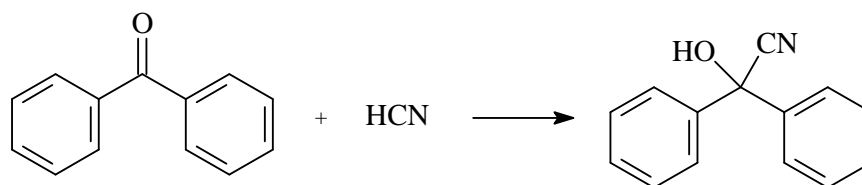
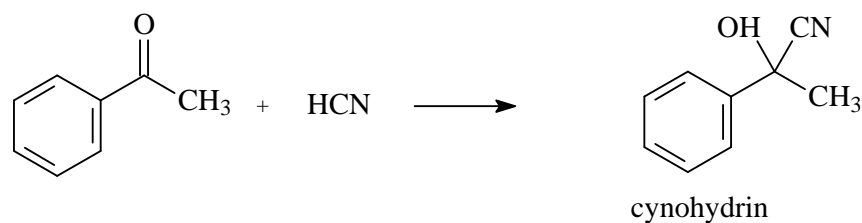


Mechanism of aldol condensation is similar to that of aldehyde which has already been discussed in aldehyde unit. However in mixed aldol condensation, when aldehydes condense with ketones in the presence of dil. alkali, it is the  $\alpha$ -carbon (having hydrogen) atom of the ketone which is the attacking nucleophile.

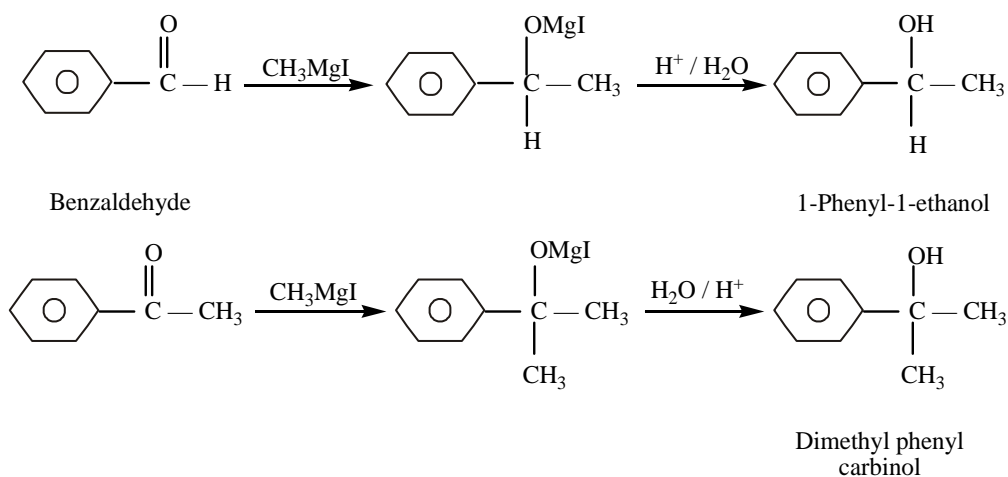


### 5.7.6 SOME REACTIONS OF AROMATIC KETONES:

Aromatic ketones show nucleophilic addition reactions. Positive part of adding reagent always goes to carbonyl oxygen while negative part to carbonyl carbon. Though the reactions have already been discussed here again we discuss some important reactions with reference to aromatic ketones only.

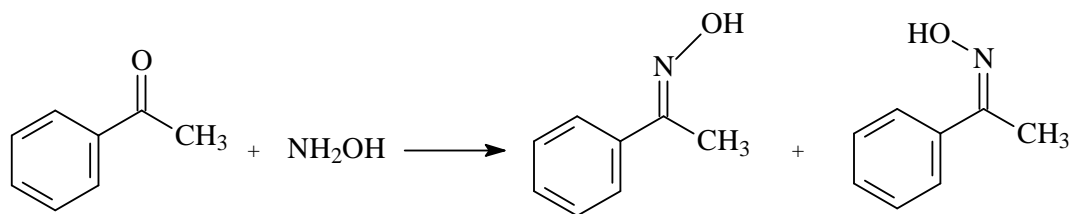
**(1) Addition of HCN:**

**(2) Addition of Grignard Reagent:** Like aliphatic ketones aromatic ketones give secondary alcohols while treated with Grignard reagent followed by hydrolysis.

**(3) Addition of sodium bisulphite:**

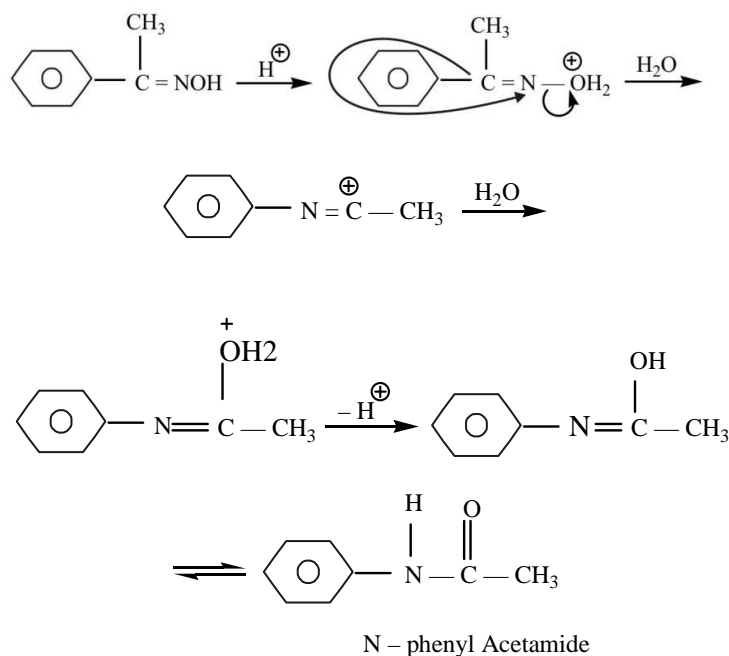
Acetophenone does not give bisulphite addition reaction due to steric hindrance.

**(4) Acetophenone reacts with hydroxylamine to form and methyl phenyl ketoxime in the presence of reagents as  $\text{PCl}_5$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$  etc. This reaction is known as **Beckmann rearrangement****



ketoxime syn and anti

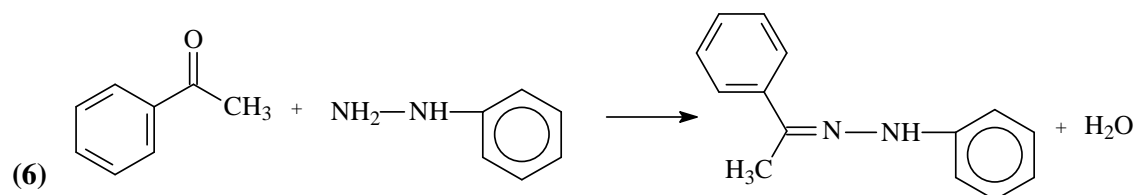
**Mechanism:**



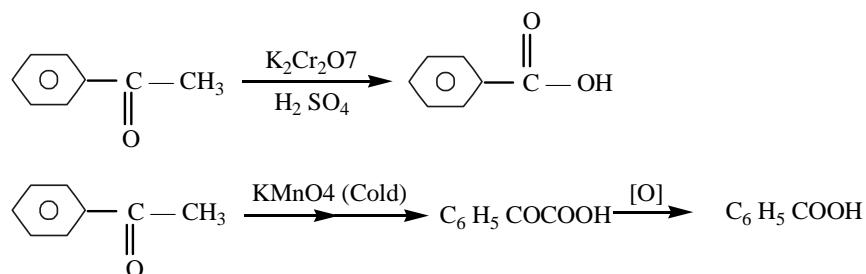
N – phenyl Acetamide

During Beckmann rearrangement it is methyl/phenyl group present in trans position migrate to the carbocation. Based on this we can distinguish syn or anti ketoxime. If phenyl group migrates, we get N-phenyl- acetamide and if methyl group migrate, the product is acetanilide.

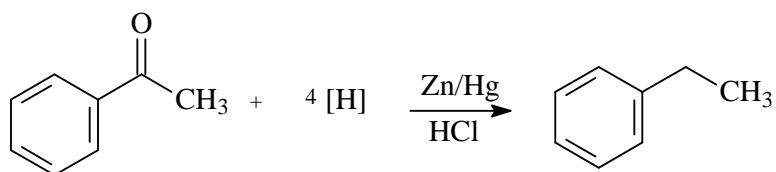
- (5) Acetophenone reacts with phenylhydrazine to give respective phenylhydrazones and eliminate water.



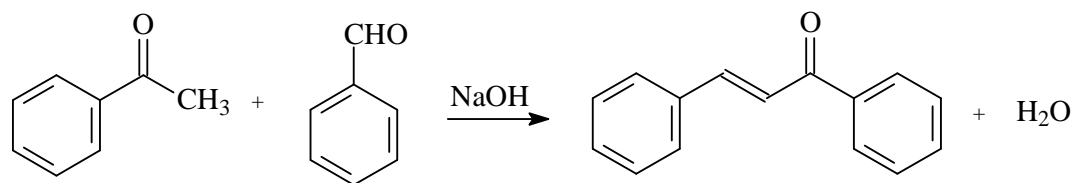
**Oxidation:** Acetophenone is oxidized by acidic  $K_2Cr_2O_7$  or  $KMnO_4$  to give benzoic acid.



**(7) Reduction:** Acetophenone undergo reduction to form ethyl benzene

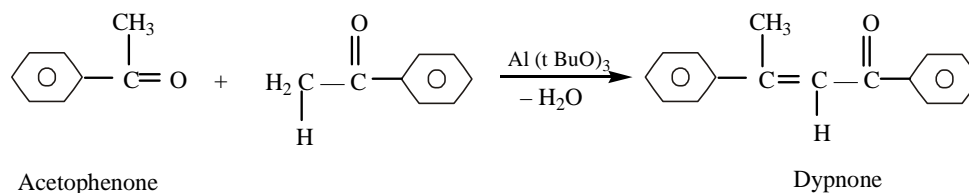


**(8) Condensation Reactions: (a) Mixed Aldol condensation:** - Acetophenone (has  $\alpha$ -hydrogen) condenses with benzaldehyde to form phenyl styaryl ketone.

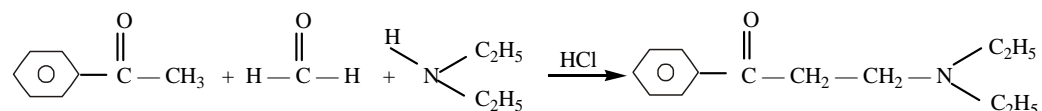


Condensation between aromatic aldehyde and aliphatic ketone (or mixed ketone) is also known as Claisen Schmidt reaction.

**(b) Aldol type condensation:** - Acetophenone undergoes self addition in the presence of aluminium t-butoxide to form dypnone.

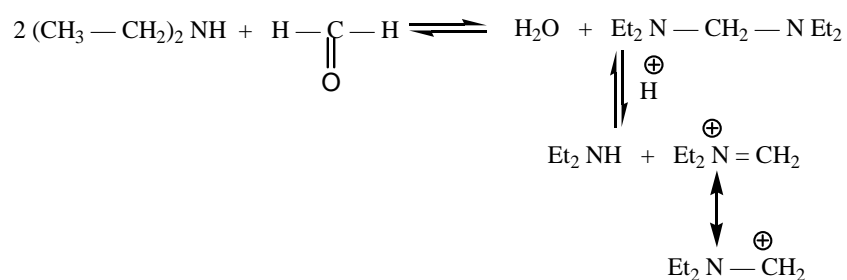


(9) **Mannich reaction:** - Acetophenone reacts with formaldehyde and ammonia or a primary amine or a secondary amine to form  $\beta$ -aminoketones.

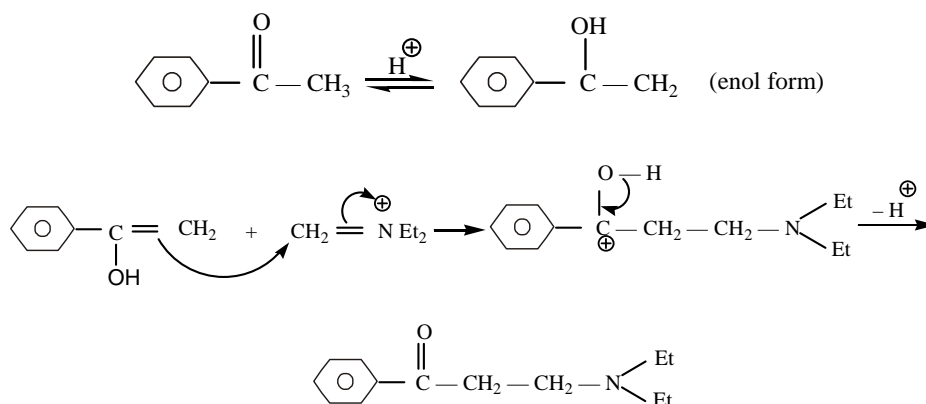


**Mechanism:**

(i) Mannich intermediate is formed by condensation of amine and formaldehyde in acidic medium

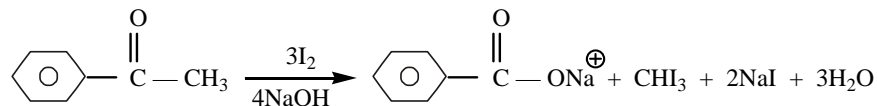


(ii) Mannich intermediate attacks acetophenone (enolic form)

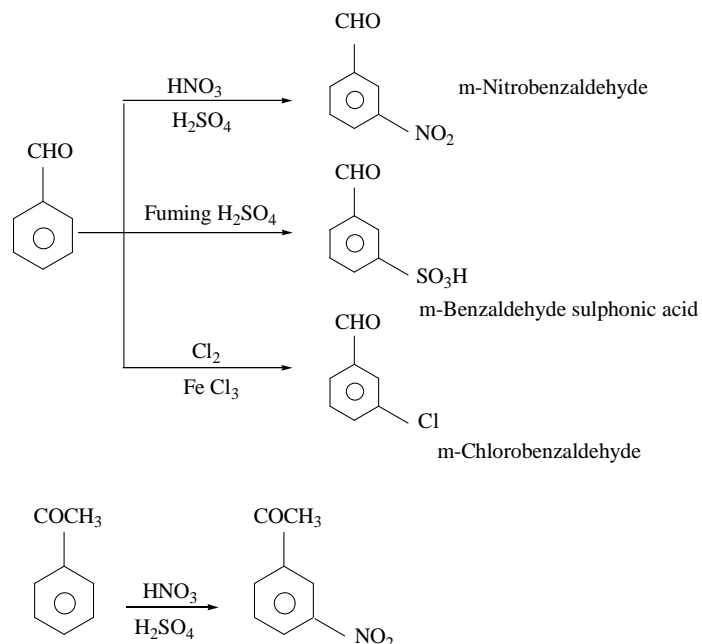


(10) **Iodoform reaction:** - Acetophenone reacts with Iodine in the presence of NaOH to form Iodoform (Reaction analogous to aliphatic aldehyde and ketones having methyl group showing haloform reaction).





(11) **Electrophillic substitution reaction:** - Acetophenone undergo electrophillic substitution reaction– COCH<sub>3</sub> group are meta directing and deactivating.



## 5.8 SUMMARY

Ketones are the compounds which have general formula of  $\text{C}_n\text{H}_{2n}$  contain oxo (carbonyl) group and its functional keto group  $>\text{C}=\text{O}$  lies within the chain. Secondary alcohols on Oppenauer oxidation (aluminium isopropoxide in presence of excess of acetone) give ketones. Ketones also show nucleophilic addition reactions but ketones are less reactive than corresponding aliphatic aldehydes as it involves change of carbon's hybridization from  $\text{sp}^2$  to  $\text{sp}^3$  and increased crowding at carbonyl carbon is sterically hindered. Also +I effect of alkyl group at carbonyl carbon reduces its nucleophilicity. Mild oxidizing agents like Tollen's reagent or Fehling's solution do not oxidize ketones. Strong oxidizing agents oxidize ketones as Conc.  $\text{HNO}_3$ ,  $\text{KMnO}_4/\text{H}_2\text{SO}_4$ . They give condensation reactions and alpha hydrogen substitution reactions. Reagents like  $\text{LiAlH}_4$ ,  $\text{NaBH}_4$  etc, can reduce ketones.

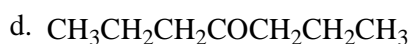
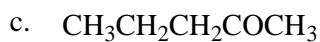
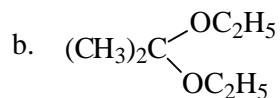
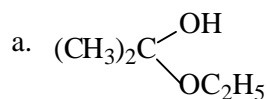
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**5.9 TERMINAL QUESTIONS**


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Q.1 Tick out the correct option in following multiple choice questions.

1. Acetone is treated with excess of ethanol in the presence of HCl. The product obtained is



Ans. :- (b)

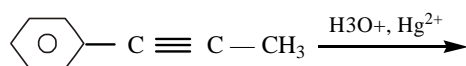
2. Clemmensen reduction of ketone is carried out in the presence of which of the following:-

(a)  $\text{H}_2$  and Pt as catalyst    (b) Glycol with KON    (c) Zn – Hg with HCl

(d) Li Al H<sub>4</sub>

Ans. :- (c)

3. Identify the product in reaction:-



(a)  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CHO}$     (b)  $\text{C}_6\text{H}_5\text{COCH}_2\text{CH}_3$     (c)  $\text{C}_6\text{H}_5\text{CH}_2\text{COCH}_3$

(d)  $\text{C}_6\text{H}_5\text{COCOCH}_3$

Ans. :- (b)

4. Compound A react with HCN and forms cyanohydrin which on hydrolysis gives carboxylic acid. So compound A is –

(a)  $\text{CH}_3\text{NH}_2$     (b)  $\text{CH}_3\text{COCH}_3$     (c)  $\text{CH}_3\text{CO}_6\text{CH}_5$     (d)  $\text{C}_6\text{H}_5\text{OH}$

Ans :- (b)

5. The compound which forms acetaldehyde when heated with dilute NaOH.

(a) 1, Chloroethane (b) 1, 1 dichloro ethane (c) 1, 2 dichloro ethane

(d) 1, 1, 1 trichloro ethane

Ans. :- (a)

6. An organic compound X is oxidized by using acidified  $K_2Cr_2O_7$ . Resultant product reacts with phenyl hydrazine but does not answer silver mirror test. So the possible compound X is

(a)  $(CH_3)_2CHON$  (b)  $CH_3CHO$  (c)  $CH_3CH_2OH$  (d)  $CH_3-C(=O)-CH_3$

Ans. :- (a)

7. To distinct 2-pentanone from 3-pentanone \_\_\_\_\_ reagent should be employed.

(a)  $K_2Cr_2O_7 / H_2SO_4$  (b)  $Zn - Hg / HCl$  (c)  $SeO_2$

(d) Iodine / NaOH

Ans. :- (d)

(WB JEE 2009)

8. In which of the following reactions new carbon – carbon bond is not formed-

(a) Cannizaro reaction (b) Wurtz reaction (c) Aldol condensation

(d) Benzoin condensation

Ans. :- (a)

(WB Jee 2009)

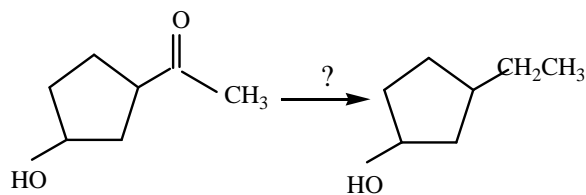
9. A strong base can abstract an a hydrogen from –

(a) Amine (b) Alkane (c) Alkene (d) Ketone

(CBSE AIPMT 2008)

Ans. :- (d)

10.



(a) Zn (Hg), HCl

(b) NH<sub>2</sub> NH<sub>2</sub>, OH

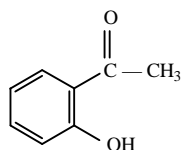
(c) H<sub>2</sub>, Ni

(d) NaBH<sub>4</sub>

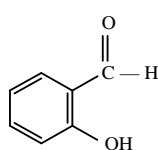
Ans.:- (b)

11. What is the correct structure for 2-hydroxy acetophenone?

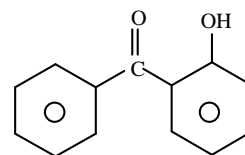
(a)



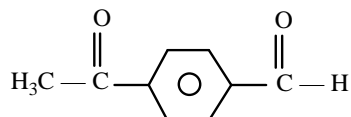
(b)



(c)

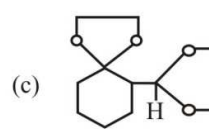
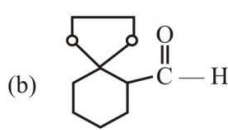
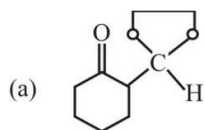
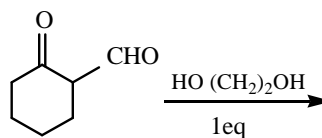


(d)



Ans. :- (a)

12. What is the major product of the following reaction ?



Ans. :- (a)

13. Cyclopentanol undergoes oxidation to give –

- (a) Cyclopentene                      (b) Cyclophentanone                      (c) Cyclopentanal

Ans. :- (b)

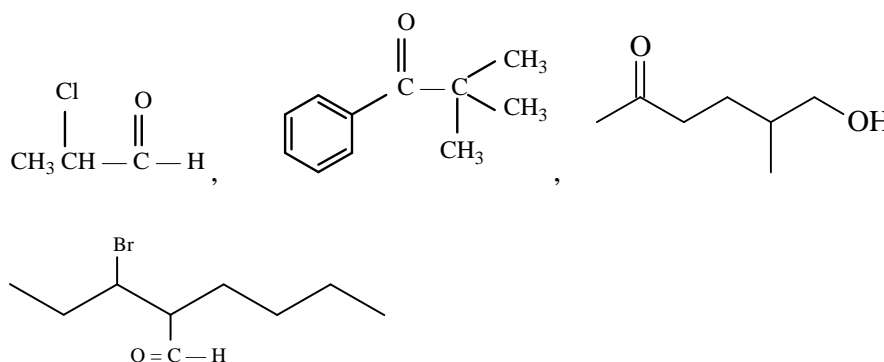
14. Which of the following compounds gives positive iodoform test ?

- (a) 3-Hexanone                      (b) 1-Pentanol                      (c) Acetone  
(d) 3-Pentanone

Ans. :- (c)

Q.2 Short answer type questions

1. Write IU PAC names of following compounds :-

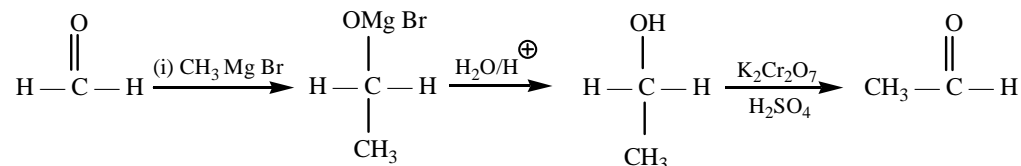


Ans: - 2-chloropropanal, 2, 2-dimethyl-1-phenyl propanone, 6-hydroxy -5 methyl -2-hexanone, 2-[1-bromophenyl] hexanal.

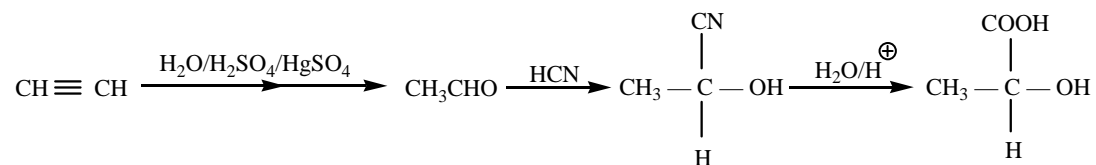
2. Why boiling points of aldehydes and ketones are higher than those of corresponding alkanes?

3. Why lower aldehydes are soluble in water?

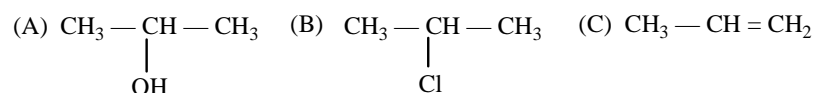
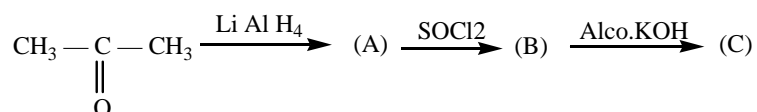
4. How will you synthesize acetaldehyde from formaldehyde?



5. How will you synthesize lactic acid from acetylene?



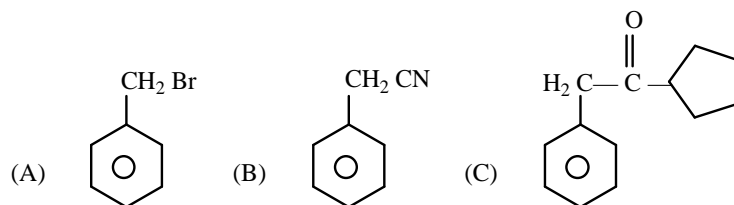
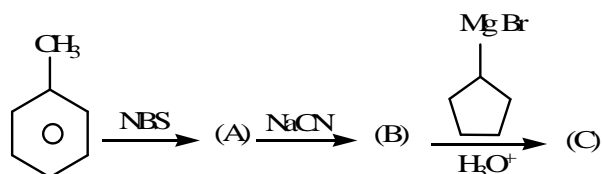
6. Identify (A), (B) and (C)



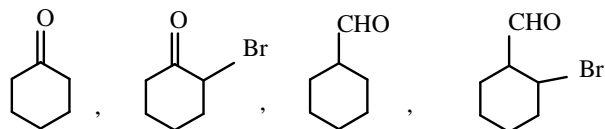
7. How did you distinguish formaldehyde from acetaldehyde?

Q.3. Complete the following reactions.

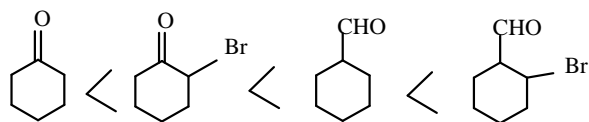
1. Identify A, B and C In the following:-



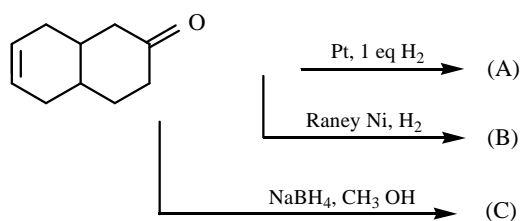
2. Arrange the following in increasing extent of hydration.



Ans – hydration increases with increasing H-bonding.

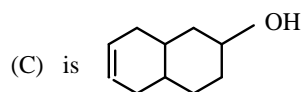
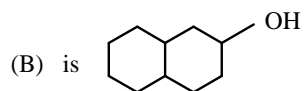
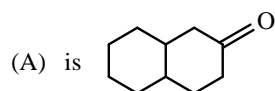


3.



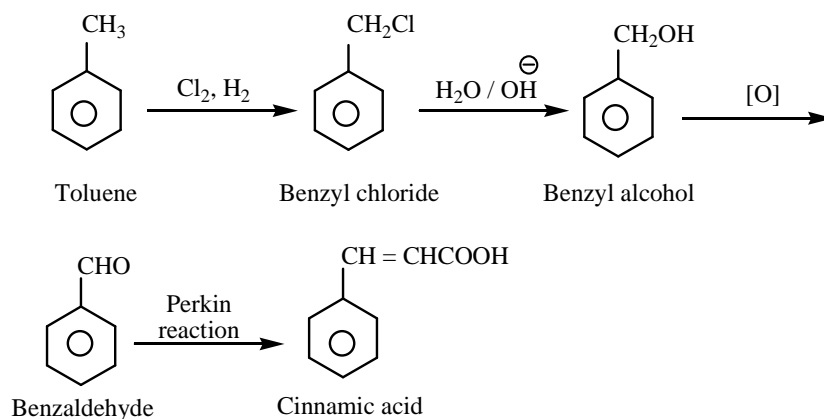
Identify (A), (B) and (C)

Ans –



4. Compound A, having the empirical formula C<sub>7</sub>H<sub>8</sub> is chlorinated in sunlight to give a product which is hydrolysed to produce B. B after oxidation reacts with acetic anhydride in the Perkin reaction to produce an acid C which has an equivalent weight of 148. Give the name and structure of A, B and C.

Ans –




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### 5.10 REFERENCES

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2. R.T.Morrison and R.N.Boyd Organic Chemistry, 6<sup>th</sup> edition, Prentice Hall Private Ltd, 1997.
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**UNIT -6 CARBOXYLIC ACIDS**

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**CONTENTS:**

- 6.1 Objectives
- 6.2 Introduction
- 6.3 Nomenclature of carboxylic acids
- 6.4 Structure and bonding
- 6.5 Physical properties
- 6.6 Acidity of carboxylic acids and effect of substituents on acid strength
- 6.7 Preparation of carboxylic acids
- 6.8 Reactions of carboxylic acids
- 6.9 Mechanism of decarboxylation
- 6.10 Methods of formation and chemical reactions of halo-acids
  - 6.10.1 Preparation of halo acids
  - 6.10.2 Chemical reactions of halo-acids
- 6.11 Hydroxy acids: malic, tartaric and citric acids
  - 6.11.1 Physical properties of hydroxyl acids
  - 6.11.2 Preparation and chemical properties of hydroxy acids
- 6.12 Summary
- 6.13 Terminal Question
- 6.14 Answers(MCQ)
- 6.15 References

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***6.1 OBJECTIVES***

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The aim of this unit is to make you aware about carboxylic acids their common names and IUPAC naming system. To explain the structure of carboxylic acids, describe the acid strength of carboxylic acids, describe boiling points and solubility of carboxylic acids in water, synthesis of carboxylic acids, describe the physical and chemical properties of carboxylic acids To discuss the methods for the conversion of carboxylic acids into acid chlorides, esters and amides. To study the reduction of carboxylic acid and understand about the mechanism of decarboxylation. To study how halo acids are

synthesized from carboxylic acids? To describe the preparation, properties and uses of hydroxyl acids: malic, tartaric and citric acids.

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## 6.2 INTRODUCTION

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Carboxylic acids are aliphatic or aromatic compounds which contain at least one carboxyl group (-COOH) in the molecule. The word “carboxyl” is derived from the names of two functional groups *i.e.* carbonyl and hydroxyl. Carboxylic acids are classified as mono, di, tri, or polycarboxylic acids according to the number of carboxyl groups present in the molecule. For example, the one -COOH group containing hydrocarbons such as formic acid, acetic acid, propionic acid, lactic acid, malic acid, benzoic acid etc. are called monocarboxylic acids whereas the two -COOH groups containing compounds such as oxalic acid, succinic acid, adipic acid, fumeric acid, malic acid, tartaric acid phthalic acid etc. are called dicarboxylic acids similarly like citric acid contains three -COOH group and termed as tri-carboxylic acid. The long chain monocarboxylic acids are also known as fatty acids such as stearic acid, palmitic acid, oleic acid etc. The general chemical formula of aliphatic carboxylic acids is  $C_nH_{2n+1}COOH$ .

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## 6.3 NOMENCLATURE OF CARBOXYLIC ACIDS

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In IUPAC system, carboxylic acids are named by replacing the suffix “-e” of the corresponding alkane with “-oic acid”. It is not necessary to indicate the position of the -COOH group because this group will be at the end of the parent chain and its carbon is assigned as C-1. The common names and IUPAC names for some straight chain saturated carboxylic acids are given in *Table-6.1*.

*Table 6.1–Common names and IUPAC names of some straight chain saturated carboxylic acids*

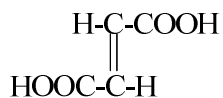
Carboxylic acids	Common name	IUPAC name
HCOOH	formic acid	methanoic acid
CH <sub>3</sub> COOH	acetic acid	ethanoic acid

$\text{CH}_3\text{CH}_2\text{COOH}$	propionic acid	propanoic acid
$\text{CH}_3(\text{CH}_2)_2\text{COOH}$	butyric acid	butanoic acid
$\text{CH}_3(\text{CH}_2)_3\text{COOH}$	valeric acid	pentanoic acid
$\text{CH}_3(\text{CH}_2)_4\text{COOH}$	caproic acid	hexanoic acid
$\text{CH}_3(\text{CH}_2)_5\text{COOH}$	enanthic acid	heptanoic acid
$\text{CH}_3(\text{CH}_2)_6\text{COOH}$	caprylic acid	octanoic acid
$\text{CH}_3(\text{CH}_2)_7\text{COOH}$	pelargonic acid	nonanoic acid
$\text{CH}_3(\text{CH}_2)_8\text{COOH}$	capric acid	decanoic acid
$\text{CH}_3(\text{CH}_2)_9\text{COOH}$	-	undecanoic
$\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$	lauric	dodecanoic

**IUPAC nomenclature of di-carboxylic acids:** If there are two  $-\text{COOH}$  groups are present in an acid; the acid is called dicarboxylic acid. To construct the IUPAC name of these compounds, add the suffix *-dioic* acid to the name of the parent alkane containing both carboxylic groups (*Table-6.2*).

*Table 6. 2-Common names and IUPAC names of some di-carboxylic acids*

<b>Carboxylic acids</b>	<b>Common name</b>	<b>IUPAC name</b>
$\text{HOOC}-\text{COOH}$	oxalic acid	ethanedioic acid
$\text{HOOC}.\text{CH}_2\text{COOH}$	malonic acid	propanedioic acid
$\text{HOOC}.\text{CH}_2\text{CH}_2\text{COOH}$	succinic acid	butanedioic acid
$\text{HOOC}(\text{CH}_2)_4\text{COOH}$	adipic acid	hexanedioic acid
$\begin{array}{c} \text{H}-\text{C}-\text{COOH} \\    \\ \text{H}-\text{C}-\text{COOH} \end{array}$	maleic acid	<i>cis</i> -2-butenedioic acid



fumaric acid

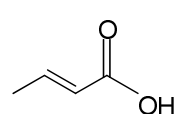
*trans*-2-butenedioic acid

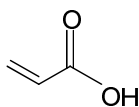
**IUPAC nomenclature of hydroxyl derivatives of carboxylic acids:** The hydroxyl derivatives of carboxylic acids are called hydroxyl carboxylic acids. In common system, the position of –OH group in a hydrocarbon chain is indicated by the *Greek alphabets*  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$  etc. whereas in IUPAC system the position of –OH group in a hydrocarbon chain is indicated by the *numbering*, 1, 2, 3, 4 etc. (Table-6.3)

Table 6.3-Common names and IUPAC names of some hydroxyl derivatives of carboxylic acids.

Carboxylic acids	Common name	IUPAC Name
HOCH <sub>2</sub> COOH	glycollic acid	hydroxyethanoic acid
CH <sub>3</sub> CHOHCOOH	lactic acid	2-hydroxypropanoic acid
HOOCCH <sub>2</sub> CHOHCOOH	malic acid	2-hydroxybutanedioic acid
HOOC(CHOH) <sub>2</sub> COOH	tartaric acid	2,3-dihydroxy butanedioic acid
HOC(COH)((CH <sub>2</sub> )COOH) <sub>2</sub>	citric acid	2-hydroxypropane-1,2,3 tri carboxylic acid

Table 6.4-If a carboxylic compound contains double bond (alkene), then replace the infix from “-an to -en” and the placement of the infix is determined by the *numbering*, 1, 2, 3, 4 etc. (Table-6.4).

Carboxylic acids	Common name	IUPAC name
	crotonic acid	<i>trans</i> -2-Butenoic acid



acrylic acid

propenoic acid

**IUPAC nomenclature of aromatic carboxylic acids:** Aromatic carboxylic acids are named by adding the suffix "*-carboxylic acid*" to the name of a parent hydride (Table-6.5).

**Table 6.5–Common names and IUPAC names of some aromatic carboxylic acids:**

Carboxylic acids	Common name	IUPAC name
	benzoic acid	benzene carboxylic acid
	salicylic acid	2-hydroxybenzene carboxylic acid

Table 6.6–If the two carboxylic acid groups are in the benzene ring it is named as "*di-carboxylic acid*".

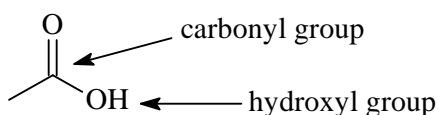
Carboxylic acids	Common name	IUPAC name
	phthalic acid	1,2-benzenedicarboxylic acid
	terephthalic acid	1,4-benzenedicarboxylic acid

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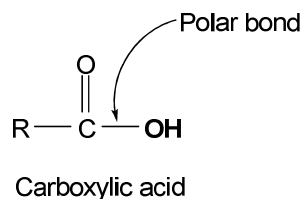
### 6.4 STRUCTURES AND BONDING

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The carboxylic group (-COOH) in a carboxylic acid is constituted by a carbonyl group (C=O) and a hydroxyl group (-OH). The carboxyl carbon atom is double bonded with one oxygen atom and single bonded with another oxygen atom in a carboxylic group as shown in figure:



The carboxylic acids can be represented by R-COOH or R-CO<sub>2</sub>H. The carboxylic carbon in a carboxylic acid is bonded with three functional groups, therefore the carboxylic carbon is sp<sup>2</sup> hybridized and hence the carboxylic group has a planar structure with bond angles of approximately 120°. In a carboxylic group, the C=O bond length is shorter than the bond length between C-O. One half filled un-hybridized *p*-orbital of the carbon and the un-hybridized *p*-orbital of the oxygen atom undergo sideways overlap. This results in the formation of the delocalized *p*-electron cloud. This is confirmed by the C-O single bond length in formic acid being shorter than the C-O bond length in ethanol. The oxygen is more electronegative than either carbon or hydrogen therefore the C-O and O-H bonds are polar.



The carboxyl group has the following resonating structures:



Carboxylic acids have higher boiling points than the organic compounds like, alcohols, ethers, aldehydes, or ketones of similar molecular weight. For example, acetic acid has higher boiling point (118°C) than the 1-propanol (97°C) although the two have similar molecular weights (60.1). Similarly, the butanoic acid and 1-pentanol have similar molecular weights (MW 88.1), but the boiling point of butanoic acid (163 °C) is more than that of 1-pentanol (137 °C). Because the two molecules of a carboxylic acid form two hydrogen bonds with each other while two alcohol molecules can only form one hydrogen bond. The boiling points of carboxylic acids increase with increase in molecular weight.

#### 4. Solubility

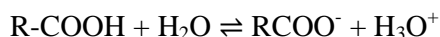
The C<sub>1</sub>-C<sub>4</sub> members are more soluble in water. This is due to the ability of the –COOH group to form hydrogen bonds with water molecules. Due to strong H..... bonding, carboxylic acids are more soluble in water than alcohols, ethers, aldehydes, or ketones of comparable molecular weight. The solubility of a carboxylic acid in water decreases as the molecular weight of carboxylic acids increases. This is due to, a carboxylic acid consists two different polarities: a polar hydrophilic carbonyl group and a non polar hydrophobic hydrocarbon chain. The hydrophilic carbonyl group increases water solubility whereas hydrophobic hydrocarbon chain decreases water solubility. Therefore, C<sub>5</sub> members are partly soluble and the higher carbon chain members are insoluble in water, but readily soluble in ethanol, ethers and benzene.

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### ***6.6 ACIDITY OF CARBOXYLIC ACIDS AND EFFECT OF SUBSTITUENTS ON ACID STRENGTH***

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A carboxylic acid can ionize in water into carboxylate ion and hydronium ion as:



The equilibrium constant K for given equation can be expressed as:

$$K = \frac{[\text{RCOO}^-][\text{H}_3\text{O}^+]}{[\text{RCOOH}][\text{H}_2\text{O}]}$$



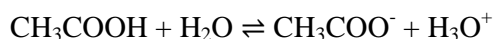
Since water is in excess therefore,  $K_a = \frac{[\text{RCOO}^-][\text{H}_3\text{O}^+]}{[\text{RCOOH}]}$ , hence the above equation can be written as:

$$K_a = \frac{[\text{RCOO}^-][\text{H}_3\text{O}^+]}{[\text{RCOOH}]}$$

$K_a$  is known as acid dissociation constant which is a measure of acid strength of an acid. The  $pK_a$  of an acid is the negative logarithm of  $K_a$ , and commonly used parameter to measure the acid strength of an acid. The low value of  $pK_a$  corresponds to more acidity and high value relates to less acidity of acids.

$$pK_a = -\log K_a$$

For example, the acetic acid is dissociated as:



The acid dissociation constant  $K_a$  for given equation can be expressed as:

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} = 1.74 \times 10^{-5}$$

$$pK_a = 4.76$$

The value of  $pK_a$  for aliphatic carboxylic acids are in the range of 4.0 -5.0. Therefore carboxylic acids are weak acids and their acidic strength decreases with increase in molecular weight.

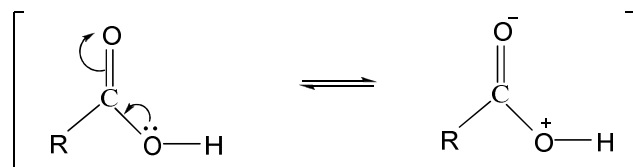
*Table 6.7 – Values of  $pK_a$  for some simple carboxylic acids:*

Compound	IUPAC name	$pK_a$
HCOOH	methanoic acid	3.75
CH <sub>3</sub> COOH	ethanoic acid	4.74
CH <sub>3</sub> CH <sub>2</sub> COOH	propanoic acid	4.87
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> COOH	butanoic acid	4.82
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> COOH	pentanoic acid	4.81

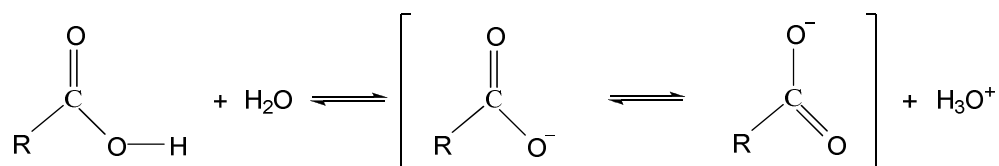
$\text{CH}_3(\text{CH}_2)_4\text{COOH}$	hexanoic acid	4.88
$\text{CH}_3(\text{CH}_2)_6\text{COOH}$	octanoic acid	4.89
$\text{CH}_3(\text{CH}_2)_8\text{COOH}$	decanoic acid	4.84
$\text{C}_6\text{H}_5\text{COOH}$	benzoic acid	4.19
$p\text{-CH}_3\text{C}_6\text{H}_4\text{COOH}$	<i>p</i> -toluic acid	4.36
$p\text{-ClC}_6\text{H}_4\text{COOH}$	<i>p</i> -chlorobenzoic acid	3.98
$p\text{-NO}_2\text{C}_6\text{H}_4\text{COOH}$	<i>p</i> -nitrobenzoic acid	3.41
$\text{FCH}_2\text{COOH}$	fluoroethanoic acid	2.59
$\text{ClCH}_2\text{COOH}$	chloroethanoic acid	2.86
$\text{BrCH}_2\text{COOH}$	bromoacetic acid	2.90
$\text{ICH}_2\text{COOH}$	iodoethanoic acid	3.18
$\text{Cl}_2\text{CHCOOH}$	di-chloroethanoic acid	1.26
$\text{Cl}_3\text{CCOOH}$	tri-chloroethanoic acid	0.64

There are two reasons of acidic nature of carboxyl compounds:

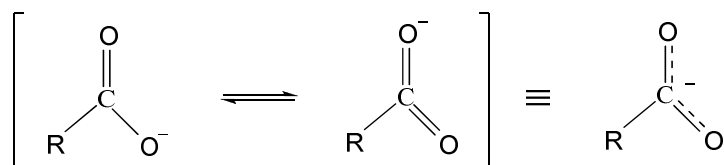
1. Resonance effect:-



Carboxyl group shows resonance structures in which the oxygen atom of  $-\text{OH}$  group contain a positive charge which is not a stable hence can lose bonded hydrogen atom in the form of proton and convert in carboxylate ion. That is the reason the equilibrium between carboxyl group and carboxylate ion lies towards right side.



The carboxylate anion is also stabilized by resonance like carboxylic acid. The stabilization of the anion is much greater than that of the neutral carboxyl group. In the carboxylate anion the C-O bonds are of equal length and the two contributing structures have equal weight in the hybrid.

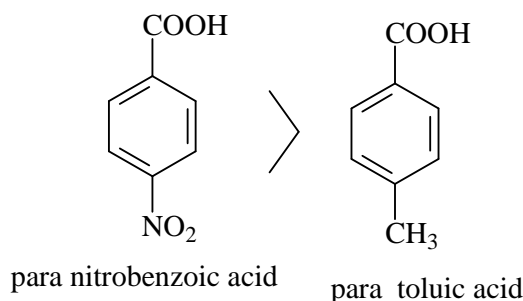


### 2. Effect of substituent's on acidity of carboxylic acids:-

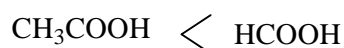
Substituent affects on the acidity of carboxylic acids by affecting the stability of carboxylate anion. A substituent that stabilizes the carboxylate anion promoted the dissociation and results in a stronger acid. Substituents on the  $\alpha$ -carbon atom are most effective in order to increase in acid strength.

*Electron withdrawing groups such as  $-\text{NO}_2$ ,  $-\text{CN}$  etc. enhance the acid strength of a carboxylic acid due to increase the stability of carboxylate anions through the delocalization of negative charge by inductive or resonance effects. However the electron releasing groups such as alkyl groups reduce the acidic strength of carboxylic acids.*

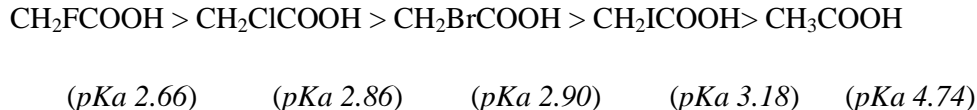
For example, *p*-nitrobenzoic acid ( $pK_a$  3.41) is stronger acid than *p*-toluic acid ( $pK_a$  4.36) because the *p*-nitrobenzoic acid has an electron withdrawing  $-\text{NO}_2$  substituent while the *p*-toluic acid has an electron releasing  $-\text{CH}_3$  substituent. The  $-\text{NO}_2$  group has a larger effect in *ortho* and *para* positions than in *meta* position.



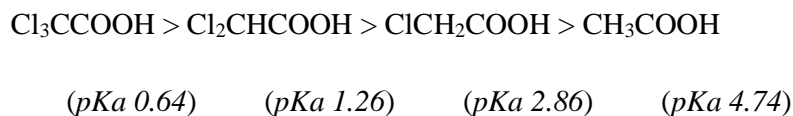
Similarly, ethanoic acid ( $pK_a$  4.74) is weaker than the methanoic acid ( $pK_a$  3.75) because it has an electron releasing  $-CH_3$  substituent.



The presence of an electron withdrawing group near the carbonyl group decreases its  $pK_a$  value. Means the magnitude of a substituent depends on its distance from the carbonyl group of a carboxylic acid. The higher electronegative substituent on the  $\alpha$ -carbon atom further increases the acidity of carboxylic acids by the inductive effect. For example, the acidity of acetic acid and their halogen derivatives.



To study the effect of multiple halogen substitution, compare the value of  $pK_a$  for acetic acid with its chloro-, dichloro-, and trichloro derivatives. The chloro, dichloro, and trichloro derivatives are successively stronger because they have more electron withdrawing chlorine. You see that a single chlorine substituent increases acid strength by nearly 100.



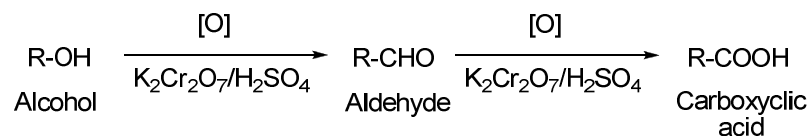
Carboxylic acids ( $pK_a$  4-5) are stronger acids than alcohols ( $pK_a$  16-18) because of delocalization of the negative charge of the carboxylate anion through resonance and the electron withdrawing inductive effect of the carbonyl group.

## 6.7 PREPARATION OF CARBOXYLIC ACIDS

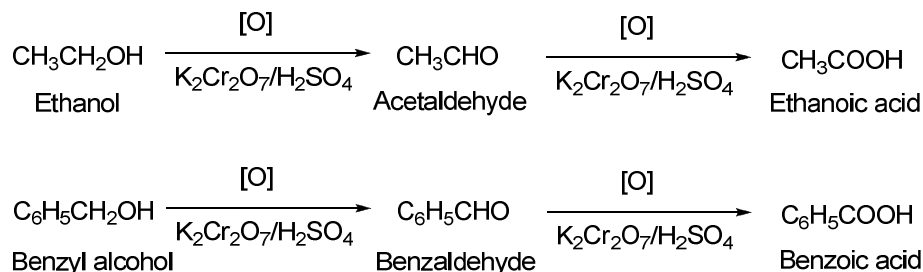
The carboxylic acids can be synthesized by various methods as follow:-

### 1. By the oxidation of primary alcohols and aldehydes

Carboxylic acids can be prepared by the oxidation of primary alcohols and aldehydes with acidic  $\text{KMnO}_4$ , or acidic  $\text{K}_2\text{Cr}_2\text{O}_7$ .

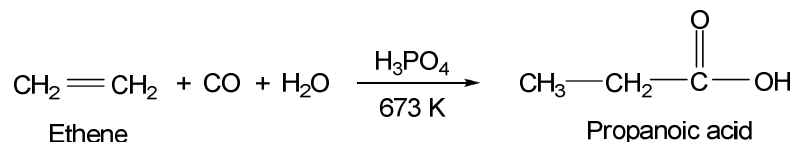


For example:



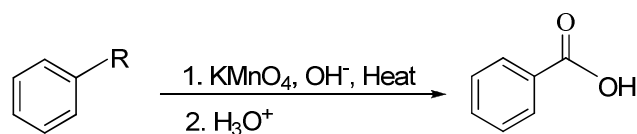
### 2. From Koch reaction

Koch reaction is an organic reaction used to convert olefins into tertiary carboxylic acids. In this reaction alkenes are treated with carbon monoxide and hydrogen in presence of strong mineral acids like phosphoric acid or hydrogen fluoride to form the tertiary carboxylic acids.

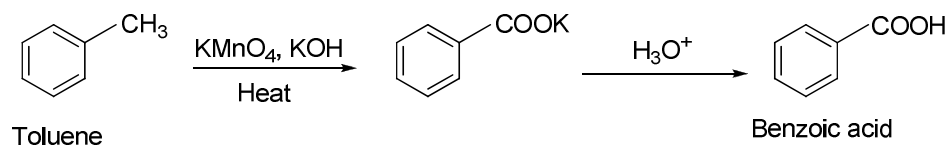


### 3. By the oxidation of alkyl benzenes

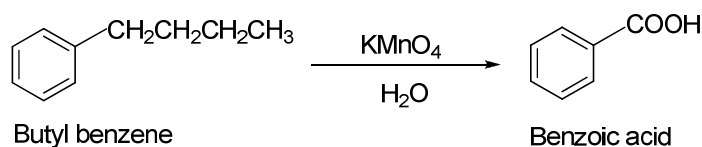
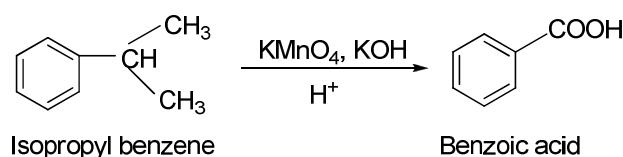
Aromatic carboxylic acids may be formed by the oxidation of alkyl benzene with  $\text{K}_2\text{Cr}_2\text{O}_7$ , or acidic or alkaline  $\text{KMnO}_4$ .



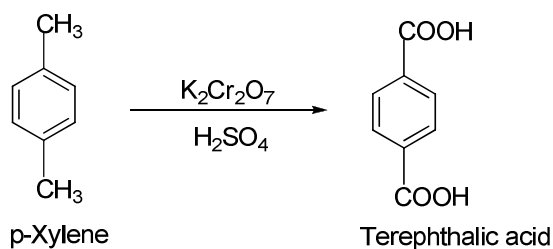
When toluene is heated with KMnO<sub>4</sub>, it is oxidized to benzoic acid.



Similarly, the isopropyl benzene is oxidized into benzoic acid with alkaline KMnO<sub>4</sub>.

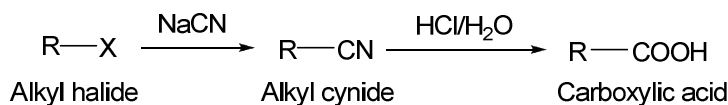


Terephthalic acid can be obtained by the oxidation of *p*-xylene with acidic K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>.

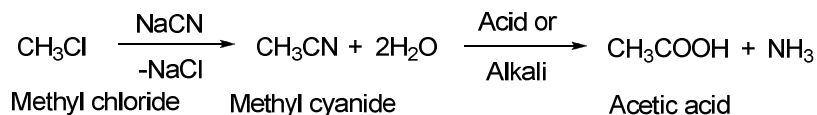


#### 4. By the hydrolysis of cyanides or nitriles

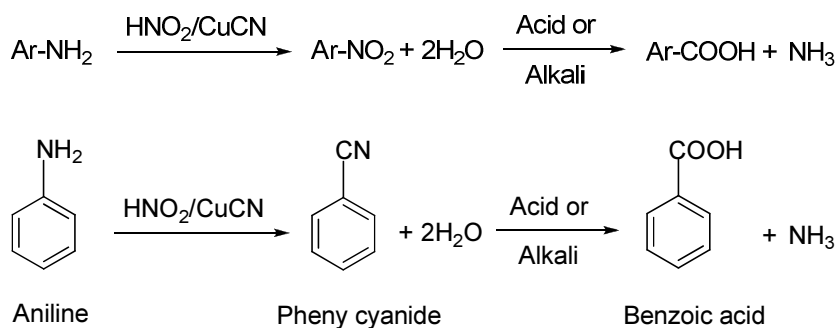
Alkyl halides react with sodium cyanide in S<sub>N</sub>2 displacement to form a nitrile which on hydrolysis converted into carboxylic acid. The cyano group contains a hydrogen bond which under acid hydrolysis converted into carboxylic group.



(Where, R is an alkyl group and X is a halide)



Aromatic amine with nitrous acid produces aromatic nitrile which on acidic hydrolysis produces aromatic carboxylic acid.



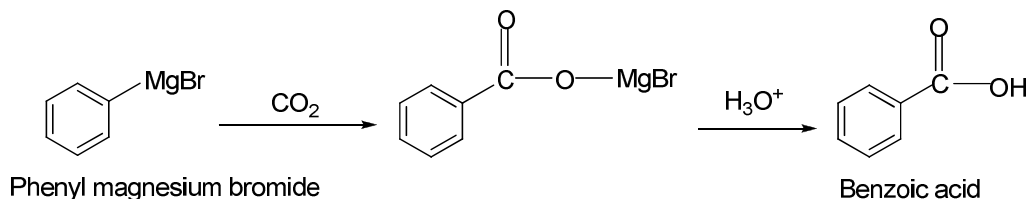
### 5. By Grignard's reagents

Grignard's reagents react with carbon dioxide to form salts of carboxylic acids which give carboxylic acids on reaction with mineral acids.



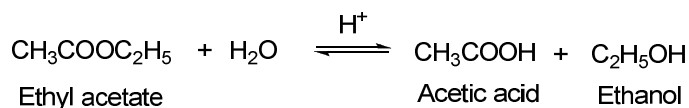
(Where, R is an alkyl or aryl group)

Benzoic acid is prepared by the action of carbon dioxide on phenyl magnesium bromide (Grignard's reagent).



### 6. By the hydrolysis of esters

Carboxylic acids can be prepared by the hydrolysis of esters either in acidic or alkaline medium. For example, the acetic acid is formed by the hydrolysis of ethyl acetate in acidic conditions.

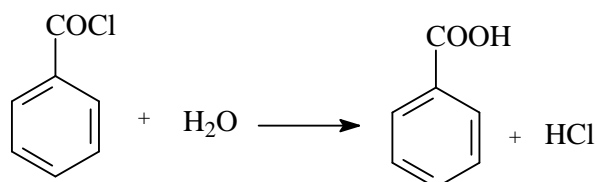
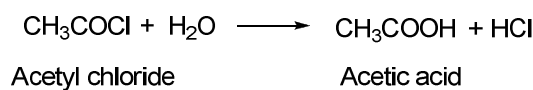
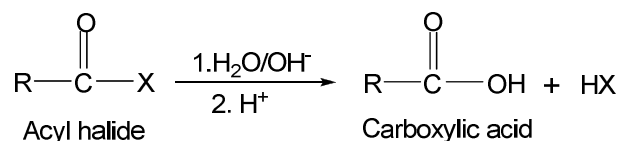


**7. By the hydrolysis of acid derivatives viz. acyl chloride, acid anhydride, esters and amides**

The acid derivatives on hydrolysis with acid or alkali form corresponding carboxylic acids.

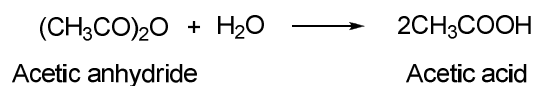
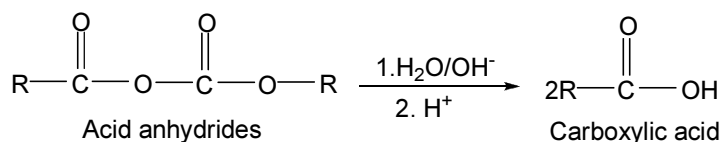
**(i) By the hydrolysis of acyl halides**

Acid chlorides are hydrolyzed with water to parent carboxylic acids.



**(ii) By the hydrolysis of acid anhydride**

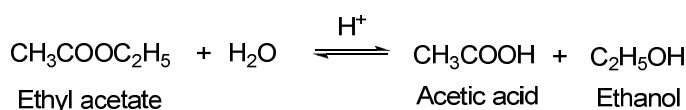
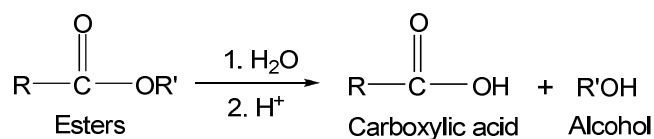
Acid anhydrides are hydrolyzed with water to acids.



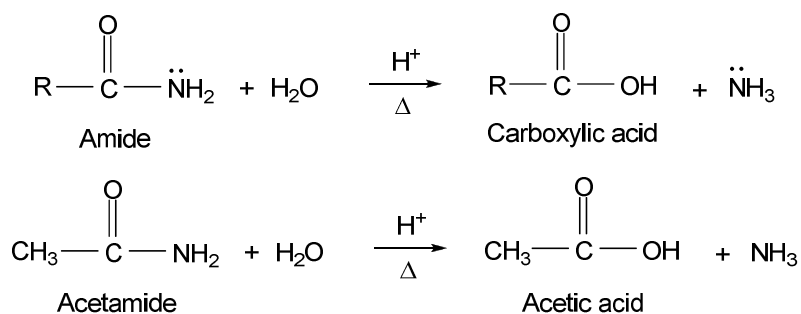


**(iii) By the hydrolysis of esters**

Esters are hydrolyzed to carboxylic acids in presence of an acid.

**(iv) By the hydrolysis of amide**

Acid amides are not easily hydrolyzed with water, but hydrolyzed easily on heating with dilute acids or alkalis.



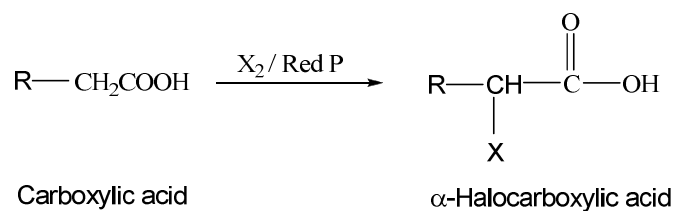

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## 6.8 REACTIONS OF CARBOXYLIC ACIDS

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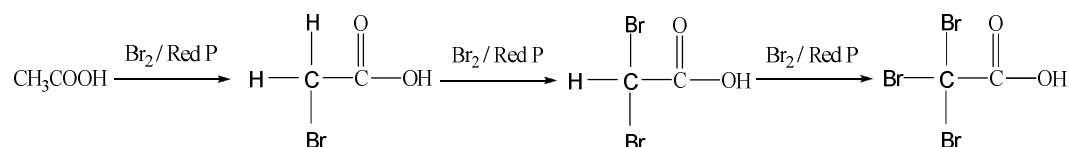
The carboxylic acids are reactive organic compounds because of –OH and –CO group and undergo many reactions some of them are as follow.

**(1) α-Halogenation of aliphatic acids:** Carboxylic acids undergo halogenation with chlorine or bromine in the presence of small amount of red phosphorus form α-halo or β-haloacids. The reaction is known as *Hell Volhard Zelinsky reaction*. In this reaction a carboxylic acids containing an α-hydrogen atom is replaced by a chlorine or bromine atom to form an α-halo carboxylic acid. The general reaction is as:



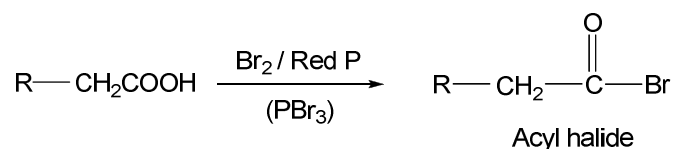
(Where, X= Cl, Br)

Bromination of acetic acid is a good example of this reaction.

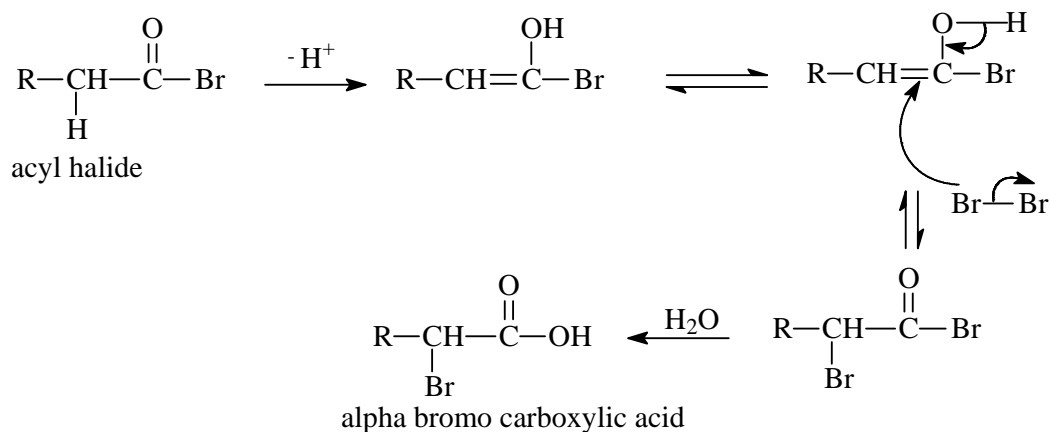


**Mechanism:** The stepwise mechanism is as follow of HVZ reaction

**Step 1:** Phosphorus reacts with bromine to form phosphorus tribromide, and in the first step this converts the carboxylic acid into an acyl bromide.



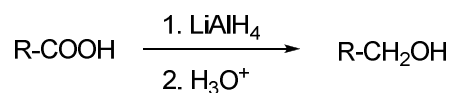
**Step 2:** The acyl bromide then tautomerizes to the enol form which subsequently attacks the halogen molecule to form a  $\alpha$ -halo acyl halide. Water hydrolysis yields the final  $\alpha$ -halo carboxylic acid product.



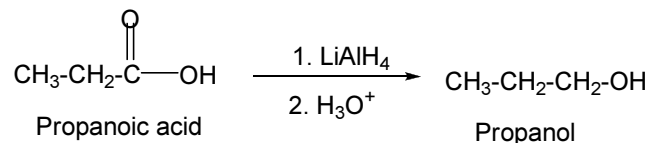
Although the  $\alpha$ -bromination of some carbonyl compounds, such as aldehydes and ketones, can be accomplished with  $\text{Br}_2$  under acidic conditions, this reaction will generally not occur with acids, esters, and amides because only aldehydes and ketones enolize to a sufficient extent to allow the reaction to occur.

## (2) Reactions of -COOH group

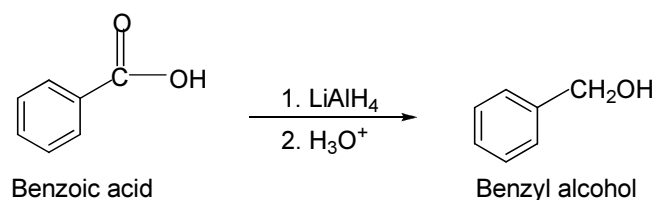
(i) a. **Reduction of carboxylic acid to alcohols by  $\text{LiAlH}_4$ :** The carboxylic acids are reduced to primary alcohols with a strong reducing agent like lithium aluminium hydride ( $\text{LiAlH}_4$ ). In this reaction the carbonyl group of a carboxyl group is reduced to - $\text{CH}_2$  group.



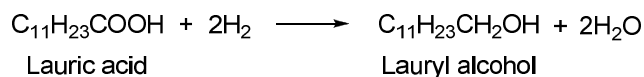
Propanoic acid is reduced to propanol in presence of lithium aluminium hydride ( $\text{LiAlH}_4$ ).



Similarly, benzoic acid is reduced to benzyl alcohol in presence of lithium aluminium hydride ( $\text{LiAlH}_4$ ).



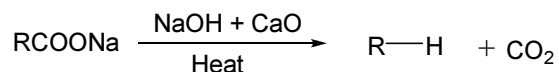
Higher carboxylic acids are also reduced to alcohols by hydrogen in presence of copper chromium oxide. This reaction is used to prepare detergents such as sodium lauryl sulphate from lauryl alcohol.



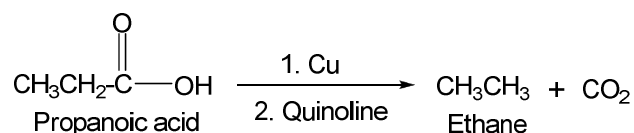
Carboxylic acids cannot be reduced by  $\text{H}_2/\text{Ni}$ , or  $\text{Na}/\text{C}_2\text{H}_5\text{OH}$ , or  $\text{NaBH}_4$ , or catalytic hydrogenation.

**b. Reduction by HI:** Carboxylic acids can be reduced to either primary alcohols or alkanes depend upon the reducing agent involve in reaction

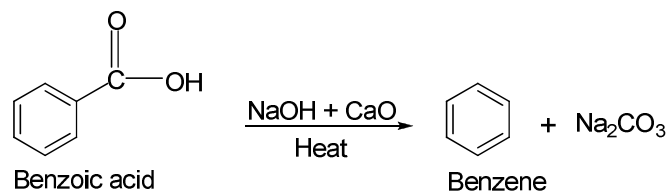
**(ii) Decarboxylation reaction:** When an anhydrous sodium salt of a fatty acid is heated with sodalime ( $\text{NaOH} + \text{CaO}$ ) or  $\text{Cu}/\text{quinoline}$ , it loses carbon dioxide to form an alkane. This reaction is known as decarboxylation reaction. The general reaction is as:



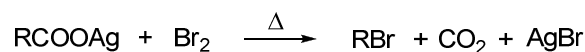
Simple copper salts such as copper chromate, copper hydroxide or copper carbonate can also be used in decarboxylation of aliphatic and aromatic acids.



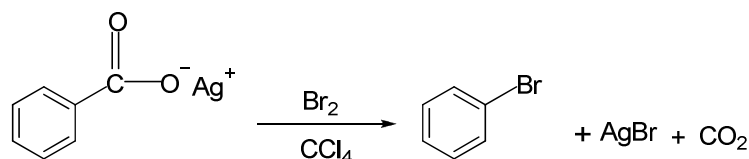
Aromatic carboxylic acids also react with sodalime to give benzene.



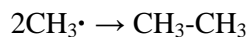
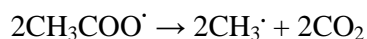
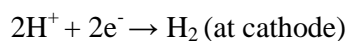
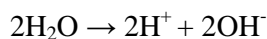
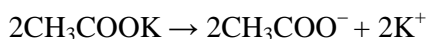
**(iii) Hunsdiecker reaction:** Silver salt of fatty acids on heating with a halogen (Cl or Br) undergo decarboxylate halogenations give alkyl or aryl halides. The general reaction is as:



For example,

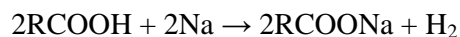


**(iv) Kolbe electrolysis:** The electrochemical oxidation of sodium or potassium salts of fatty acids give alkanes having twice the number of carbon atoms present in the alkyl group of the acid. This process is known as *Kolbe's electrolysis*. For example; the electrolysis of potassium ethanoate forms ethane with carbon dioxide gas and hydrogen gas as side products.

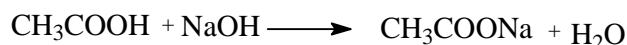
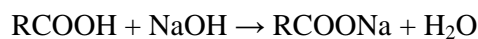


**(3) Reactions with metals and alkalis:** Some reactions which show the acidic character of carboxylic compounds are as follow:

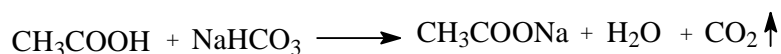
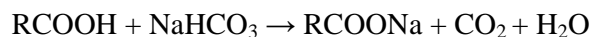
**(i) Reaction with metal:** Carboxylic acids react with active metals like K, Ca, Mg to form salts by releasing hydrogen gas.



**(ii) Reaction with alkalis:** Carboxylic acids react with alkalis like sodium hydroxide to form salts and water.



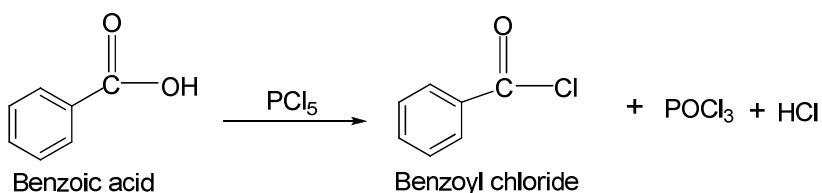
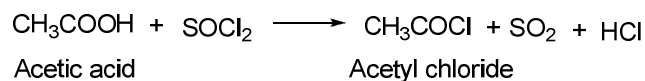
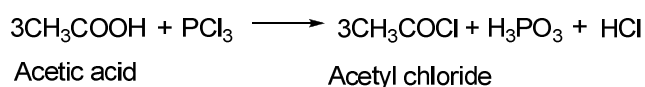
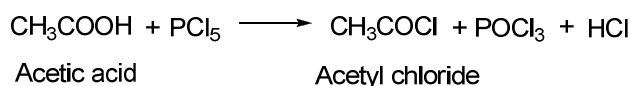
**(iii) Reaction with sodium bicarbonate:** Carboxylic acids are weaker than mineral acids like sulphuric acid or nitric acid and able to react with weaker bases like carbonates and bicarbonates to evolve carbon dioxide with water.

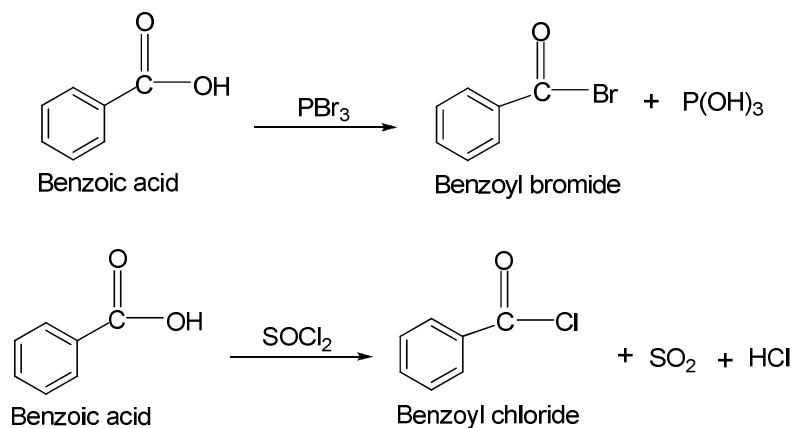


The reaction with sodium bicarbonate is also used as functional group determination of carboxylic acid

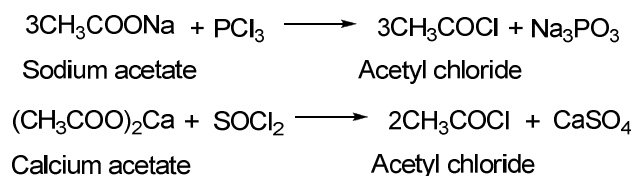
**(4) Formation of acid derivatives:** The carboxylic acid derivatives *viz.*, acyl halides(RCOCl), acid anhydrides(RCOOCOR), esters(RCOOR) and acid amides(RCONH<sub>2</sub>) can be derived from carboxylic acids(RCOOH) by the replacement of -OH part of a -COOH group by some other groups like -Cl, -OR, -NH<sub>2</sub>.

**(i) Formation of acid halides:** Carboxylic acids react with halide derivatives like phosphorous trichloride (PCl<sub>3</sub>), phosphorous tribromide (PBr<sub>3</sub>), phosphorous pentachloride (PCl<sub>5</sub>), and thionyl chloride (SOCl<sub>2</sub>) to form acyl halides. Acyl halides are formed by the replacement of -OH part of -COOH group by a -Cl or -Br group.

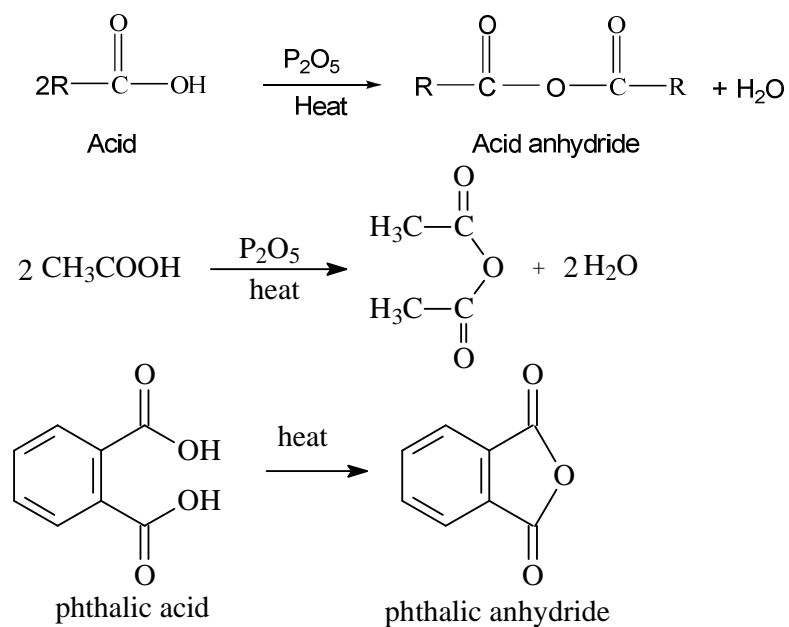




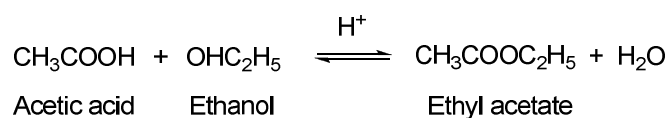
Acyl halides like acyl chlorides are also prepared by the reaction of sodium salts of carboxylic acids with phosphorous trichloride ( $\text{PCl}_3$ ) or thionyl chloride ( $\text{SOCl}_2$ ).



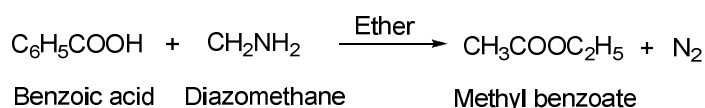
**(ii) Formation of acid anhydride:** The acid anhydrides can be obtained by the dehydration of carboxylic group in the presence of strong dehydrating agents like  $\text{P}_2\text{O}_5$  or concentrated  $\text{H}_2\text{SO}_4$ .



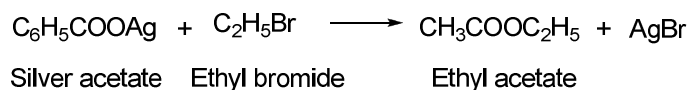
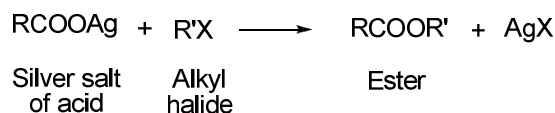
(iii) **Formation of esters:** Carboxylic acids react with alcohols to form esters in presence of concentrated  $\text{H}_2\text{SO}_4$ . This reaction involves the replacement of  $-\text{OH}$  group by  $-\text{OR}$  group of alcohol or phenol and also known as Fischer-speier esterification. For example, ethanoic acid reacts with ethanol to form ethylethanoate.



Esters can also be prepared by the action of the ethereal solution of diazomethane on carboxylic acid.

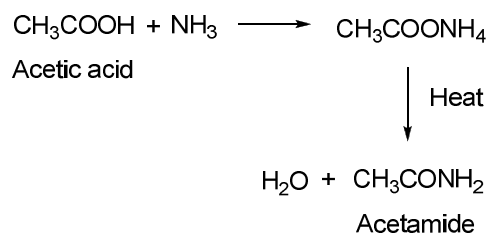


Esters can also be prepared by the reaction of silver salt of acids on alkyl halides.



#### (iv) Formation of amides

Carboxylic acids react with ammonia to form ammonium salts which on heating lose water molecule to form amides.



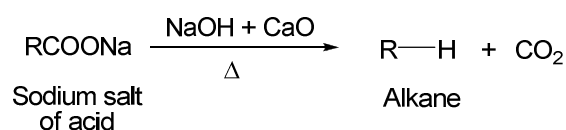


### 6.9 MECHANISM OF DECARBOXYLATION

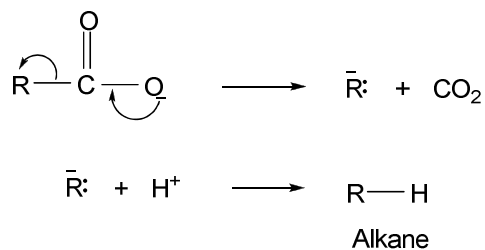
When anhydrous sodium salt of a fatty acid is heated with sodalime (NaOH + CaO) or Cu/quinine, it loses carbon dioxide to form an alkane. This reaction is known as decarboxylation reaction.

Decarboxylation is of two types:

#### 1. Simple carboxylic acids

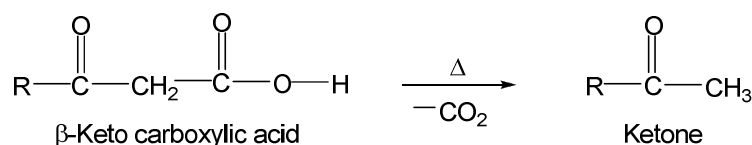


*Mechanism*



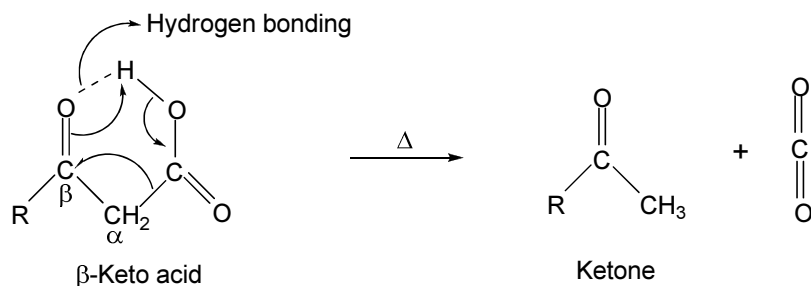
#### 2. $\beta$ -carbonyl carboxylic acids

The  $\beta$ -keto carboxylic acids lose  $\text{CO}_2$  readily on heating at about  $100^\circ\text{C}$ .

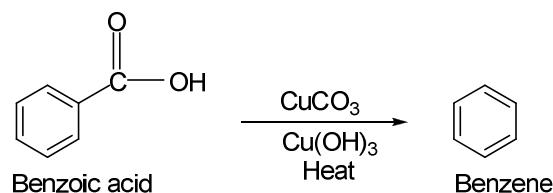


*Mechanism*

Decarboxylation of  $\beta$ -keto acid takes place via a six membered cyclic transition state.



Note: Simple copper salts such as copper hydroxide and copper carbonate can also be used in decarboxylation of aliphatic and aromatic acids. For example:




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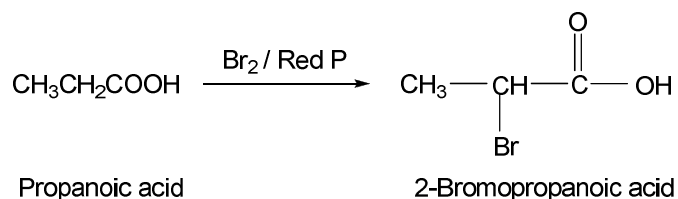
## 6.10 METHODS OF FORMATION AND CHEMICAL REACTIONS OF HALO ACIDS

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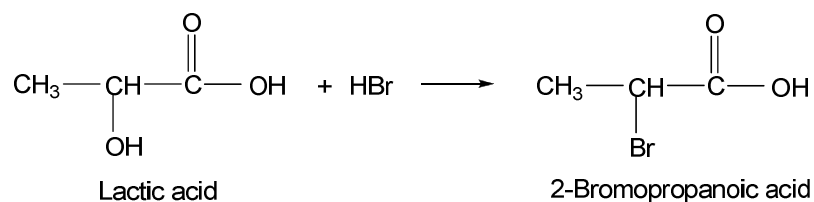
Hydroxy acids, halo acids, amino acids and nitro acids are the derivatives of monocarboxylic acids and known as substituted carboxylic acids.

### 6.10.1 PREPARATION OF HALO ACIDS:

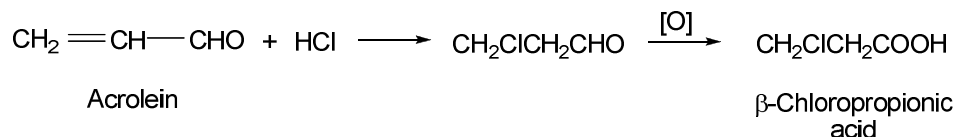
**1. Hell Volhard Zelinski reaction:** Aliphatic carboxylic acids on reaction with bromine in the presence of phosphorous produce  $\alpha$ -halo acids. This reaction is known as Hell Volhard Zelinski reaction.



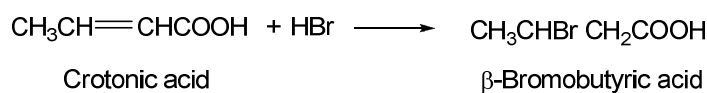
**2. By hydroxy acids:**  $\alpha$ -halo acids can be obtained by the treatment of  $\alpha$ -hydroxy acids with HCl or HBr.



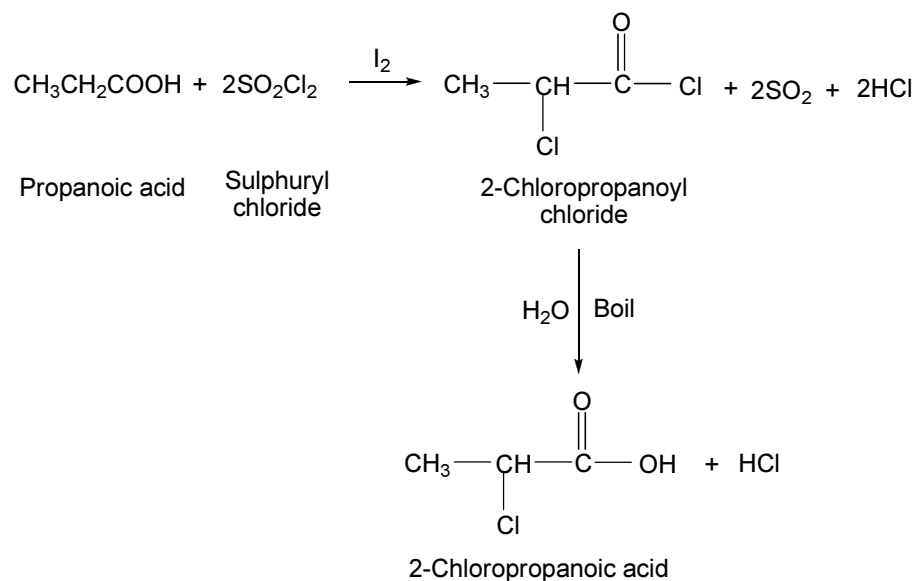
3. By  $\alpha$ ,  $\beta$ -unsaturated aldehydes:  $\alpha$ ,  $\beta$ -unsaturated aldehydes on reaction with halogen acids followed by oxidation produce  $\beta$ -halo acids.



4. By  $\alpha$ ,  $\beta$ -unsaturated carboxylic acids:  $\alpha$ ,  $\beta$ -unsaturated carboxylic acids on reaction with halogen acids produce halo acids.



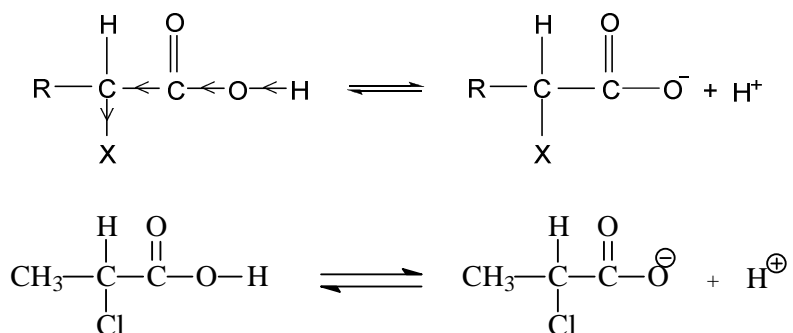
5. By the reaction of sulphuryl chloride on carboxylic acids: Reaction with  $\text{SO}_2\text{Cl}_2$  in presence of iodine carboxylic acid gives halo acid.



## 6.10.2 CHEMICAL REACTIONS OF HALO ACIDS:

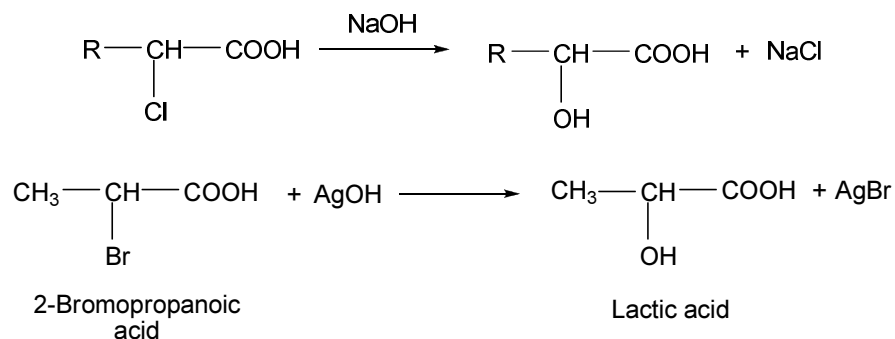
Halo acids show the similar properties as carboxylic acids. Halo acids are also gives the reactions of halogen group. The main reactions of halo acids are as follows:

**1. Acidic strength:** The halo acids are more acidic than carboxylic acids because halogens are more electronegative than other atoms therefore a halogen atom withdraws the electron pairs towards it and help to release the proton; since the halo acids are more acidic than the normal acids.

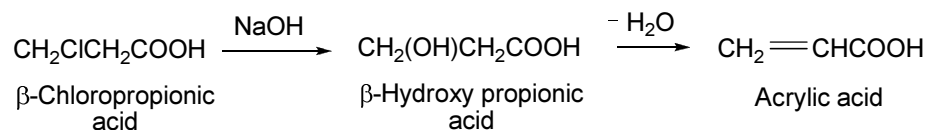


## 2. Reaction due to halogen atom

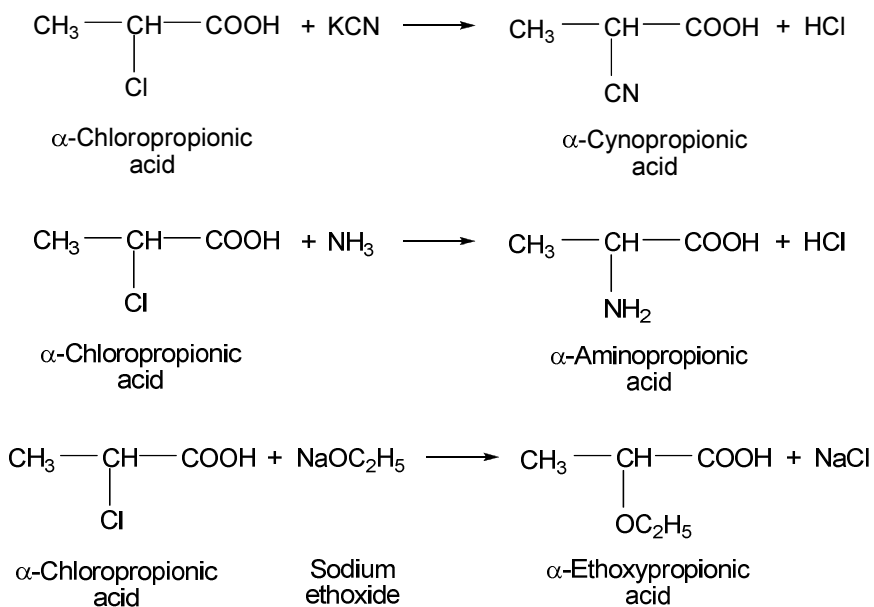
(i) **Reaction with alkali;**  $\alpha$ -halo acids undergo alkaline hydrolysis form the  $\alpha$ -hydroxy acids.



While,  $\beta$ -halo acids on reaction with alkali form  $\beta$ -hydroxy acid and  $\alpha, \beta$ -unsaturated acid.

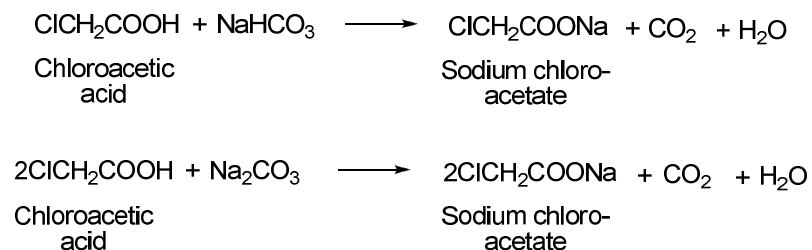


(ii) **Nucleophilic substitution reactions:** The halogen group present in a halo acid can be replaced by nucleophiles such as  $-\text{CN}$ ,  $\text{NH}_3$ , or  $-\text{OC}_2\text{H}_5$ .

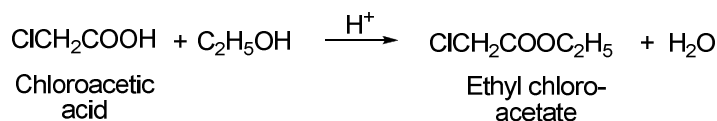


### 3. Reaction due to $-\text{COOH}$ group

(i) **Action with  $\text{NaHCO}_3$  or  $\text{Na}_2\text{CO}_3$ :** On reaction with  $\text{NaHCO}_3$  or  $\text{Na}_2\text{CO}_3$  halo acids decompose to release carbon dioxide.



(ii) **Reaction with alcohols:** Halo acids react with alcohols to form the esters.



(iii) **Reaction with  $\text{PCl}_5$ :** They also react with  $\text{PCl}_5$  to form the acid chlorides.




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### 6.11 HYDROXY ACIDS: MALIC, TARTARIC AND CITRIC ACIDS

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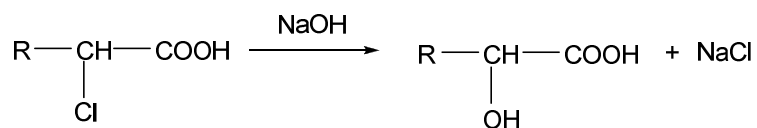
Hydroxy acids contain a -OH group and a -COOH group. They may be mono or polybasic. The monocarboxylic acids are classified as  $\alpha$ -hydroxy acids,  $\beta$ -hydroxy acids,  $\gamma$ -hydroxy acids and  $\delta$ -hydroxy acids depending on whether the -OH group is bounded to the  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$  carbon atom of the hydrocarbon chain with respect to -COOH group (Table-6.8). Glycolic acid, lactic acid, tartaric acid, malic acid, citric acid, mandelic acid etc. are  $\alpha$ -hydroxy acids while salicylic acid,  $\beta$ -hydroxybutanoic acid etc. are  $\beta$ -hydroxy acids.  $\alpha$ -Hydroxy acids are naturally occurring carboxylic acids found in many foods including glycolic acid (sugar cane), lactic acid (milk), citric acid (citrus fruits), and malic acid (apples) among others. The most commonly used  $\alpha$ -hydroxy acids are glycolic and lactic acids.

*Table 6.8 – Common name of some hydroxyl acids*

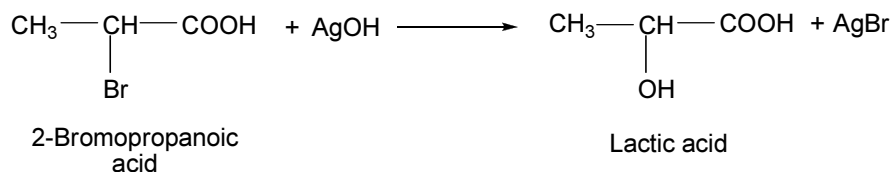
Chemical formula	name
CH <sub>2</sub> (OH).COOH	hydroxyl acetic acid
CH <sub>3</sub> CH(OH).COOH	$\alpha$ -hydroxy propionic acid
CH <sub>2</sub> (OH)CH <sub>2</sub> .COOH	$\beta$ -hydroxy propionic acid
CH <sub>2</sub> (OH).CH <sub>2</sub> CH <sub>2</sub> COOH	$\gamma$ -hydroxy butric acid

**A. Preparation of  $\alpha$ -hydroxy acids:** The hydroxyl carboxylic acids are synthesized by using different methods as:

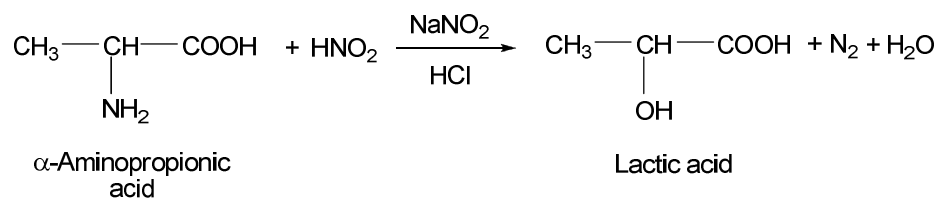
**1. By the hydrolysis of  $\alpha$ -halo acids:**  $\alpha$ -hydroxy acids can be prepared by the alkaline hydrolysis of  $\alpha$ -halo acids.



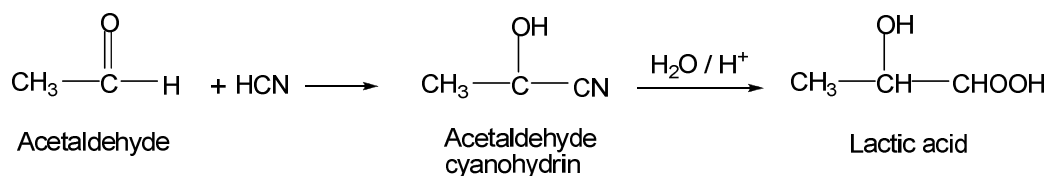
Lactic acid is obtained by the alkaline hydrolysis of  $\alpha$ -bromopropionic acid.



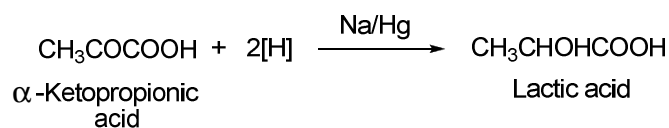
**2. By the action of nitrous acid:**  $\alpha$ -aminopropionic acid on treatment with nitrous acid in presence of sodium nitrite and hydrochloric acid.



**3. By the hydrolysis of cyanohydrins:**  $\alpha$ -hydroxy acids can be obtained by the reaction of aldehydes with cyanohydrins followed by acid hydrolysis.

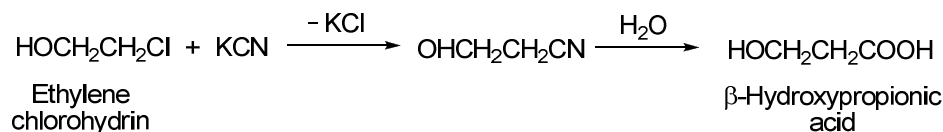


**4. By the reduction of keto acids:**  $\alpha$ -hydroxy acids can be obtained by the reduction of ketonic acids in presence of Na/Hg.

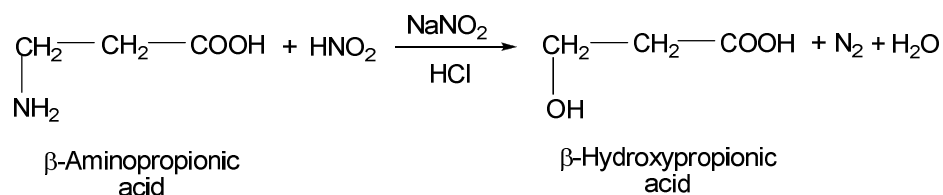


**B. Preparation of  $\beta$ -hydroxy acids:** like  $\alpha$ -hydroxy acids,  $\beta$ -hydroxy acid can be synthesized using following methods:-

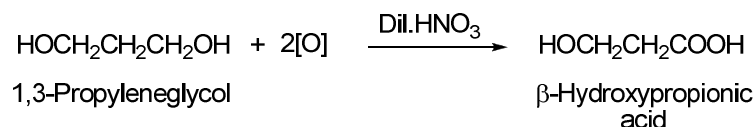
1. **From chlorohydrins:**  $\beta$ -hydroxypropionic acid can be produced by the reaction of ethylene chlorohydrins with potassium cyanide followed by hydrolysis.



2. **By the action of nitrous acid:**  $\beta$ -hydroxypropionic acid is prepared by the action of nitrous acid on  $\beta$ -aminopropionic acid in presence of sodium nitrite and hydrochloric acid form lactic acid.



3. **By the oxidation of 1,3-dihydroxy compounds:**  $\beta$ -Hydroxypropionic acid is obtained by the reaction of 1,3-propyleneglycol with oxygen in presence of dilute nitric acid.



### 6.11.1 PHYSICAL PROPERTIES OF HYDROXY ACIDS:

1. **Physical state:** Most of the hydroxy acids occur naturally and have several important biological properties. They are colorless, crystalline solids or syrupy liquids. Hydroxy acids are more acidic than normal carboxylic acids.

2. **Solubility:** The hydroxyl derivatives are containing  $-\text{OH}$  and  $-\text{COOH}$  groups which form hydrogen bond with water, therefore they are more soluble in water than the corresponding carboxylic acids.

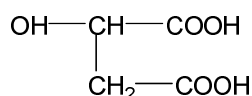
3. **Boiling points:** The boiling or melting points of hydroxyl acids are also higher than the corresponding carboxylic acids.



### 6.11.2 PREPARATION AND CHEMICAL PROPERTIES OF HYDROXY ACIDS:

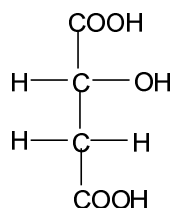
The method of preparation, physical and chemical properties of some of the individual hydroxyl acids alongwith their uses are being described as follow.

#### A. MALIC ACID

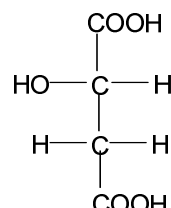


Malic acid

Malic acid is an organic compound with the molecular formula  $\text{C}_4\text{H}_6\text{O}_5$ . It is also known as hydroxyl butanedioic acid. It is a dicarboxylic acid that is made by all living organisms, contributes to the pleasantly sour taste of fruits, and is used as a food additive. Malic acid is a colorless crystalline solid, soluble in water and alcohol but sparingly soluble in ether, it melts at  $130^\circ\text{C}$ . Malic acid contains one asymmetric carbon, hence it exists in two optically active (two stereoisomeric forms: L- and D-enantiomers) and one inactive form, though only the L-isomer exists naturally.



D-malic acid

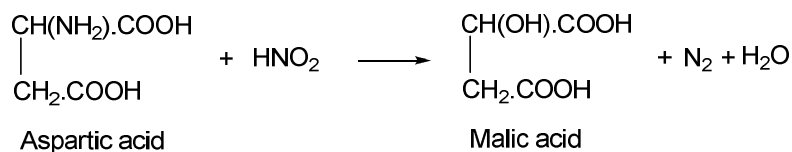


L-malic acid

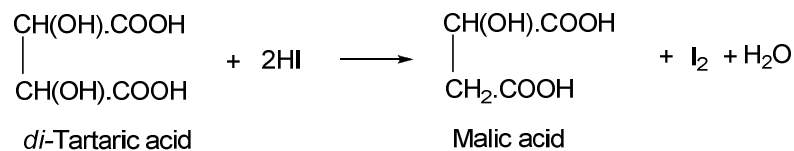
**Preparation of malic acid:** Malic acid can be prepared by the following methods:

#### 1. By the action of nitrous acid on $\alpha$ -amino succinic acid (aspartic acid).

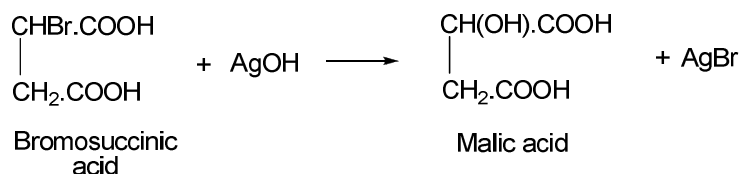
Malic acid can be obtained by the reaction of nitrous acid on Aspartic acid.



**2. By the partial reduction of tartaric acid:** Malic acid can be prepared by the reduction of tartaric acid with HI.

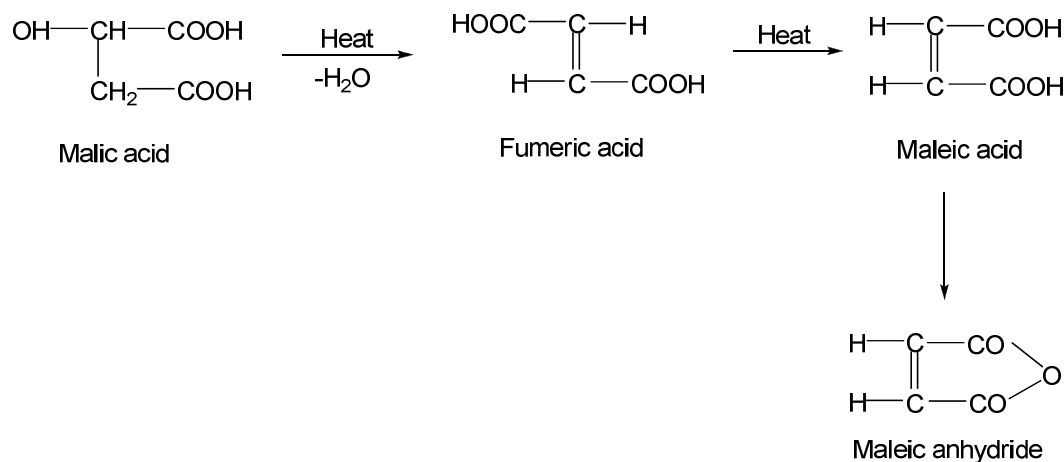


**3. From bromosuccinic acid:** When bromosuccinic acid is treated with moist silver oxide, malic acid is obtained.

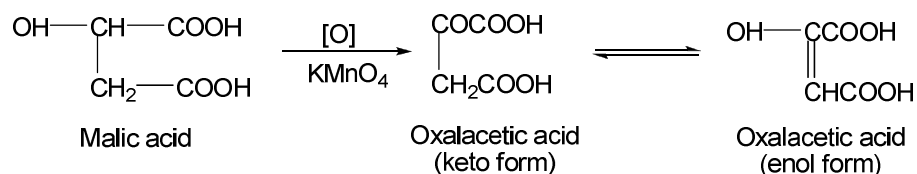


**Chemical properties of malic acid:** Malic acid possesses following chemical properties.

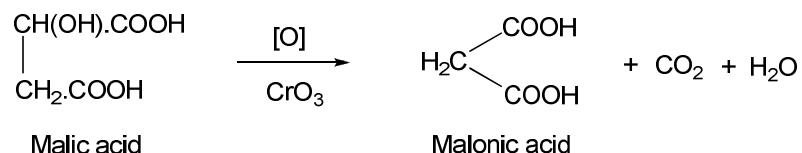
**1. Action of heat:** Malic acid undergoes dehydration on heating to form maleic anhydride.



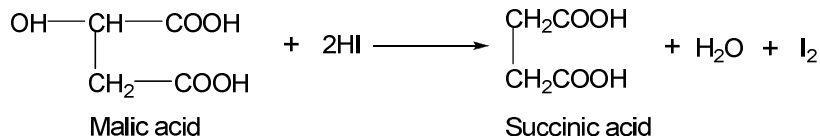
**2. Oxidation with KMnO<sub>4</sub>:** On oxidation with KMnO<sub>4</sub> malic acid forms oxalacetic acid, which exists in keto-enol tautomerism.



**3. Oxidation with H<sub>2</sub>CrO<sub>4</sub>:** On oxidation with chromic acid, malic acid converts into malonic acid.



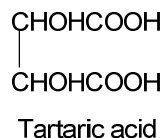
**4. Reduction:** Malic acid reduces with HI to form succinic acid.



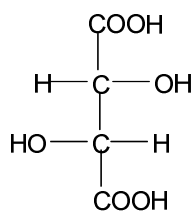
**Uses:** Malic acid is used:

1. In the preparation of several esters and salts.
2. As a substitute of citric acid in drinks.
3. In the preparation of medicine of sore throat.

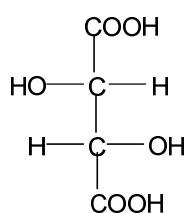
## B. TARTARIC ACID



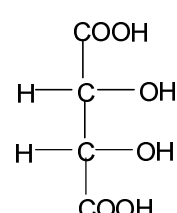
Tartaric acid, HOOC(CHOH)<sub>2</sub>COOH, is a dicarboxylic acid, found in many plants particularly tamarinds and grapes. Tartaric acid is also known as α,α'-dihydroxy succinic acid (IUPAC name : 2,3-dihydroxybutanedioic acid). It is a colorless crystalline solid, soluble in water and alcohol, and melt at 170 °C. It has an acidic taste. Tartaric acid has two identical asymmetric carbon atoms and exists in four stereoisomeric forms dextro, laevo, meso and racemic:



D-tartaric acid



L-tartaric acid

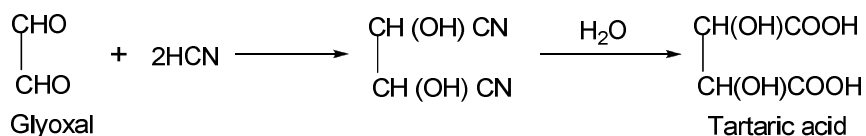


meso-tartaric acid

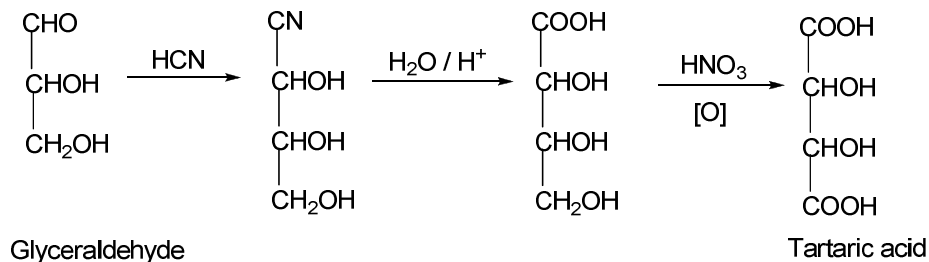
1. Dextrorotatory tartaric acid (d-tartaric acid) is found naturally in grapes berries, plums and several other fruits.
2. Levorotatory tartaric acid (l-tartaric acid) is obtained chiefly by resolution of racemic tartaric acid.
3. Racemic tartaric acid (an equal mixture of d- and l-tartaric acid) is prepared commercially by the molybdenum- or tungsten-catalyzed oxidation of maleic anhydride with hydrogen peroxide.

**Preparation of tartaric acid:** Tartaric acid can be prepared by the following general methods:

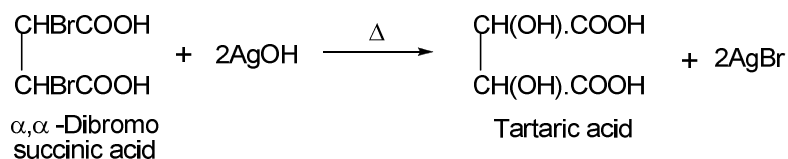
**1. From glyoxal:** On treatment with hydrogen cyanide, glyoxal produces glyoxal cyanohydrin which on hydrolysis gives tartaric acid.



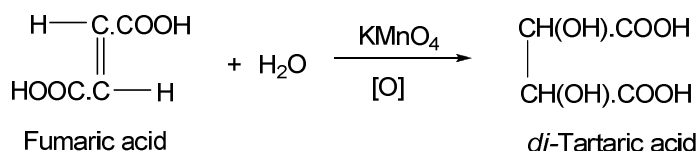
**2. From Kiliani-Fisher synthesis: Kiliani-** Fisher synthesis is one of the methods to increase no of carbons in compounds. Tartaric acid can also be formed from glyceraldehydes.



**3. From  $\alpha, \alpha'$ -dibromosuccinic acid :** Both ( $\pm$ ) and meso tartaric acids are prepared by boiling  $\alpha, \alpha'$ -dibromosuccinic acid with moist silver oxide.

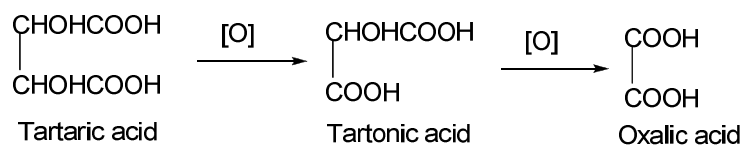


**4. By the oxidation of fumeric acid:** Tartaric acid can be prepared by the oxidation of fumeric acid with alkaline  $\text{KMnO}_4$ .

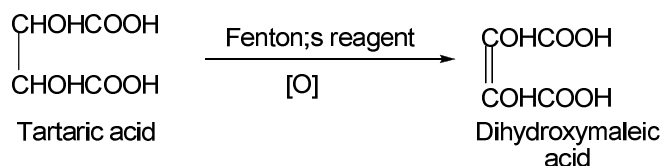


**Chemical properties of tartaric acid:** The chemical properties of tartaric acids are as under.

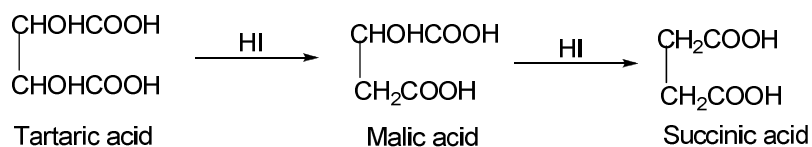
**1. Oxidation:** With mild oxidizing agents tartaric acid yields tartaric acid while with strong oxidizing agents, tartaric acid forms oxalic acid.



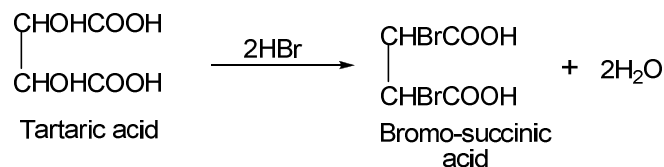
However, on oxidation with Fenton's reagent (alkaline  $\text{H}_2\text{O}_2 + \text{FeSO}_4$ ), tartaric acid is oxidized into dihydroxy maleic acid.



**2. Reduction:** Tartaric acid with HI is reduced into malic acid and then to succinic acid.



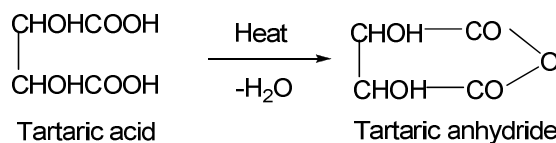
With HBr, the tartaric acid is reduced to bromosuccinic acid.



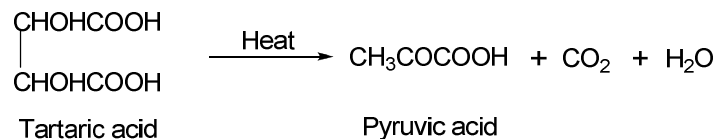
**3. Salt formation:** Tartaric acid forms two series of salts with the reactions of alkali.



**4. Action of heat:** When tartaric acid is heated at 150°C, it decomposes into tartaric anhydride.



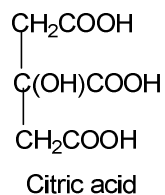
On strong heating, it decomposes into pyruvic acid with the evolution of CO<sub>2</sub>.



**Uses:** Tartaric acid is used:

1. In the preparation of baking powder and effervescent beverages.
2. In mirror silvering in the form of sodium potassium tartrate.
3. As mordant in dyeing and calico printing.

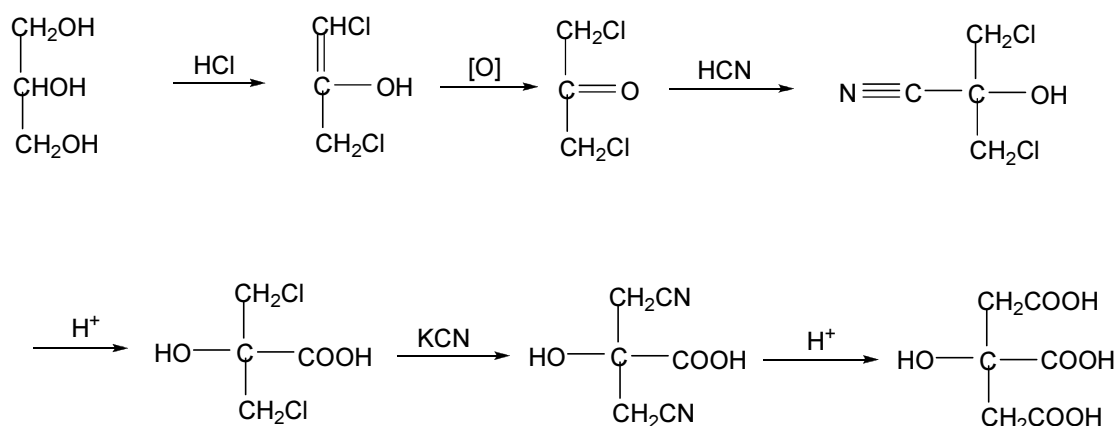
**C. CITRIC ACID**



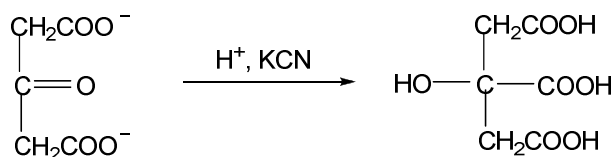
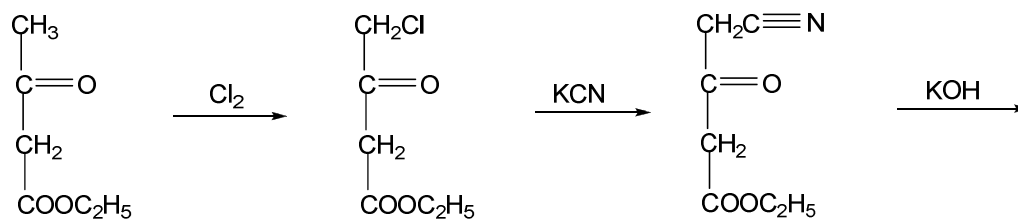
Citric acid is a weak organic tri-basic acid having the chemical formula  $C_6H_8O_7$ . The IUPAC name of citric acid is 2-hydroxypropane-1,2,3-tricarboxylic acid. It occurs naturally in citrus fruits like lemon, orange, tomato etc. Citric acid is crystalline solid containing one water molecule. It is soluble in water and alcohols but sparingly in ether. At 130 °C it loses water molecule and the anhydrous acid melts at 153 °C.

**Synthesis of citric acid:** Citric acid can be synthesized by the following methods:

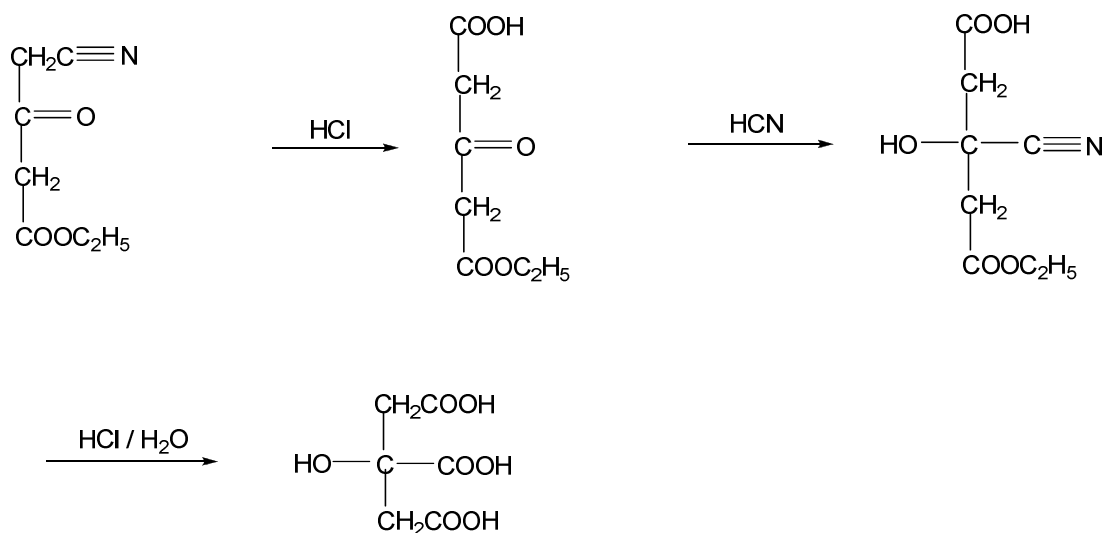
**1. By Grimaux and Adam synthesis (1880):** The sequential steps in this synthesis are: 1,2,3-hydroxy propane  $\rightarrow$  1,3-dichloro-2-propenol  $\rightarrow$  1,3-dichloro-2-propanone  $\rightarrow$  1,3-dichloro-2-cyno-2-hydroxypropane  $\rightarrow$   $\alpha$ -chloromethyl- $\alpha$ -hydroxypropionic acid  $\rightarrow$   $\beta$ -cyno- $\alpha$ -cynomethyl- $\alpha$ -hydroxypropionic acid  $\rightarrow$  2-hydroxy-1,2,3-tricarboxylic acid.



**2. By Haller and Held synthesis (1890):** This synthesis can be represented as: Ethyl- $\beta$ -keto butyrate  $\rightarrow$  ethyl- $\gamma$ -chloro- $\beta$ -ketobutyrate  $\rightarrow$  ethyl- $\gamma$ -cyno- $\beta$ -ketobutyrate  $\rightarrow$   $\beta$ -keto glutaric acid  $\rightarrow$  2, hydroxyl-1,2,3-tricarboxy acid.

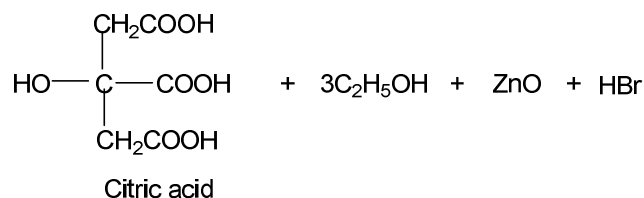
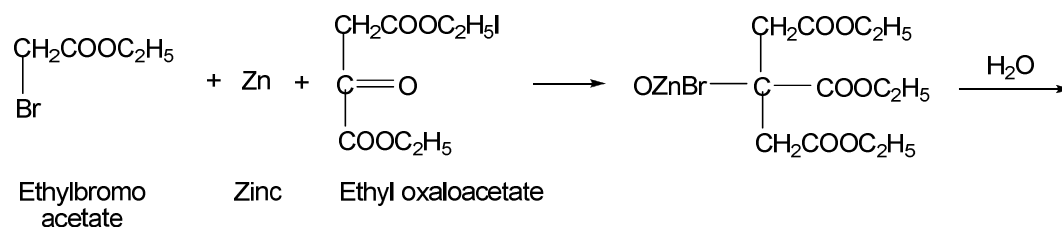


**3. By Dunschmann and Pechmann synthesis (1891):** This synthesis can be represented as: Ethyl- $\gamma$ - chloro- $\beta$ -ketobutyrate  $\rightarrow$  ethyl- $\beta$ -ketoglutarate  $\rightarrow$  ethyl- $\beta$ -cyno- $\beta$ -hydroxy glutarate.

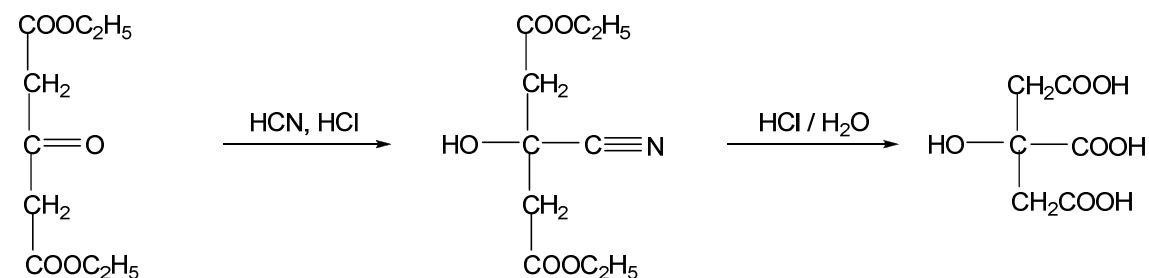


**4. By Reformatsky' reaction:** Citric acid is obtained by the reaction of ethylbromo acetate with oxaloacetate in presence of zinc followed by hydrolysis.



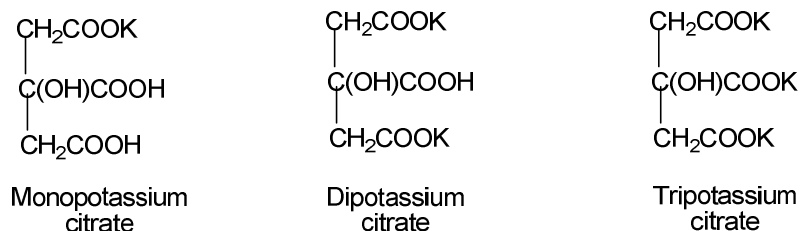


**5. From diethyl β-ketoglutarate:** This synthesis is progress as: Diethyl β-ketoglutarate → diethyl β-cyno-β-hydroxy glutarate.

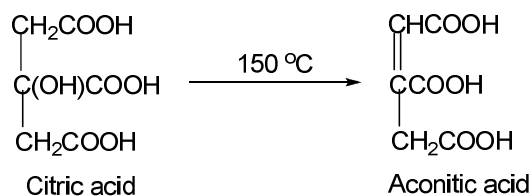


**Chemical reactions of citric acid:** Citric acid undergo the following types of chemical reactions

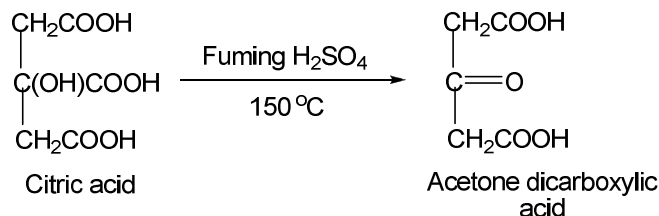
**1. Citric acid forms three types of salts:** Citric acid is a tricarboxylic acid therefore it forms three series of salts on reaction with alkalies *e.g.*, monopotassium citrate, dipotassium citrate and tripotassium citrate.



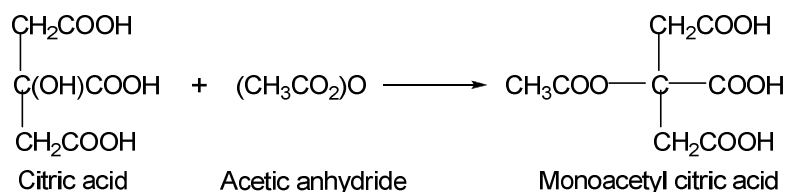
**2. Action of heat:** On heating at 150 °C, citric acid undergoes dehydration as:



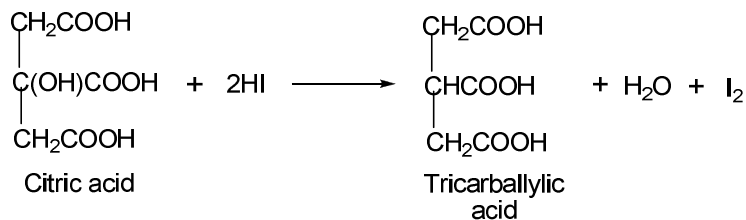
On heating with fuming sulphuric acid at 150 °C, citric acid gives acetone dicarboxylic acid.



**3. Reaction with acetic anhydride:** Citric acid produces monoacetyl derivatives.



**4. Reduction:** In presence of hydrogen iodide citric acid reduced to tricarballylic acid.



**Uses:** Citric acid is used:

1. As flavor compound in the preparation of synthetic fruit drinks.
2. As laxative in form of magnesium citrate.
3. As solvent in polymer synthesis.
4. As an iron supplement in the form of ferric ammonium citrate.
5. As mordant in printing and dyeing.

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### 6.12 SUMMARY

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The unit containing organic compounds carboxylic acids with –OH and –COOH group together can be summarized as: The carboxylic acids are known as mono, di, tri, or polycarboxylic acids according to number of carboxyl groups present in the molecule. Long chain monocarboxylic acids are also known as fatty acids such as stearic acid, palmitic acid, oleic acid etc. The carboxylic acids can be represented by –RCOOH or –RCO<sub>2</sub>H. In IUPAC system, monocarboxylic acids are named by replacing the suffix “-e” of the corresponding alkane with “-oic acid”, dicarboxylic acids named by add the suffix –*dioic* acid to the name of the parent alkane containing both carboxylic groups. Aromatic carboxylic acids are named by adding the suffix “-carboxylic acid” to the name of a parent hydride. The carboxylic carbon in a carboxylic acid is bonded with three functional groups, therefore the carboxylic carbon is sp<sup>2</sup> hybridized and hence the carboxylic group has a planer structure with bond angles of approximately 120°. The carboxylic acids are associated by hydrogen bonding into dimers (pairs of molecules) in liquid state or gaseous state. Carboxylic acids have higher boiling points than other hydrocarbons such as alcohols, ethers, aldehydes, or ketones of comparable molecular weight. The C<sub>1</sub>-C<sub>4</sub> members are more soluble in water. This is due to the ability of the –COOH group to form hydrogen bonds with water molecules. The C<sub>5</sub> members are partly soluble, and the higher carbon chain members (C<sub>10</sub> onwards) are insoluble in water, but readily soluble in ethanol, ethers and benzene. The carboxylic acids are weak acids, their acidic strength decreases with increase in molecular weight. Electron withdrawing groups enhance the acid strength due to increase the stability of carboxylate anions through the delocalization of negative charge by inductive or resonance effects. However the electron releasing groups reduce the acidity of carboxylic acids. The carboxylic acids (*pK<sub>a</sub>* 4-5) are stronger acids than alcohols (*pK<sub>a</sub>* 16-18) because of delocalization of the negative charge of the carboxylate anion through resonance and the electron withdrawing inductive effect of the carbonyl group. The carboxylic acids can be prepared, by various methods viz; by the oxidation of primary alcohols and aldehydes with acidic KMnO<sub>4</sub> or acidic K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. By alkenes on treatment with carbon monoxide and steam in presence of phosphoric acid. By the oxidation of alkyl benzene with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> or acidic or alkaline KMnO<sub>4</sub>. By the reaction of Grignard’s reagents on carbon dioxide. By the hydrolysis of esters and other

functional derivatives either in acidic or alkaline medium. The carboxylic acids undergo halogenations with chlorine or bromine, are reduced to alcohol with a suitable reducing agent like lithium aluminium hydride ( $\text{LiAlH}_4$ ) can be decarboxylated, undergo Kolbe's electrolysis, release hydrogen gas while reacting with active metals such as K, Ca, Mg. The carboxylic acids react with alkalis like sodium hydroxide to form salts and water. This unit also describes functional derivatives like acyl chlorides, esters and amides, anhydrides and their methods of preparation by various methods along with physical and chemical reactions. Hydroxy acids like malic acid, tartaric acid and citric acid are very important compounds. This unit also makes the readers aware about the methods of preparations, properties and uses of these hydroxyl acids.

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### ***6.13 TERMINAL QUESTIONS***

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#### **Section-A**

Q.1 Long answered questions: Answer the following questions

1. What are carboxylic acids? Describe the structure and nomenclature of aliphatic and aromatic carboxylic compounds.
2. What are carboxylic acids? Give the general methods of preparation of carboxylic acids.
3. Describe the reduction and decarboxylation reactions of carboxylic acids.
4. What are halo acids? Give the general methods of preparation and chemical properties of halo acids.
5. What are hydroxyl acids? Give the general methods of preparation and properties of malic acid.
6. Describe the general methods of preparation, physical and chemical properties of tartaric acid.
7. How is citric acid synthesized? Describe the important chemical properties of citric acid.

**Section-B**

## Q.2 Short answered questions

1. How can you synthesize carboxylic acids from cyanides?
2. Write a short note on the acid strength of carboxylic acids.
3. Write the physical properties of carboxylic acids.
4. Why the monochloroacetic acid is stronger than acetic acid?
5. Explain benzoic acid is more acidic than phenol.
6. Compare the acidic strength of acetic acid and halo acids.
7. Give the mechanism of Hell Volhard Zelinsky reaction.
8. How can you obtain halo acids from Hell Volhard Zelinsky reaction?
9. Give the mechanism of decarboxylation.
10. How can you synthesize esters and amides from carboxylic acids?
11. How can you prepare succinic acid from tartaric acid?
12. Give the method of preparation of hydroxyl acids.
13. How can you convert tartaric acid into oxalic acid, and tartaric acid into malic acid?
  
14. How will you obtained?
  - a. Carboxylic acids from acyl chlorides
  - b. Carboxylic acids from aldehydes
  - c. Carboxylic acids from alkyl benzene
  - d. Carboxylic acids from nitriles
  
15. How can you convert?
  - a) Carboxylic acids into halo acids
  - b) Carboxylic acids into alcohols
  - c) Carboxylic acids into alkanes
  - d) Carboxylic acids into acid anhydrides

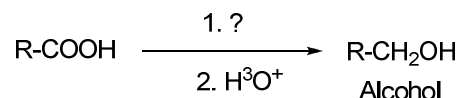
## Section-C

## Q.3 Multiple choice questions(MCQ)

- Which functional group is present in a carboxylic acid?  
(a)  $-\text{COOH}$  (b)  $-\text{NH}_2$   
(c)  $-\text{RCOOR}'$  (d)  $-\text{OR}'$
- Which one of the followings is a monocarboxylic acid?  
(a) Oxalic acid (b) Succinic acid  
(c) Formic acid (d) Citric acid
- What is the IUPAC name of  $\text{HOOC}(\text{CHOH})_2\text{COOH}$  ?  
(a) 2-Hydroxypropionic acid (b) 2, 3-Dihydroxybutanedioic acid  
(c) 2-Hydroxybutanedioic acid (d) Butanedioic acid
- Carboxylic acids are more soluble in water than alcohols and ethers due to  
(a) Their high molecular weight (b) Hydrogen bonding  
(c) More reactive carboxyl carbon (d) Their acidic character
- Carboxylic acid and alcohols both are formed hydrogen bonding with water but why carboxylic acids have higher boiling points than alcohols?  
(a) Because acids are more reactive than alcohols.  
(b) Because carboxylic acids are weak acids.  
(c) Because alcohols are not ionized completely.  
(d) Because the two molecules of a carboxylic acid form two hydrogen bonds.
- Which of the following is the strongest acid?  
(a)  $\text{CH}_2\text{ClCOOH}$  (b)  $\text{CH}_2\text{BrCOOH}$   
(c)  $\text{CH}_2\text{FCOOH}$  (d)  $\text{CH}_2\text{ICOOH}$
- The weakest acid among the following is  
(a)  $\text{Cl}_3\text{CCOOH}$  (b)  $\text{Cl}_2\text{CHCOOH}$   
(c)  $\text{ClCH}_2\text{COOH}$  (d)  $\text{CH}_3\text{COOH}$
- Primary alcohols are oxidized with acidic  $\text{KMnO}_4$  into  
(a) Carboxylic acid (b) Amide  
(c) Acid anhydride (d) Alcohols

9. Derivatives of carboxylic acids are hydrolyzed into
- (a) Alcohols (b) Acyl chlorides  
(c) Thioethers (d) Carboxylic acids
10. With  $\text{LiAlH}_4$  the carboxylic acid reduced to
- (a) Acids (b) Alcohols  
(c) Amines (d) Ketones
11. Anhydrides can be converted into carboxylic acids by
- (a) Oxidation (b) Ammonolysis  
(c) Hydrolysis (d) Decarboxylation
12. Carboxylic acids react with  $\text{SO}_2\text{Cl}_2$  in presence of iodine to form
- (a) Halo acids (b) Alcohols  
(c) Hydroxy acids (d) Ketones
13. Carboxylic acids can be prepared by the  $\text{S}_{\text{N}}2$  nucleophilic substitution reaction of
- (a) Alkyl halide with HI (b) Alkyl halide with CO  
(c) Acid anhydrides with NaCN (d) Alkyl halide with NaCN
14. Which of the following gives malic acid on reaction with  $\alpha$ -aminosuccinic acid?
- (a) Hydrogen iodide (b) Nitrous oxide  
(c) Acidic  $\text{KMnO}_4$  (d) Lithium aluminium hydride
15. The major product (?) of the reaction is an:
- $$\text{RCOONa} \xrightarrow[\Delta]{\text{NaOH} + \text{CaO}} ? + \text{CO}_2$$
- (a) Alcohol (b) Amine  
(c) Alkane (d) Ester
16. Malic acid on reduction with chromic acid produce
- (a) Succinic acid (b) Tartaric acid  
(c) Citric acid (d) Malonic acid
17. Malic acid can be reduced with HI into
- (a) Succinic acid (b) Tartaric acid  
(c) Citric acid (d) Malonic acid
18. Citric acid is
- (a) Halo acid (b)  $\alpha$ -Hydroxy acid  
(c)  $\beta$ -Hydroxy acid (d) Mineral acid

19. On reduction with strong oxidizing agent tartaric acid forms
- (a) Maleic acid (b) Succinic acid  
(c) Oxalic acid (d) Citric acid
20. Formation of  $\alpha$ -chloropropionic acid to  $\alpha$ -aminopropionic acid is an example of
- (a) Electrophilic substitution (b) Ammonolysis  
(c) Friedel Craft acylation (d) Nucleophilic substitution
21. What is the reagent for the following reaction?



- (a)  $\text{LiAlH}_4$  (b)  $\text{KMnO}_4$   
(c)  $\text{NaOH}$  (d)  $\text{HI}$
22. A primary alcohol can be oxidized to which of the following?
- (a) An aldehyde (b) A ketone  
(c) A carboxylic acid (d) A hemiacetal
23.  $\alpha$ - bromination of carboxylic acid by a mixture of  $\text{Br}_2$  and  $\text{PBr}_3$  is called
- (a) Michael reaction (b) Hell-Volhard Zelinskii reaction  
(c) Friedel Craft acylation (d) Claisen- condensation reaction
24. Which of the following acids is used in making baking powder?
- (a) Oxalic acid (b) Citric acid  
(c) Tartaric acid (d) Lactic acid
25. Acid present in lemon is
- (a) Oxalic acid (b) Citric acid  
(c) Tartaric acid (d) Lactic acid



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**6.14 ANSWERS (MCQ):**

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1. (a)	2. (c)	3. (b)	4. (b)	5. (d)
6. (c)	7. (d)	8. (a)	9. (c)	10. (b)
11. (c)	12. (a)	13. (d)	14. (b)	15. (c)
16. (d)	17. (a)	18. (b)	19. (c)	20. (d)
21. (a)	22. (c)	23. (b)	24. (c)	25. (b)

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## UNIT-7 FUNCTIONAL DERIVATIVES OF MONOCARBOXYLIC ACIDS

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### CONTENTS:

- 7.1 Objectives
- 7.2 Introduction
- 7.3 Structure and nomenclature of acid chlorides, esters, amides and acidhydrides
- 7.4 Relative stability of acyl derivative
- 7.5 Physical properties
- 7.6 Preparation of carboxylic acid derivatives
- 7.7 Chemical reactions of carboxylic acid derivatives
- 7.8 Mechanism of esterification and hydrolysis (acidic and basic)
- 7.9 Summary
- 7.10 Terminal Question
- 7.11 Answers (MCQ)
- 7.12 References

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### ***7.1 OBJECTIVES***

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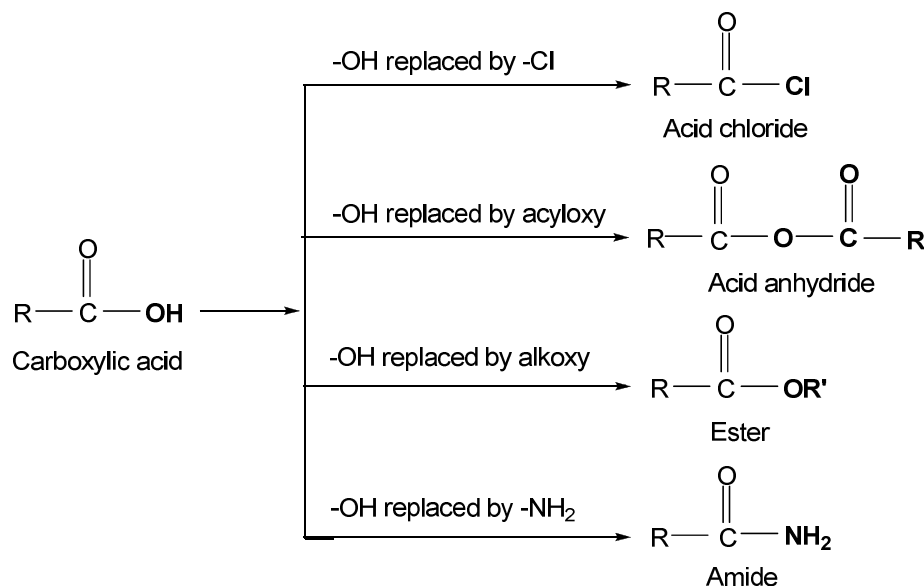
The objectives of this unit are to study carboxylic acid derivatives *viz.* acid halides, acid anhydrides, esters and amides using IUPAC naming system. Describe the structure; acid strength and reactivity of carboxylic acid derivatives. To synthesize carboxylic acid derivatives: acyl halides, acid anhydrides, esters, and amides. Describe the physical properties of carboxylic acid derivatives. To describe the chemical properties of carboxylic acid derivatives. To describe the mechanism of esterification, and acidic and alkaline hydrolysis.

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### ***7.2 INTRODUCTION***

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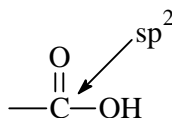
The most important functional derivatives of carboxylic acids are acyl chlorides (RCOCl), acid anhydrides ((RCO)<sub>2</sub>O), esters (RCOOR' where R and R' may be same or different), and amides (RCONH<sub>2</sub>) which are obtained by the replacement of -OH part of carboxyl group of acids by -Cl, -OCOR, -OR' or -NH<sub>2</sub> groups respectively.



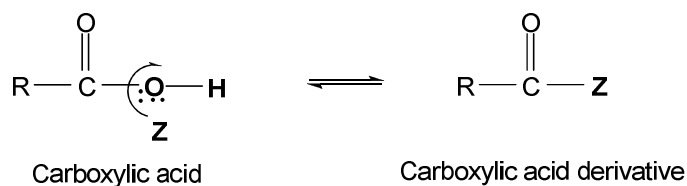
### 7.3 STRUCTURE AND NOMENCLATURE OF ACID

#### *CHLORIDES, ACID ANHYDRIDES, ESTERS, AMIDES AND ANHYDRIDES*

A carboxylic group contains a carbonyl group (C=O) and a hydroxyl group (-OH) bonded to the carbonyl carbon. The structure of carboxylic group is:

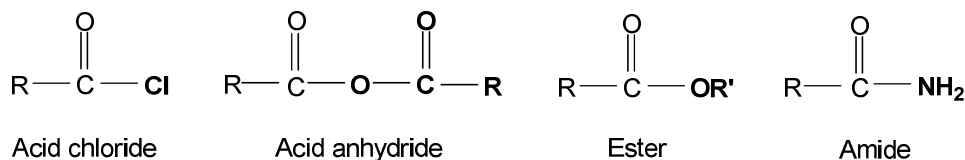


The carboxylic carbon in a carboxylic acid is bonded with three functional groups, therefore the carboxylic carbon is  $sp^2$  hybridized and hence the carboxylic group has a planer structure with bond angles of approximately  $120^\circ$ . Carboxylic acid derivatives are the organic compounds that are synthesized from the carboxylic acids by the replacement of -OH group of carboxyl group by -Cl, -OCOR (acyloxy group), -OR' (alkoxy group) or -NH<sub>2</sub> groups.



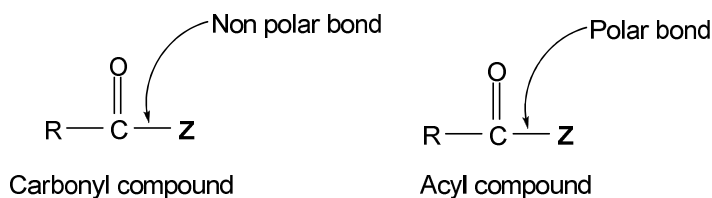
Where, Z may be chlorine atom, acyloxy group, alkoxy group or amide group.

The four important carboxylic acid derivatives are acid chlorides, acid anhydrides, esters and amides. These acid derivatives are distinguished from each other by the group attached to the carbonyl carbon atom.



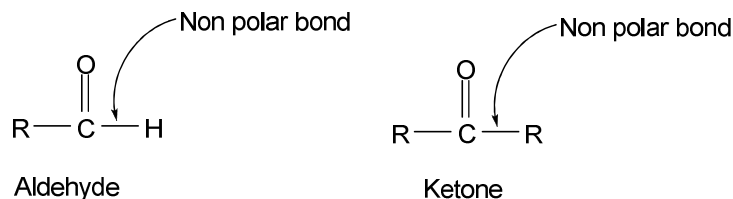
Hence, the carboxylic acids and their derivatives contain a  $sp^2$  hybridized carbonyl group which consists an O atom bonded to a C atom via a double bond in a planar model with bond angles of approximately  $120^\circ$ . In carboxylic acids derivatives, the hetero atom group (-Cl, N, or O) is connected to the carbonyl carbon via a  $\sigma$  bond. The resonance interaction of the carbonyl group with the lone pair of the adjacent heteroatom has important implications on the reactivity.

*Polarity of carboxylic acid derivatives:* Structurally, the carboxylic acid and their derivatives differ by only the substituent Z attached to the carboxylic carbon as shown in their structures. Carboxylic acid and their derivatives have a common group *i.e.*, acyl group (R-C=O). The chemical reactions of those organic compounds containing an acyl group depend on the nature of bond (polar or nonpolar) between the carbonyl carbon of acyl group and the substituent (Z) attached to it. The organic compounds containing an acyl group are called acyl compounds. On the basis of polarity, acyl compounds can be classified into two types: nonpolar carbonyl compounds and polar acyl compounds.

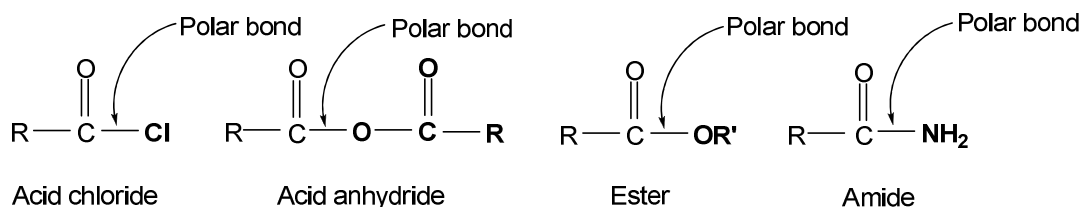


The carbonyl carbon of acyl group in carbonyl compounds is attached directly to a hydrogen atom or any other carbon atom. The carbon-carbon bond and carbon-hydrogen bonds are non polar because the electronegativities of the carbon and

hydrogen are almost same. For example, aldehydes and ketones are nonpolar carbonyl compounds.



The carbonyl carbon in acyl compounds is attached directly to an oxygen, nitrogen, or halogen atom. Such bonds, C-O, C-N, and C-halogen, are polar because oxygen, nitrogen and halogen are more electronegative than that of carbon. The carboxylic acid and their derivatives are the examples of acyl compounds.

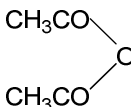
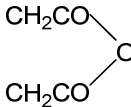
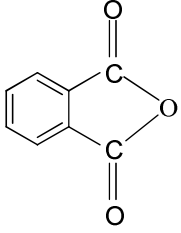


### *IUPAC nomenclature of carboxylic acid derivatives*

1. **Acyl chlorides:** In IUPAC system, acid chlorides are named by replacing the “e” ending of the parent alkane by “-oyl chloride”.

Structure	Common name	IUPAC name
HOCl	formyl chloride	methanoyl chloride
CH <sub>3</sub> COCl	acetyl chloride	ethanoyl chloride
C <sub>2</sub> H <sub>5</sub> COCl	propionyl chloride	propanoyl chloride
C <sub>3</sub> H <sub>7</sub> COCl	butyryl chloride	butanoyl chloride
C <sub>4</sub> H <sub>9</sub> COCl	valeryl chloride	pentanoyl chloride

2. **Acid anhydrides:** Acid anhydrides are named by adding the word “anhydride” after the IUPAC name of the acid.

Structure	Common name	IUPAC name
	acetic anhydride	ethanoic anhydride
	succinic anhydride	butanedioic anhydride
	Phthalic anhydride	o-Benzenedioic anhydride

3. **Acid esters:** In IUPAC system, esters are generally named by first naming the alkyl group followed by the name of the acid and changing the “*ic*” by “*ate*”.

Structure	Common name	IUPAC name
HCOOCH <sub>3</sub>	methyl formate	methyl methanoate
CH <sub>3</sub> COOC <sub>2</sub> H <sub>5</sub>	ethyl acetate	ethyl ethanoate
C <sub>2</sub> H <sub>5</sub> COOCH <sub>3</sub>	methyl propionate	methyl propanoate
CH <sub>3</sub> COOC <sub>6</sub> H <sub>5</sub>	phenyl acetate	phenyl ethanoate
C <sub>6</sub> H <sub>5</sub> COOC <sub>6</sub> H <sub>5</sub>	phenyl benzoate	phenyl benzoate
C <sub>6</sub> H <sub>5</sub> COO CH <sub>3</sub>	methyl benzoate	methyl benzoate

4. **Amides:** In IUPAC system, amides are named by replacing the ending “*-e*” of the parent alkane by *amide*.

Structure	Common name	IUPAC name
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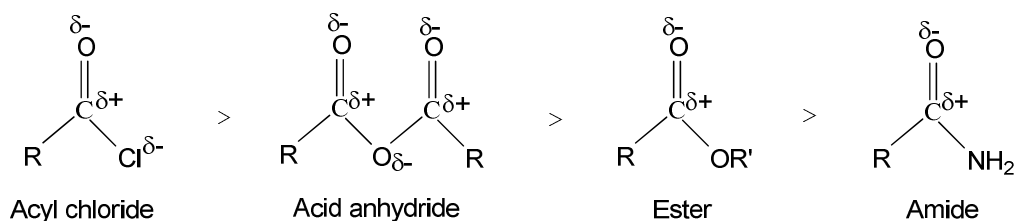
HCONH <sub>2</sub>	formamide	methanamide
CH <sub>3</sub> CONH <sub>2</sub>	acetamide	ethanamide
C <sub>2</sub> H <sub>5</sub> CONH <sub>2</sub>	propionamide	propanamide
C <sub>3</sub> H <sub>7</sub> CONH <sub>2</sub>	butyramide	butanamide
C <sub>4</sub> H <sub>9</sub> CONH <sub>2</sub>	valeramide	pentanamide

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### 7.4 RELATIVE STABILITY OF ACYL DERIVATIVES

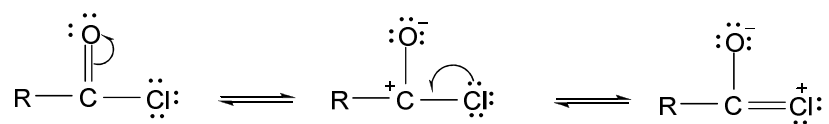
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Acid derivatives can be listed in order of their reactivity towards nucleophilic acyl substitution as:

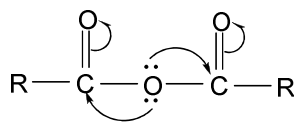


The magnitude of the  $\delta^+$  charge on the carbonyl carbon depends on the electron releasing or electron attracting power of the substituent. The substituent groups of acid chlorides and anhydrides have an ability to withdraw electrons from the carbonyl carbon, making these derivatives more reactive than carboxylic acids. On the other hand in esters and amides, the substituent (Z group) release electrons onto the carbonyl carbon which makes these derivatives less reactive. The reactivity of the carboxylic acid derivatives can be explained in details as:

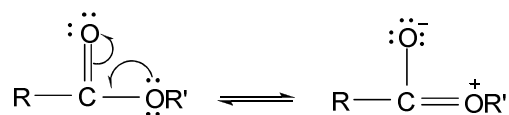
- A. Acyl chlorides:** The electron withdrawing inductive effect of an acyl chloride is not stabilized by electron pair donation; the electron withdrawing inductive effect of chlorine makes it more electrophilic and more reactive towards nucleophilic acyl substitution.



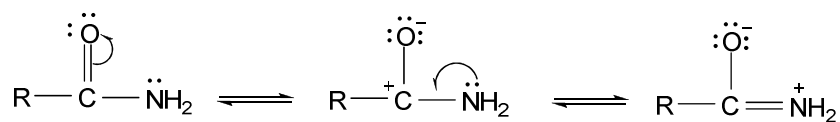
**B. Acid anhydrides:** In acid anhydrides, the carbonyl group is better stabilized by electron donation than acyl chlorides. Here electron pair orbital (2p) of oxygen overlap with the orbital of carbonyl group but the presence of two carbonyl groups create competition for the same electron pair. Thus, the extent of stabilization in resonance is decreased.



**C. Esters:** The carbonyl group of esters is stabilized more effectively by the electron pair of oxygen than acid anhydride. Because, only one carbonyl group is present in esters, this increases the stability of carbonyl group of ester and decreases the reactivity towards nucleophilic substitution than acid anhydrides.



**D. Amides:** Acid amides are less reactive towards nucleophilic substitution. This is due to the positive charge on acyl carbon atom, which is so necessary for nucleophilic substitution. They are at least 10 times less reactive than acyl chlorides.




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## 7.5 PHYSICAL PROPERTIES

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**A. Acyl chlorides:** The lower members are colorless, volatile liquid having irritating smell. Higher members are colorless liquids. The boiling points of acid derivatives are lower than that of carboxylic acids due to the absence of intermolecular hydrogen bonding. They also fume in moist air.



**B. Acid anhydrides:** Acid anhydrides are colorless liquids or solids with irritating smell. They are soluble in organic solvents, although the lower members are readily soluble in water. They have higher boiling points than parent acids due to their larger size.

**C. Esters of acids:** Esters are colorless liquids or solids having fruity or flowery odor. Low molecular weight esters are soluble in water. The solubility of esters decreases with increase the molecular weight. All esters are soluble in organic solvents like benzene, ethers etc. Ester do not form hydrogen bonding, so they have lower melting and boiling points than corresponding carboxylic acids. Boiling points of normal chain esters are higher than those of branched chain isomers.

**D. Acid amides:** Except formamide ( $\text{HCONH}_2$  which is a liquid), all amides are colorless crystalline solids. The intermolecular hydrogen bonding is associated in amides, so their melting points are much higher than parent carboxylic acids. Lower members of amides homologous series are water soluble.

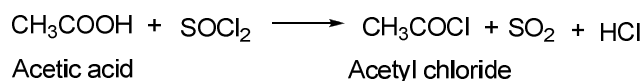
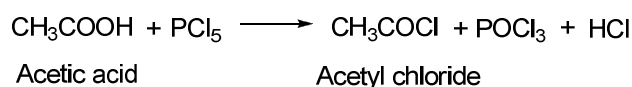
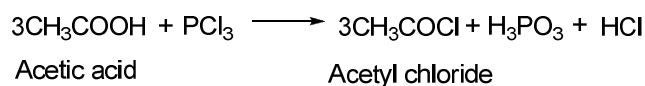
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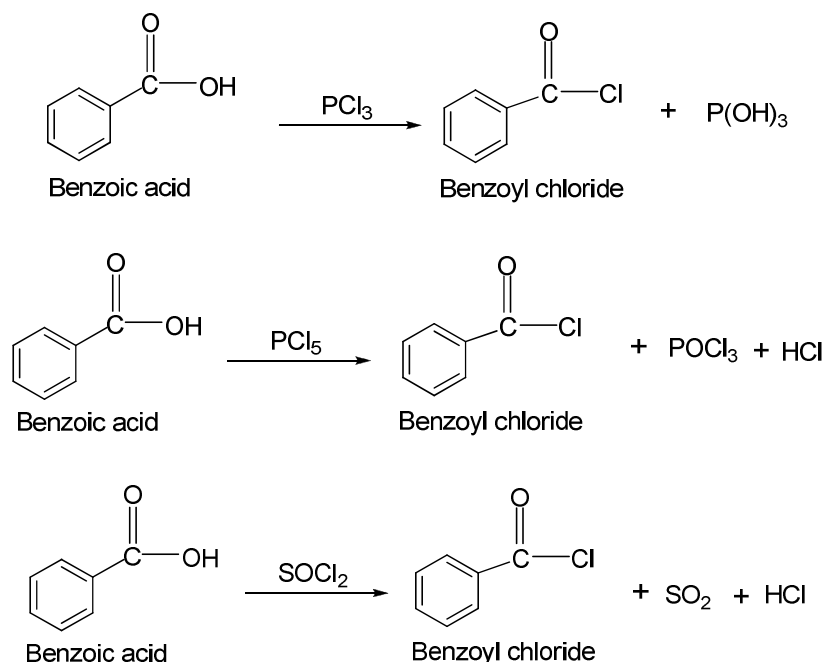
## 7.6 PREPARATION OF CARBOXYLIC ACID DERIVATIVES

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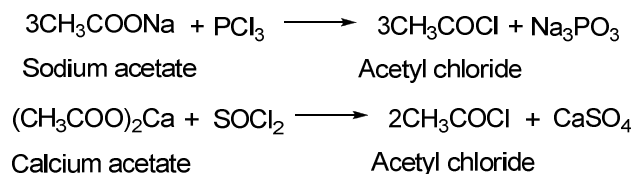
**(A) ACYL CHLORIDE:** Acid chlorides are also known as acyl chlorides have the general formula  $\text{R-COCl}$ . They are obtained by the replacement of a  $-\text{OH}$  group by a  $\text{Cl}$  atom. They can be formed by heating carboxylic acids or their salts with phosphorous trichloride ( $\text{PCl}_3$ ), phosphorus penta chloride ( $\text{PCl}_5$ ), or thionyl chloride ( $\text{SOCl}_2$ ).

**1. From acids:** Acyl chlorides are prepared by heating carboxylic acids with phosphorous trichloride ( $\text{PCl}_3$ ), phosphorus penta chloride ( $\text{PCl}_5$ ), or thionyl chloride ( $\text{SOCl}_2$ ).



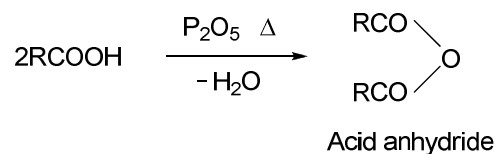


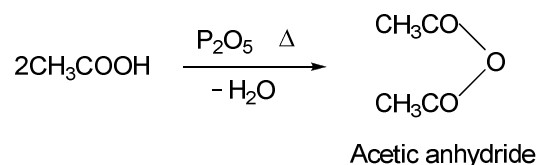
**2. From salts:** Acyl chlorides are prepared by the treatment of sodium salts of carboxylic acids with phosphorous trichloride ( $\text{PCl}_3$ ) or thionyl chloride ( $\text{SOCl}_2$ ).



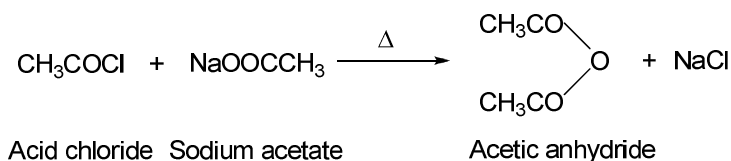
**(B) ACID ANHYDRIDE:** Acid anhydrides are formed by the dehydration of carboxylic acids. They are obtained by the elimination of one water molecule from the two molecules of monocarboxylic acids. Ethanoic anhydride is the most common acid anhydride. They can be prepared by the following general methods:

**1. Dehydration of anhydrous acids:** Acid anhydride can be obtained by heating anhydrous acids in presence of a dehydrating agent like  $\text{P}_2\text{O}_5$ .

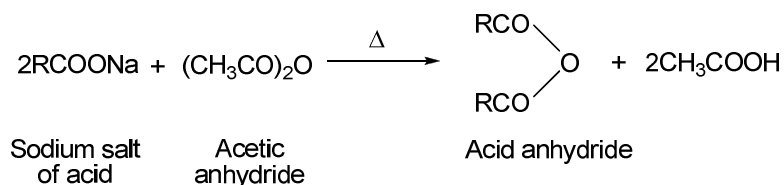




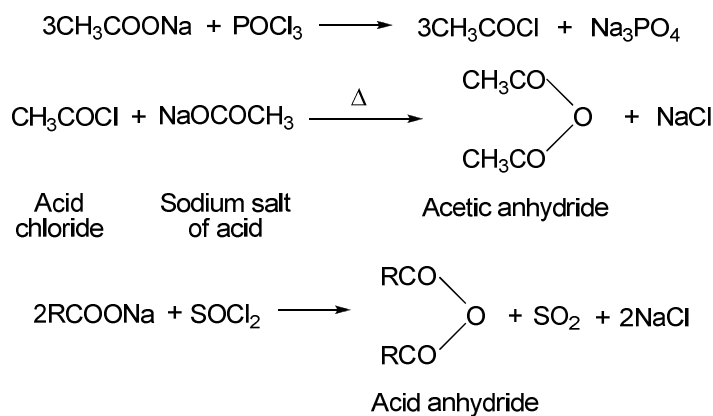
**2. By heating acid chlorides with anhydrous salts of acid:** Acid anhydride can be prepared by heating an acid chloride with anhydrous sodium salts of a carboxylic acid.



**3. By heating sodium salts of carboxylic acids with acetic anhydride:** Anhydrides of higher acids can be obtained by heating sodium salts of carboxylic acids with acetic anhydride.



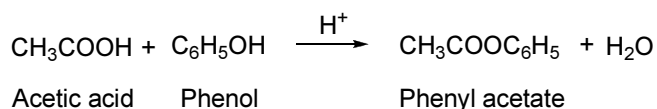
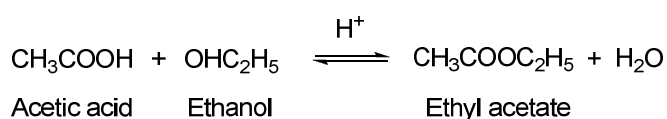
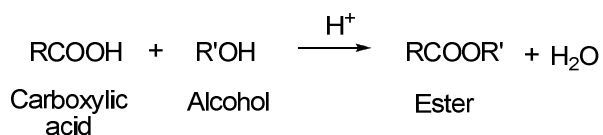
**4. By the reaction of excess amount of anhydrous sodium salts of acid with phosphorus oxy-chloride or thionyl chloride:** Acid anhydrides are synthesized by treating sodium salt of carboxylic acid with  $\text{POCl}_3$  or  $\text{SOCl}_2$ .



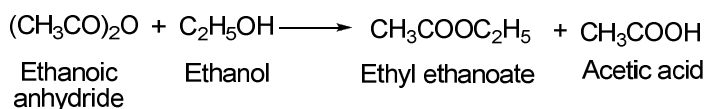
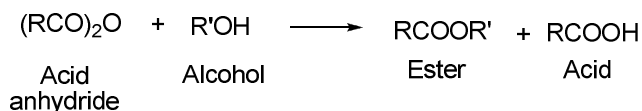
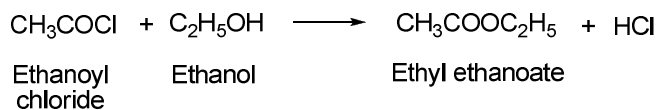
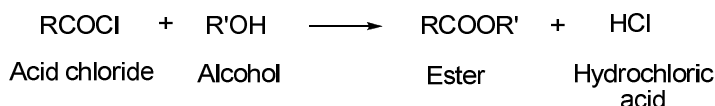
**(C) ESTERS OF ACIDS:** Esters are carboxylic acid derivatives which are formed by the replacement of hydroxyl (-OH) part of  $-\text{COOH}$  group by an alkoxy group (-OR). They are found naturally in several plants, fruits and flowers. Orange, banana, apple, pineapple, mango etc. are the chief source of esters. Oils, fats and waxes are also

composed by the esters of higher fatty acids like stearic acid, palmitic acid, oleic acid and cerotic acid etc. Esters can be formed by the following general methods:

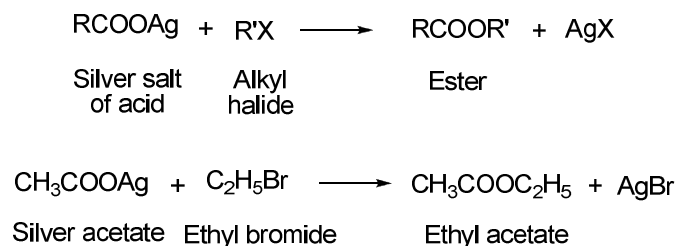
**1. By direct esterification:** When an alcohol interacts with an acid in presence of a suitable acid catalyst, esters are formed by the elimination of a water molecule. This process is known as esterification.



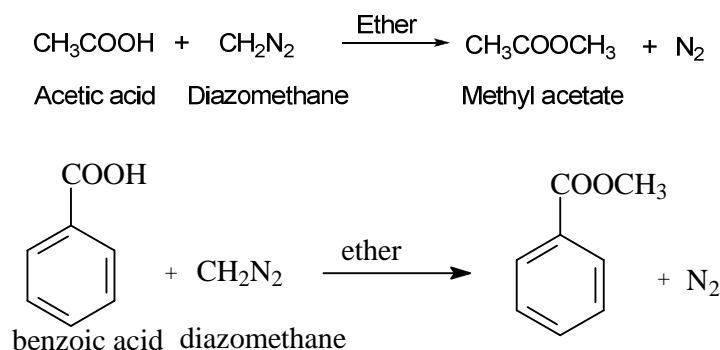
**2. By the action of alcohols on acid chlorides or anhydrides:** Esters are prepared by the nucleophilic substitution of acid chlorides or acid anhydrides with alcohols.



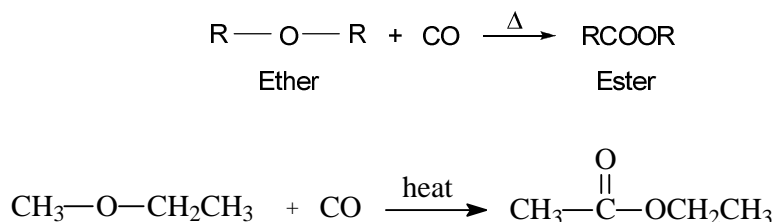
**3. By heating silver salts of carboxylic acids with alkyl halides :** Esters are prepared by the reaction of silver salt of acids on alkyl halides.



**4. By the action of diazomethane on carboxylic acids:** Methyl esters are prepared by the action of the ethereal solution of diazomethane on carboxylic acid.

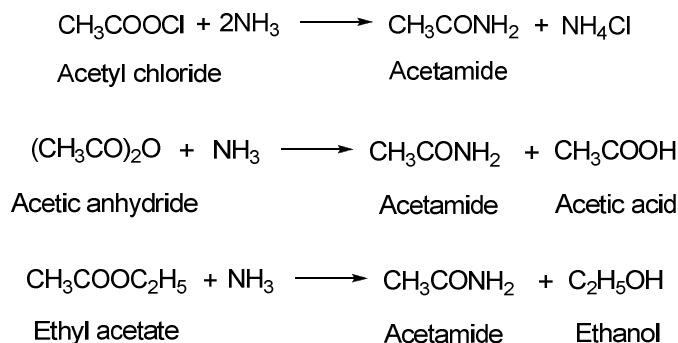


**5. From ethers and carbon monoxide:** When ether interacts with carbon monoxide at 125-180 °C under 500 atmospheric pressure in presence of boron trifluoride catalyst, an ester is formed.

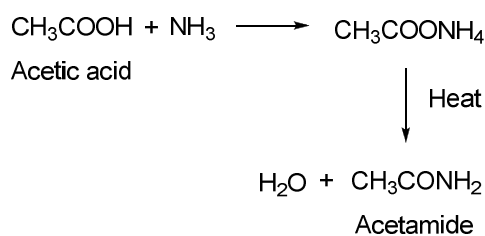


**(D) ACID AMIDES:** Amides are regarded as carboxylic acid derivatives in which the hydroxyl group (-OH) is replaced by an amino group (-NH<sub>2</sub>). For example, the most common amides are methanamide (HCONH<sub>2</sub>) and ethanamide (CH<sub>3</sub>CONH<sub>2</sub>). They have the general formula R-CONH<sub>2</sub>. The acid amides can be prepared by the following general methods:

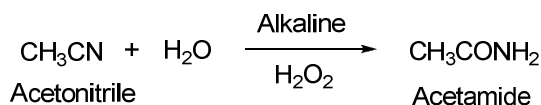
**1. Action of ammonia on acyl chloride, acid anhydride or ester:** Acid amides can be prepared by the acylation of ammonia with acyl chlorides, acid anhydrides or esters.



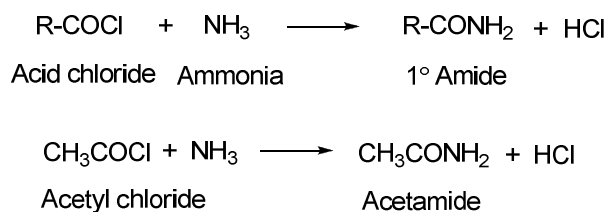
**2. By heating ammonium salts of fatty acids:** The ammonium salts of carboxylic acids on heating give amides.

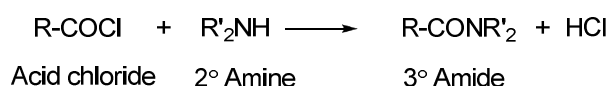
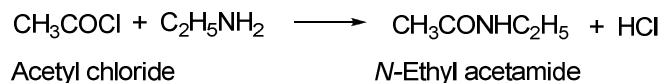
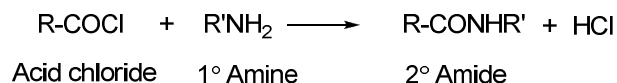
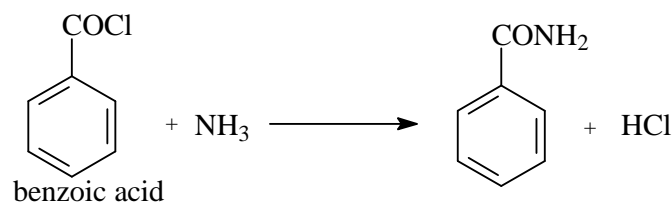


**3. Partial hydrolysis of cyanides:** The partial hydrolysis of cyanides with concentrated hydrochloric acid, polyphosphoric acid or alkaline peroxide produces amides.



**4. Reaction of an acid chloride with an amine:** Acid chlorides are converted into primary, secondary and tertiary amides by the reaction with ammonia, primary amines and secondary amines respectively.



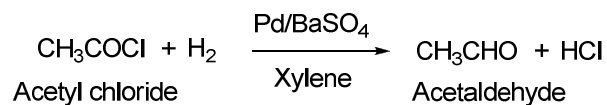


## 7.7 CHEMICAL REACTIONS OF CARBOXYLIC ACID DERIVATIVES

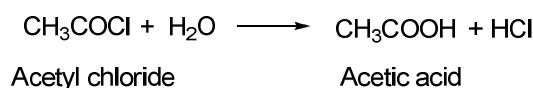
**(A) ACYL CHLORIDE:** Acyl chlorides are most reactive derivatives of carboxylic acids. They easily undergo nucleophilic acyl substitutions to form acid anhydrides, esters and amides. The most common acyl chlorides are methanoyl chloride (CH<sub>3</sub>COCl) and ethanoyl chloride (CH<sub>3</sub>COCl). The acyl chlorides give the following chemical properties:

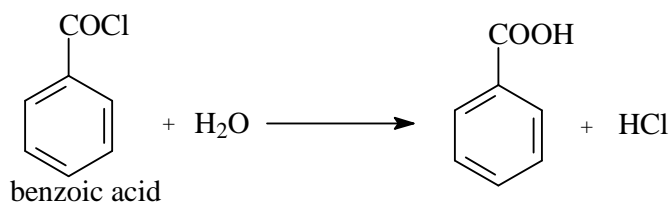
**1. Basic character:** Acyl chlorides are very much less basic because the chlorine atom is not effective at stabilizing a positive charge.

**2. Reduction:** Acid chlorides get reduced to aldehydes by the action of hydrogen in presence of Pd/BaSO<sub>4</sub>.

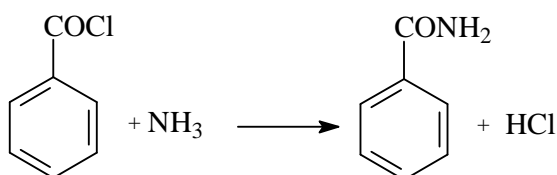
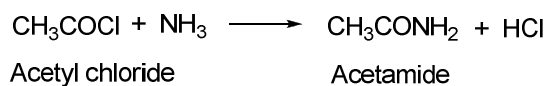


**3. Hydrolysis:** Acid chlorides are hydrolyzed with water to parent carboxylic acids.

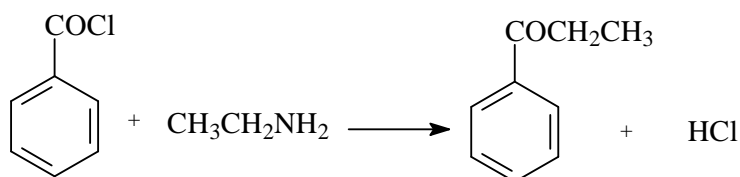
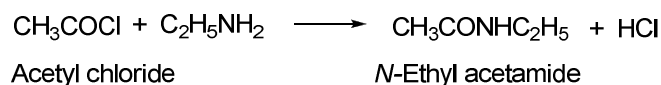




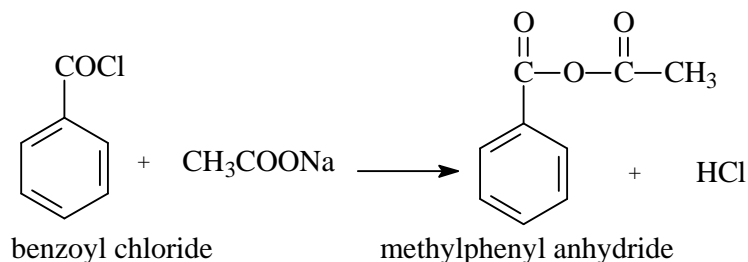
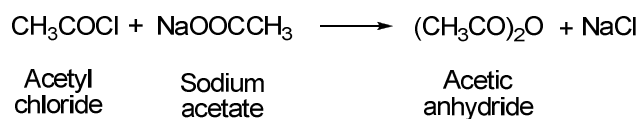
**4. Action with ammonia:** Acid chlorides react with ammonia to form acid amides.



**5. Action of amines:** Acid chlorides on reaction with primary and secondary amines give acid amides.

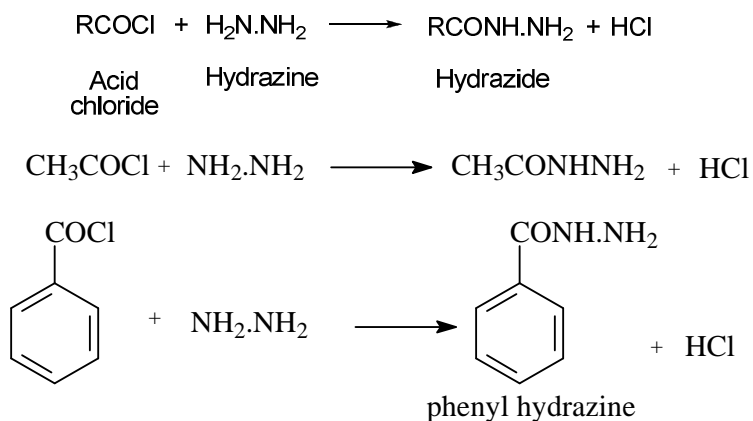


**6. Formation of acid anhydride:** Acid chlorides by treating with sodium salts of fatty acids produce anhydrides.

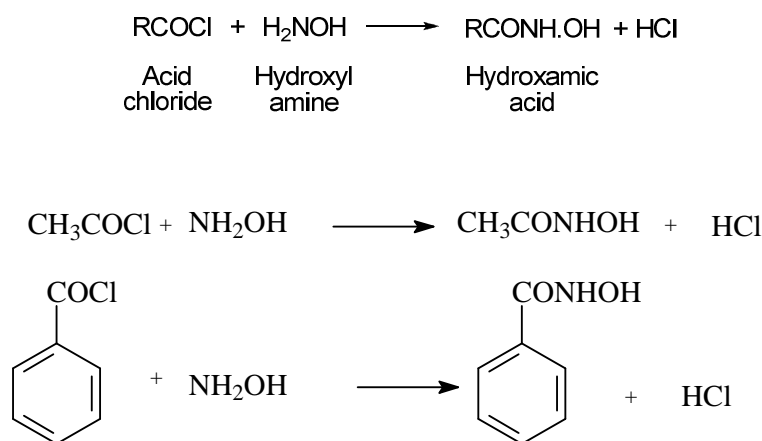




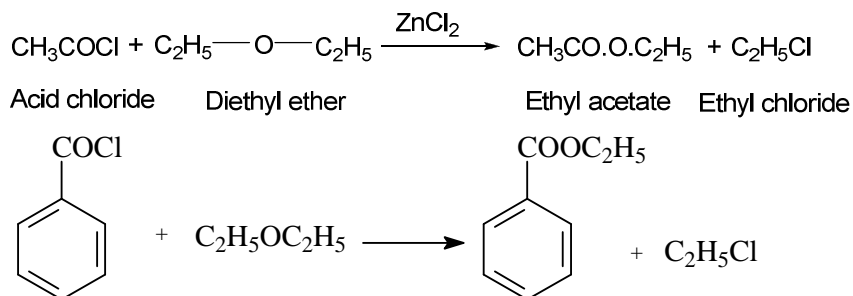
**7. Action of hydrazine:** On treatment with hydrazine acid chlorides form hydrazides.



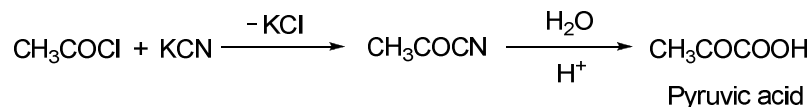
**8. Action of hydroxyl amine:** On reaction with hydroxyl amine the acid chlorides form hydroxamic acid.



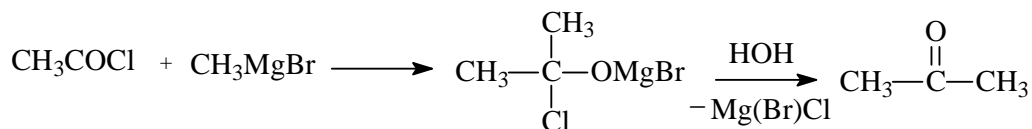
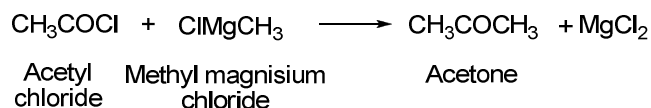
**9. Action of ethers:** Acid chlorides on reaction with diethyl ether in presence of zinc chloride form esters.



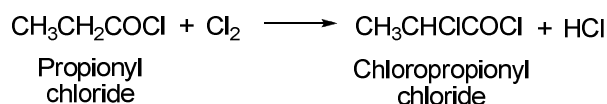
**10. Action of potassium cyanide:** Acid chlorides react with potassium cyanide to form acetyl cyanide which on acid catalyzed hydrolysis gives pyruvic acid.



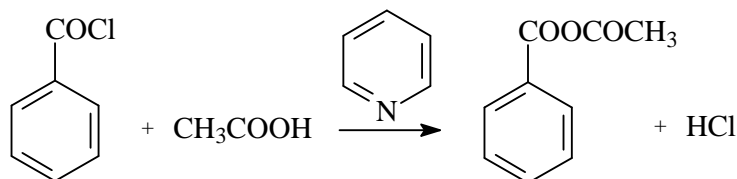
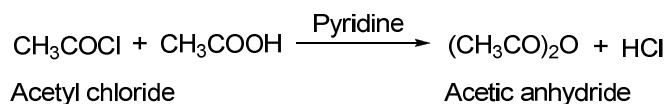
**11. Reaction with Grignard' reagent:** Acid chlorides on reaction with Grignard's reagent give tertiary alcohols.



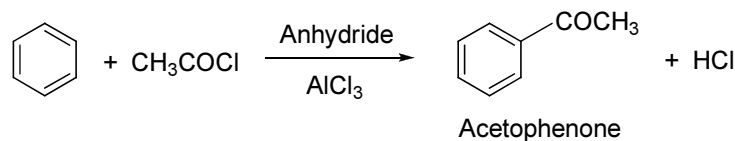
**12. Action with halogens:** Acid chlorides react with chlorine to form monochloroacetic acid.



**13. Reaction with carboxy acid:** Acid chlorides react with carboxylic acids in presence of pyridine to form acid anhydrides.



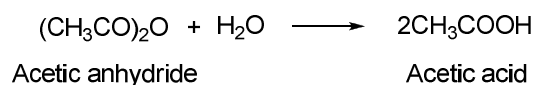
**14. Friedel Craft's reaction:** Acyl chlorides on reaction with aromatic hydrocarbons in presence of Lewis acid ( $\text{AlCl}_3$ ) in Friedel Craft acylation form aromatic ketones.



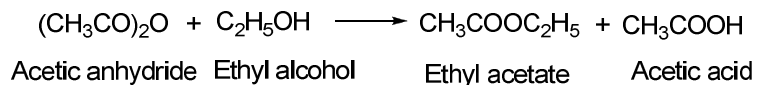
**Uses:** Acyl chlorides are used in the preparation of acetic anhydride, acetamide and acetanilide, and as acetylating agents in many reactions. They are also used in the detection and determination of  $-\text{OH}$ ,  $-\text{NH}_2$ ,  $>\text{NH}$  and functional groups in a molecule.

**(B) ACID ANHYDRIDES:** Acid anhydrides are less reactive than acyl chlorides towards nucleophilic substitution. The most common acid anhydride is acetic anhydride. The important chemical reactions of acetic anhydride are:

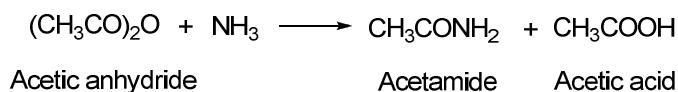
**1. Hydrolysis:** Acid anhydrides are hydrolyzed with water to acids.



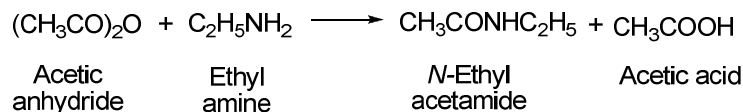
**2. Alcoholysis:** Acid anhydrides react with ethyl alcohol to produce esters.



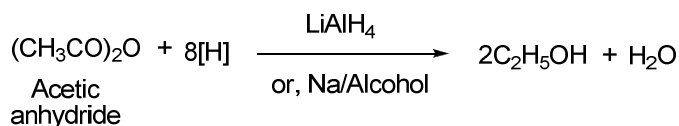
**3. Ammonolysis:** Ammonia rapidly reacts with acetic anhydrides to give acetamide.



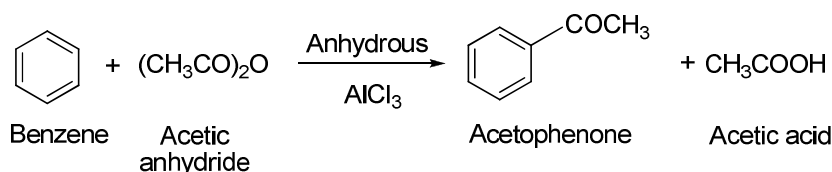
**4. Action with primary amines:** Primary amines react with acid anhydride to form amides.



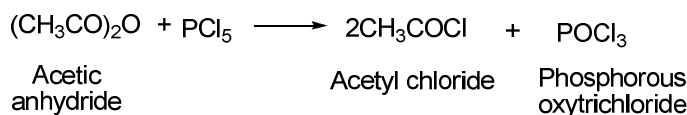
**5. Reduction:** On reduction with  $\text{LiAlH}_4$ , or Na and alcohol, acetic anhydrides produce alcohols.



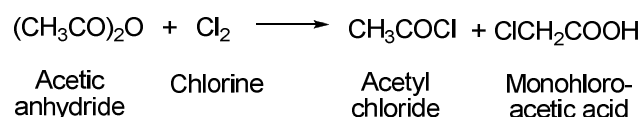
**6. Friedel Craft acylation:** Acetic anhydrides on treatment with benzene in presence of anhydrous  $\text{AlCl}_3$  form aromatic ketones.



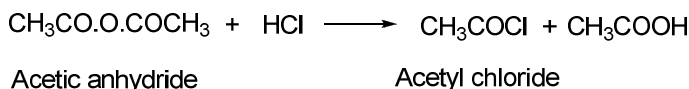
**7. Action with phosphorous pentachloride:** Acetic anhydride reacts with phosphorous pentachloride to form acetyl chloride and phosphorous oxy-trichloride.



**8. Action of chlorine:** Acid anhydride reacts with chlorine to form acetyl chloride and monochloroacetic acid.



**9. Action with dry hydrogen chloride:** On reaction with dry hydrogen chloride, acetic anhydride forms acetyl chloride and acetic acid.

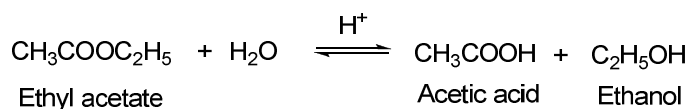


**Uses:** Acid anhydrides are used in the preparation of amyl acetate, aspirin, dyes also acetate rayon. They are also used as acetylating agent.

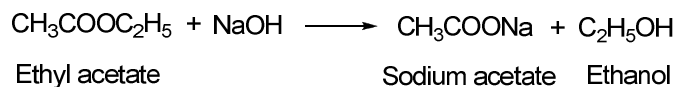
**(C) Esters:** Esters are less reactive than acyl chloride and acid anhydrides. Methyl methanoate ( $\text{HCOOCH}_3$ ) and ethyl ethanoate ( $\text{CH}_3\text{COOC}_2\text{H}_5$ ) are the most common esters. They can be converted into carboxylic acid by acid or base hydrolysis, into amides with ammonia and can be reduced into alcohols with  $\text{LiAlH}_4$ .

**1. Hydrolysis:** Esters are hydrolyzed to carboxylic acids in presence of an acid whereas in presence of an alkali they produce sodium salts of carboxylic acids.

*Acid hydrolysis:*

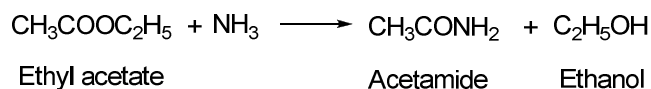


*Alkaline hydrolysis:*

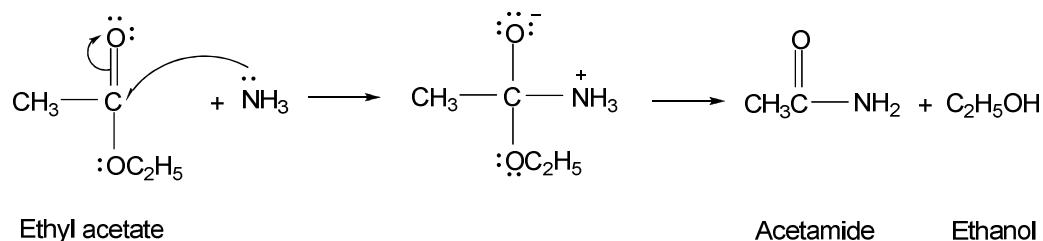


**2. Action of ammonia:** Esters slowly react with ammonia to form amides and alcohols.

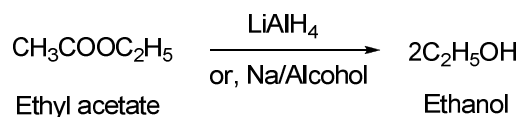
This process is called *ammonolysis*.



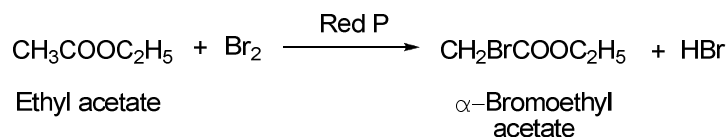
*Mechanism:*



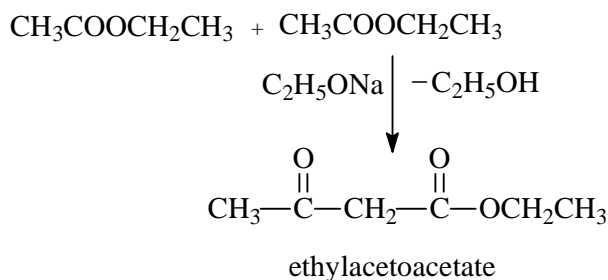
**3. Reduction:** On reduction with LiAlH<sub>4</sub> or Na and alcohol, esters produce alcohols.



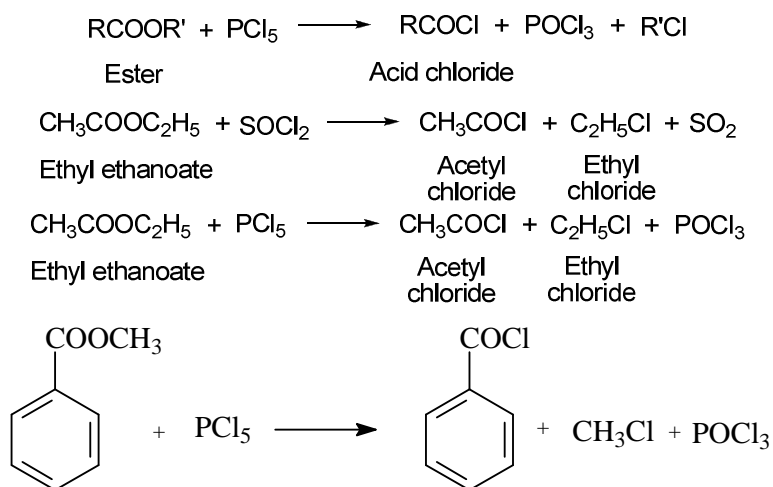
**4. Halogenation:** Esters on reaction with chlorine or bromine in presence of red phosphorous give the α-halogenated esters (*Hell Volhard Zelinsky reaction*).



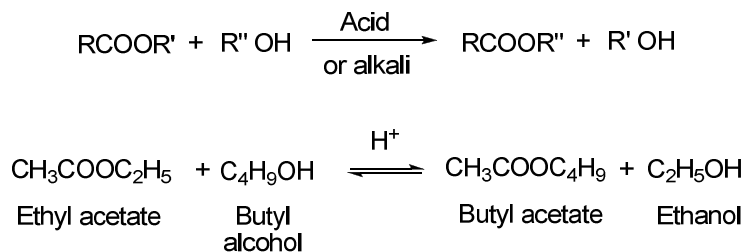
**5. Claisen condensation:** One molecule of an ester combines with second molecule of that ester in presence of sodium alkoxide to give an aldehyde or an ketone. This reaction is known as Claisen condensation.



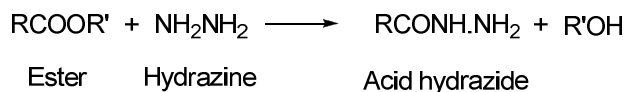
**6. Action of phosphorous pentachloride or thionyl chloride:** On reaction with phosphorous pentachloride or thionyl chloride, esters are converted into acid chlorides and alkyl halides.



**7. Trans-esterification:** Trans-esterification is the conversion of a carboxylic acid ester into a different carboxylic acid ester. When an ester is treated with the excess amount of an alcohol in presence of either an acid or a base there can be an exchange of alkoxy groups.



**8. Reaction with hydrazine:** Esters react with hydrazine to form acid hydrazides.

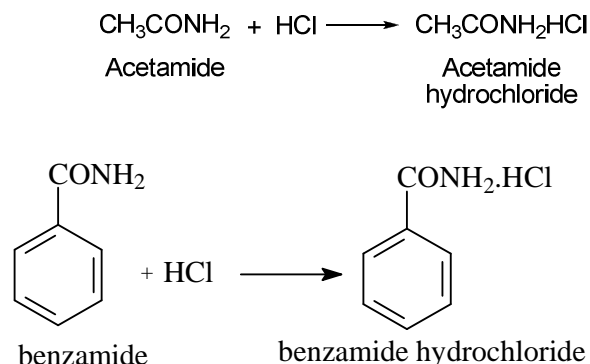


**Uses:** Esters are used as solvent in perfumes, plasticizers, gums, resins, cellulose, paints, varnishes, oils and fats. They are commercially used in making artificial flavors and essence.

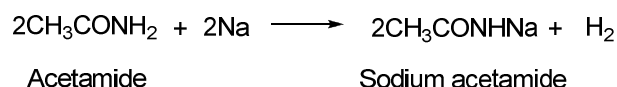
**(D) ACID AMIDES:** Amides are least reactive derivatives of carboxylic acids. They are also converted into carboxylic acid by acid or alkaline hydrolysis. They can be dehydrated into nitriles. The important chemical reactions of acid amides are:

**1. Amphoteric character:** Amides are weak acids as well as weak base. They are most basic than other derivatives because nitrogen is an effective donor of electrons in comparison to oxygen. They are neutral to litmus.

*(a) Basic property:* Acetamide behaves as a base and reacts with hydrochloric acid to produce a salt (acetamide hydrochloride).

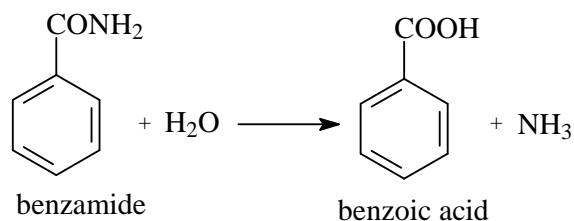
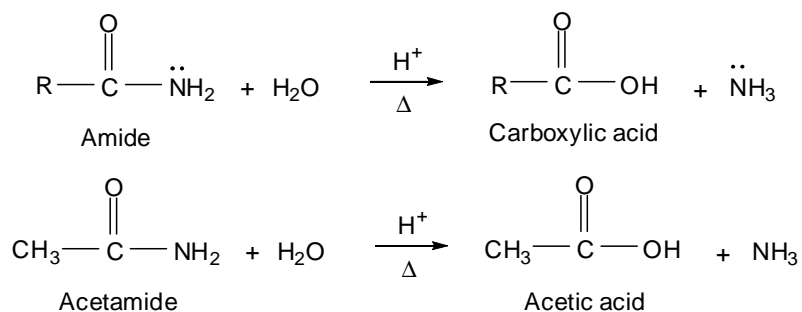


*(b) Acidic property:* Acetamide as an acid reacts with sodium (Na) or mercury oxide (HgO) to form corresponding salts.

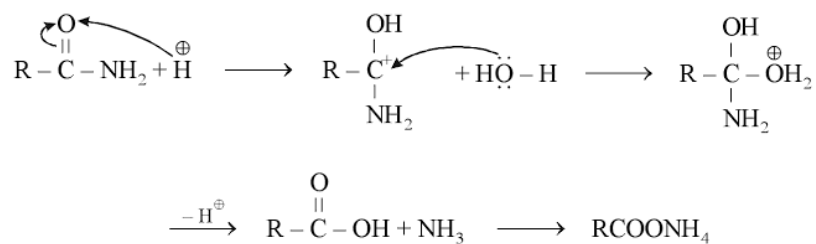


**2. Hydrolysis:** Acid amides are not easily hydrolyzed with water, but hydrolyzed easily on heating with dilute acids or alkalies.

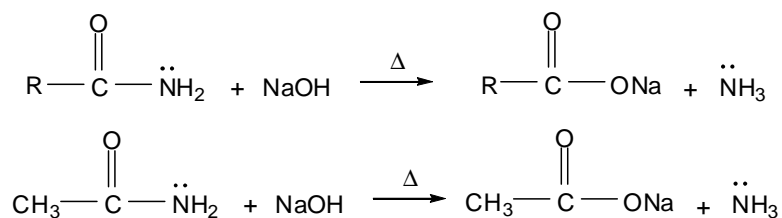
*Acid hydrolysis*



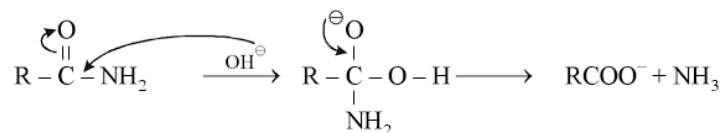
*Mechanism*



*Alkaline hydrolysis*

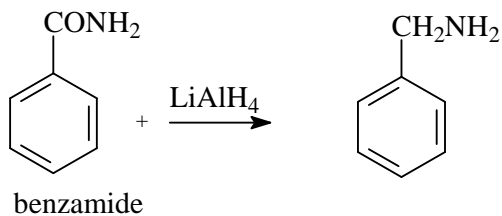
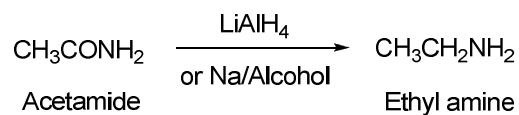


*Mechanism*

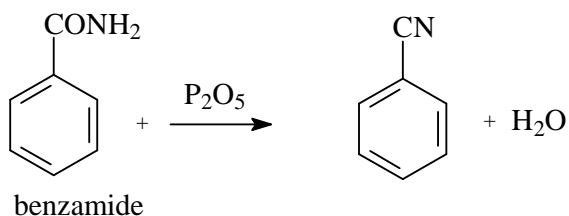
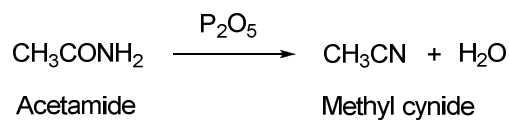


**3. Reduction:** Acid amides are reduced to primary amines with  $\text{LiAlH}_4$  or  $\text{Na}$  and alcohol.

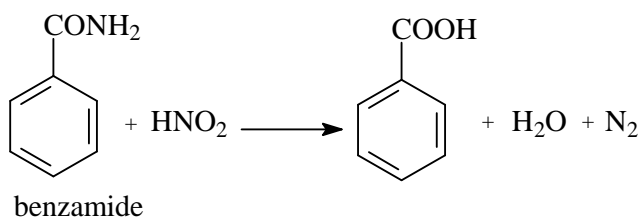
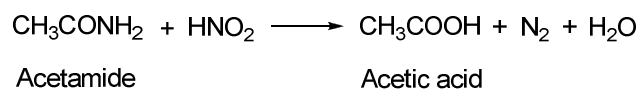




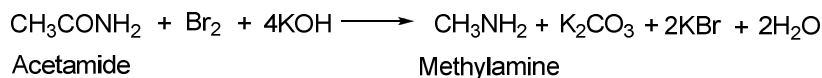
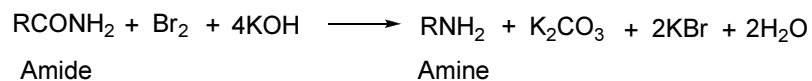
**4. Dehydration:** On heating with phosphorous pentoxide, amides lose a water molecule to produce cyanides or nitriles.



**5. Action of nitrous acid:** On treatment with nitrous acid, amides form acids with the evolution of nitrogen gas.



**6. Hoffmann's bromamide or Hoffmann's degradation reaction:** Amides on reaction with bromine and alcoholic potassium hydroxide form primary amines. This reaction is known as *Hoffmann bromamide or Hoffmann degradation reaction*.



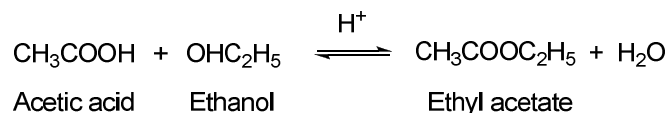
**Uses:** Amides are used as a solvent for several organic and inorganic compounds, wetting agent, plasticizer in cloths etc. They are also used in making explosives and leather tanning.

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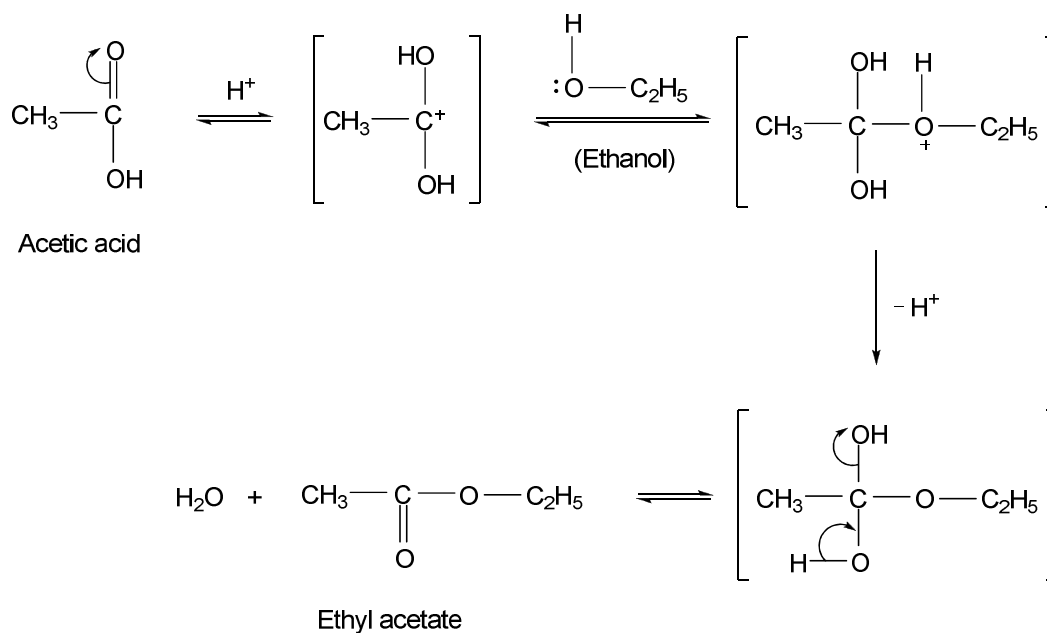
### ***7.8 MECHANISM OF ESTRIFICATION AND HYDROLYSIS (ACIDIC AND BASIC)***

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**(a) ESTERIFICATION:** When a carboxylic acid is treated with an alcohol in presence of an acid catalyst, an ester is formed along with water. This reaction is known as *Fischer esterification*.

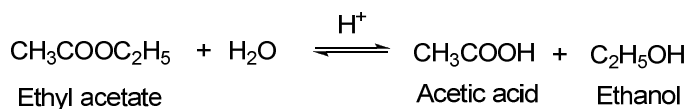


**Mechanism:** The sequential mechanism of esterification under acidic condition is as under:



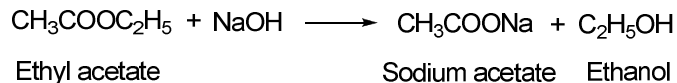
**(b) HYDROLYSIS:** Esters are not hydrolyzed easily with water, but hydrolyzed rapidly in acidic or alkaline medium. Both acid hydrolysis and alkaline hydrolysis are the examples of acyl nucleophilic substitution reactions.

*i. Acid hydrolysis:* When esters are boiled with water in presence of a strong acid like sulphuric acid or hydrochloric acid then carboxylic acids and alcohols are produced.



*ii. Alkaline hydrolysis:* When esters are boiled with an aqueous solution of a strong base like sodium hydroxide then sodium salts of carboxylic acids and alcohols are formed.

This reaction is known as *saponification reaction*.



*(i) Mechanism of acid hydrolysis:* The esters are hydrolysed in following steps.

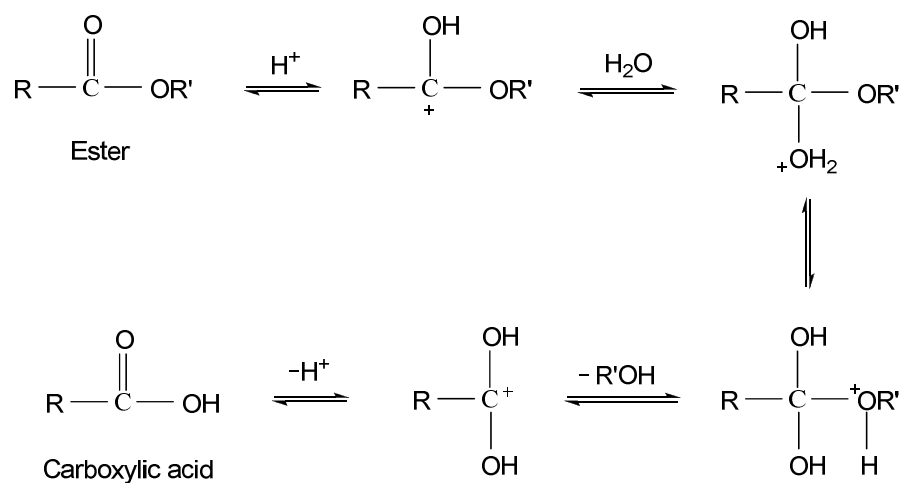
**Step 1:** Protonation of the ester carbonyl makes it more electrophilic.

**Step 2:** The 'O' atom of water acts as a nucleophile which attacks on the electrophilic C in the C=O group, with the electrons moving towards the oxonium ion, creating the tetrahedral intermediate.

**Step 3:** Deprotonate the oxygen that came from the water molecule to neutralize the charge.

**Step 4:** The  $-OR'$  group converts into a good leaving group by protonation, and  $R'OH$  is eliminated.

**Step 5:** Deprotonation of the oxonium ion reveals the carbonyl  $C=O$  group in the carboxylic acid product and regenerates the acid catalyst.

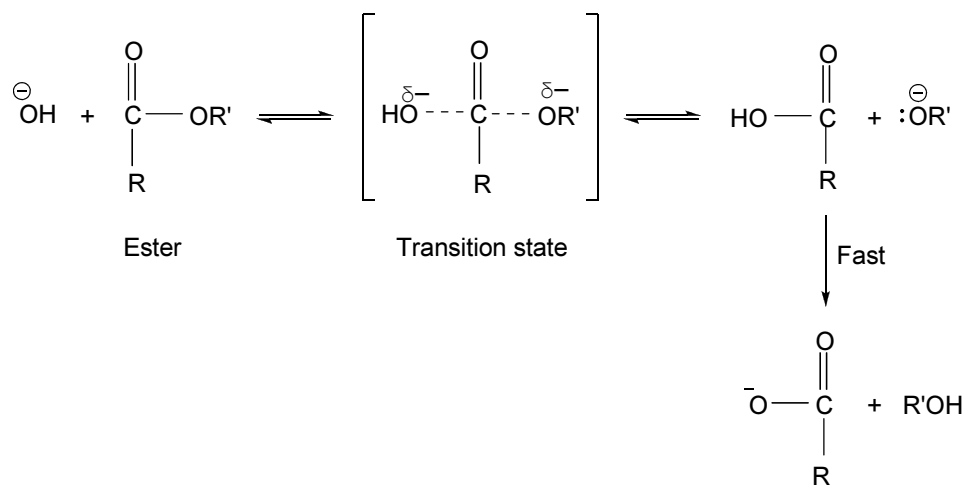


(ii) **Mechanism of alkaline hydrolysis:** In alkaline medium esters are hydrolysed in following sequential steps.

**Step 1:** The hydroxide nucleophile attacks at the electrophilic carbon of the ester  $C=O$ , and breaks the  $\pi$  bond to create a tetrahedral intermediate.

**Step 2:** This intermediate collapses to reform the  $C=O$  bond results the loss of alkoxide ( $RO^-$ ) group.

**Step 3:** A very rapid equilibrium coexist where the alkoxide ion ( $RO^-$ ) acts as a base for deprotonating the carboxylic acid.




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### 7.9 SUMMARY

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In continuation to unit 6 carboxylic acids, this unit make aware the readers about the most important functional derivatives of carboxylic acids like acyl chlorides (RCOCl), acid anhydrides ((RCO)<sub>2</sub>O), esters (RCOOR' where R and R' may be same or different), and amides (RCONH<sub>2</sub>) which are obtained by the replacement of -OH part of carboxyl group of acids by -Cl, -OCOR, -OR' or -NH<sub>2</sub>, groups respectively. This unit describes the methos of preparation, physical and chemical properties of functional derivatives of carboxylic acids, viz; a cyl chlorides can be prepared by by heating carboxylic acids with phosphorous trichloride (PCl<sub>3</sub>), phosphorus penta chloride (PCl<sub>5</sub>), or thionyl chloride (SOCl<sub>2</sub>),by the reaction of sodium salts of carboxylic acids with phosphorous trichloride (PCl<sub>3</sub>) or thionyl chloride (SOCl<sub>2</sub>). Acid anhydride can be obtained by the dehydration of carboxylic acids, by heating an acid chloride with a carboxylate salt,by heating sodium salts of carboxylic acids with acetic anhydride,by the reaction of excess amount of anhydrous ammonium salts of acid with phosphorus oxy-chloride or thionyl chloride etc. Esters can be prepared by the interaction of an alcohol with an acid in presence of a suitable acid catalyst, by the nucleophilic substitution of acid chlorides or acid anhydrides with alcohols, by the reaction of silver salt of acids on alkyl halides, by the action of the ethereal solution of diazomethane on carboxylic acid, by the interaction of an ether with carbon monoxideetc. Similarly amides are formed by the acylation of ammonia/amines with acyl chlorides, acid anhydrides or esters,by heating the ammonium salts of carboxylic acids,by the partial

hydrolysis of cyanides with concentrated hydrochloric acid, polyphosphoric acid or alkaline peroxide. This unit also describes the chemical properties of carboxylic acids derivatives, like hydrolysis, oxidation, reduction, reactions with hydrazine and its derivatives, reactions with  $P_2O_5$ ,  $PCl_5$ ,  $NH_2OH$ , diazomethane, ammonia, amines, action of heat etc. The uses of function derivatives of carboxylic acids has also been included.

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### ***7.10 TERMINAL QUESTIONS***

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#### **Section-A**

##### **Q.1 Long answered questions**

1. Describe the general methods of preparation, physical and chemical properties of acyl chlorides.
2. Give the preparation, physical and chemical properties of acid anhydrides.
3. How are acid esters prepared? Describe the important chemical properties of esters.
4. Describe the general methods of preparation, physical and chemical properties of amides.
5. Describe the mechanism of the acid and alkaline hydrolysis of esters.

#### **Section-B**

##### **Q.2 Short answered questions**

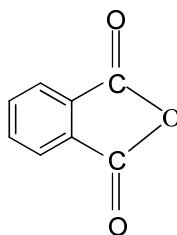
1. Explain the followings:
  - a) Acetyl chloride has lower boiling point than acetic acid.
  - b) Acetyl chloride is more reactive than acetic anhydride.
2. Compare the reactivity of carboxylic acid derivatives towards nucleophilic substitution.
3. How can you prepare acetyl chloride from carboxylic acids?
4. How can you prepare esters from silver salts of carboxylic acids?
5. How can you synthesize amides from cyanides?
6. Give the mechanism of esterification.
7. How can you convert:
  - a) Acyl chlorides into esters

- b) Esters into amides
  - c) Amides into amines
  - d) Amides into carboxylic acids
8. How will you obtained:
- a) Amides from acetyl chloride
  - b) Tertiary alcohol from acetyl chloride
  - c) Alcohols from acetic anhydrides
  - d) Acyl chlorides from esters

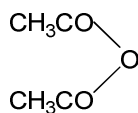
## Section-C

## Multiple choice questions (MCQ)

1. Which functional group is present in a carboxylic acid?
  - (a) -COOH
  - (b) -NO<sub>2</sub>
  - (c) C-O-C
  - (d) -SH
2. Which one of the followings is an ester?
  - a) RCOCl
  - (b) RCOOR'
  - (c) RCOOH
  - (d) RCONH<sub>2</sub>
3. What is the IUPAC name of the given compound?



- (a) *o*-Benzenedioic anhydride
  - (b) Butanedioic anhydride
  - (c) Ethanoic anhydride
  - (d) Phthalic anhydride
4. The given structure is for



- (a) Succinic anhydride
- (b) Diethyl ether
- (c) Acetic anhydride
- (d) Acetone

5. Acyl chloride can be obtained
- (a) By direct estrification.
  - (b) By the dehydration of acids.
  - (c) From cynohydrin reaction.
  - (d) From carboxylic acids.
6. Acyl chlorides are more reactive than other carboxylic acid derivatives
- (a) Because their boiling points are higher.
  - (b) Because they are heavier than water.
  - (c) Because they have a pleasant odor.
  - (d) Due to electron withdrawing inductive effect of chlorine atom.
7. On reaction with  $\text{NH}_3$  acid chloride forms
- (a) Carboxylic acid
  - (b) Amide
  - (c) Acid anhydride
  - (d) Alcohols
8. Esters undergo acid-hydrolysis form
- (a) Carboxylic acids
  - (b) Acyl chlorides
  - (c) Thioethers
  - (d) Alcohols
9. With  $\text{LiAlH}_4$  amides reduced to
- (a) Acids
  - (b) Alcohols
  - (c) Primary amines
  - (d) None of these
10. Anhydrides can be converted into esters with the reaction of
- (a) Acids
  - (b) Alcohols
  - (c) Amines
  - (d) Thionyl chloride
11. Reduction of acetyl chloride with  $\text{Pd/BaSO}_4$  will produce
- (a) Alcohols
  - (b) Ketones
  - (c) Acid
  - (d) Acetaldehyde
12. Amide reacts with nitrous acid ( $\text{HNO}_2$ ) to form
- (a) Acids
  - (b) Alcohols
  - (c) Amines
  - (d) Ketones
13. Esters can be prepared by the nucleophilic substitution of
- (a) Thiols
  - (b) Amides
  - (c) Acid anhydrides
  - (d) Acid chlorides



14. Which of the following gives a ketone on reaction with benzene?  
 (a) Tertiary amine (b) Acetyl chloride  
 (c) Alcohol (d) Esters
15. The major product (?) of the reaction is:  

$$\text{CH}_3\text{COOC}_2\text{H}_5 + \text{Br}_2 \xrightarrow{\text{Red P}} ? + \text{HBr}$$
 (a)  $\text{CH}_3\text{COOC}_2\text{H}_5\text{Br}$  (b)  $\text{CH}_2\text{CHBrCOOC}_2\text{H}_5$   
 (c)  $\text{CH}_2\text{BrCOOC}_2\text{H}_5$  (d)  $\text{CH}_3\text{BrCOOC}_2\text{H}_5$
16. Esters on reduction with alkali produce  
 (a) Carboxylic acids (b) Primary amines  
 (c) Sodium salts of carboxylic acids (d) Amides
17. Which one of the followings derivatives is most reactive towards nucleophilic substitution  
 (a) Acyl chloride (b) Acid anhydride  
 (c) Ester (d) Amide
18. Acid amides can be obtained by the  
 (a) Estrification (b) Partial hydrolysis of cyanides  
 (c) Reduction of Acetyl chloride (d) Hydrolysis of acyl chlorides
19. On reduction with  $\text{LiAlH}_4$  acetic anhydride produces  
 (a) Acids (b) Amides  
 (c) Alcohols (d) Ketones
20. On reaction with thionyl chloride ( $\text{SOCl}_2$ ), esters are converted into  
 (a) Acid anhydrides (b) Alcohols  
 (c) Amines (d) Acid chlorides

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### 7.11 ANSWERS (MCQ):

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26. (a)	27. (b)	28. (a)	29. (c)	30. (d)
31. (d)	32. (b)	33. (a)	34. (c)	35. (b)
36. (d)	37. (b)	38. (d)	39. (b)	40. (c)
41. (c)	42. (a)	43. (b)	44. (c)	45. (d)

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**7.12 REFERENCES**

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**UNIT-8 ORGANIC COMPOUNDS CONTAINING  
NITROGEN**

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**CONTENTS:**

- 8.1 Objectives
- 8.2 Introduction
- 8.3 Structure of nitro-compounds
- 8.4 Nomenclature of nitro compounds
- 8.5 Nitroarenes
- 8.6 Preparation of nitroarenes
- 8.7 Physical properties of nitroalkanes
- 8.8 Chemical reactions of nitroalkanes
- 8.9 Mechanism of nucleophilic substitution in nitroarenes
- 8.10 Reduction of nitroarenes in different conditions
- 8.11 Picric acid (2, 4, 6- trinitrophenol)
- 8.12 Physical properties of picric acid
- 8.13 Chemical properties of picric acid
- 8.14 Summary
- 8.15 Terminal questions
- 8.16 Answers (MCQ)
- 8.17 References

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## 8.1 OBJECTIVES

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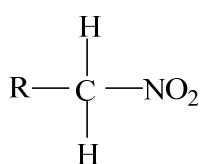
The main objectives of this unit are: To make the students aware about the organic compounds containing nitrogen particularly the aliphatic and aromatic nitro compounds, chemical properties of nitroalkanes, mechanism of nucleophilic substitution in nitroarenes. To explain the reduction of nitroarenes in different media and to describe the preparation, chemical properties and uses of picric acid.

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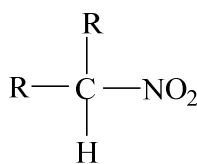
## 8.2 INTRODUCTION

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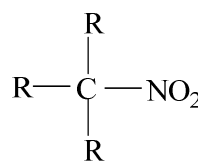
Nitro-compounds are those organic compounds which contain at least one nitro (-NO<sub>2</sub>) functional group in the molecule. These compounds are obtained by replacing one or more hydrogen in the hydrocarbon with nitro (-NO<sub>2</sub>) group. Nitro-compounds may be aliphatic or aromatic according to the nitro group attached to an alkyl or aryl group. The organic compounds where nitro group (-NO<sub>2</sub>) is directly attached to the carbon of hydrocarbon chain are known as aliphatic nitro compounds *e.g.* nitromethane (CH<sub>3</sub>NO<sub>2</sub>), nitroethane (C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub>), 1-nitropropane (NO<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), whereas the compounds where nitro group (-NO<sub>2</sub>) is directly attached to an aromatic ring are known as aromatic nitro compounds or nitroarenes such as nitrobenzene (C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>), *m*-dinitrobenzene, 2-nitroethylbenzene, *p*-nitrotoluene, *o*-nitroaniline, 2,4,6-trinitrophenol etc. The aliphatic nitro compounds may be further classified into primary, secondary or tertiary nitro compounds as the nitro group is attached to primary, secondary or tertiary carbon atom respectively.



Primary



Secondary



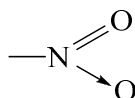
Tertiary

Nitro compounds are found naturally in plants and animals, and can be synthesized. These compounds are associated in many hormones, vitamins, and amino acids and proteins. These compounds possess wide chemical reactivity and used in the synthesis of several important products like drugs, agrochemicals, polymers (nylon), dyes and

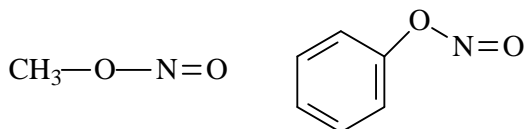
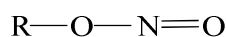
explosives. There are many functional groups, which contain one or more nitrogen atoms includes nitro compounds, amines, cyanides, isocyanides, diazo compounds etc.

### 8.3 STRUCTURE OF NITRO COMPOUNDS

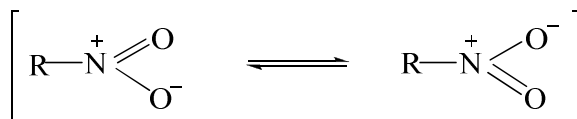
The nitro group is an ambident group and is capable of getting attached to carbon chain through nitrogen as well as through oxygen (-O-N = O) atom.



The compound in which the -NO<sub>2</sub> group is linked to the alkyl or aryl group through oxygen atom are called nitrites. Nitrites are isomeric with nitro compounds. These compounds are also known as alkyl esters of nitrous acid. The general formula of an alkyl nitrite is as:



The nitrogen is trigonal planar with a bond angles of 120°, there are two resonance forms so implying that the two oxygen's are equivalent.



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**8.4 NOMENCLATURE OF NITRO COMPOUNDS**


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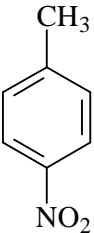
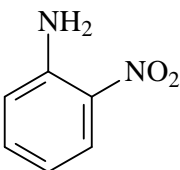
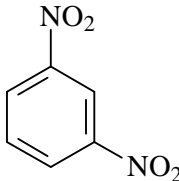
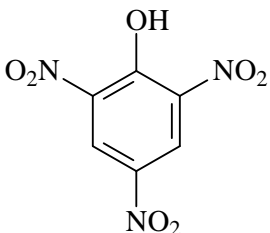
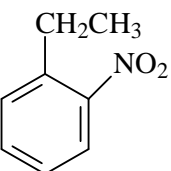
In IUPAC system, nitro compounds are named by prefixing "nitro" before the name of hydrocarbon in which the nitro group is substituted. Arabic numerals are used to indicate the position of nitro group and other substitutes if any.

***Aliphatic nitro compounds:***

COMPOUNDS	IUPAC NAME
↓	↓
$\text{CH}_3\text{NO}_2$	nitromethane
$\text{CH}_3\text{CH}_2\text{NO}_2$	nitroethane
$\text{CH}_3\text{CH}_2\text{CH}_2\text{NO}_2$	1- nitropropane
$\begin{array}{c} \text{NO}_2 \\   \\ \text{CH}_3-\text{CH}-\text{CH}_3 \end{array}$	2- nitropropane
$\begin{array}{c} \text{NO}_2 \\   \\ \text{CH}_3-\text{C}-\text{CH}_3 \\   \\ \text{CH}_3 \end{array}$	2- methyl - 2- nitropropane

***Aromatic nitro compounds***

COMPOUNDS	IUPAC NAME
↓	↓
$\begin{array}{c} \text{NO}_2 \\   \\ \text{C}_6\text{H}_5 \end{array}$	nitrobenzene
$\begin{array}{c} \text{NO}_2 \\   \\ \text{C}_6\text{H}_4 \\   \\ \text{NO}_2 \end{array}$	m- nitrobenzene

COMPOUNDS	IUPAC NAME
	p - nitrotoluene
	o - nitroaniline
	m - dinitrobenzene
	2, 4, 6 - trinitrophenol
	2 - nitroethylbenzene

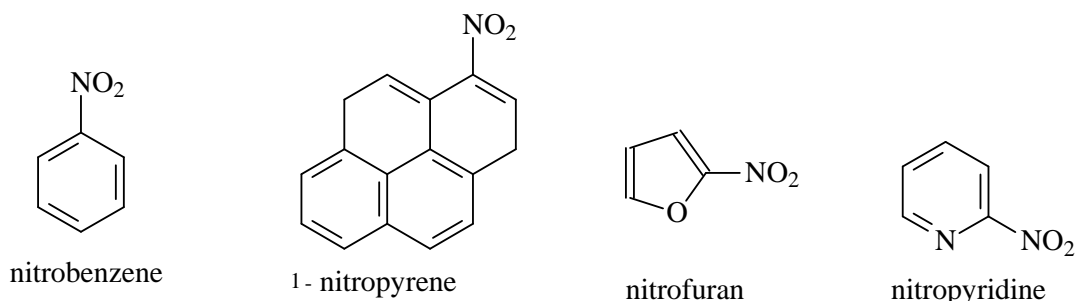
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## 8.5 NITROARENES

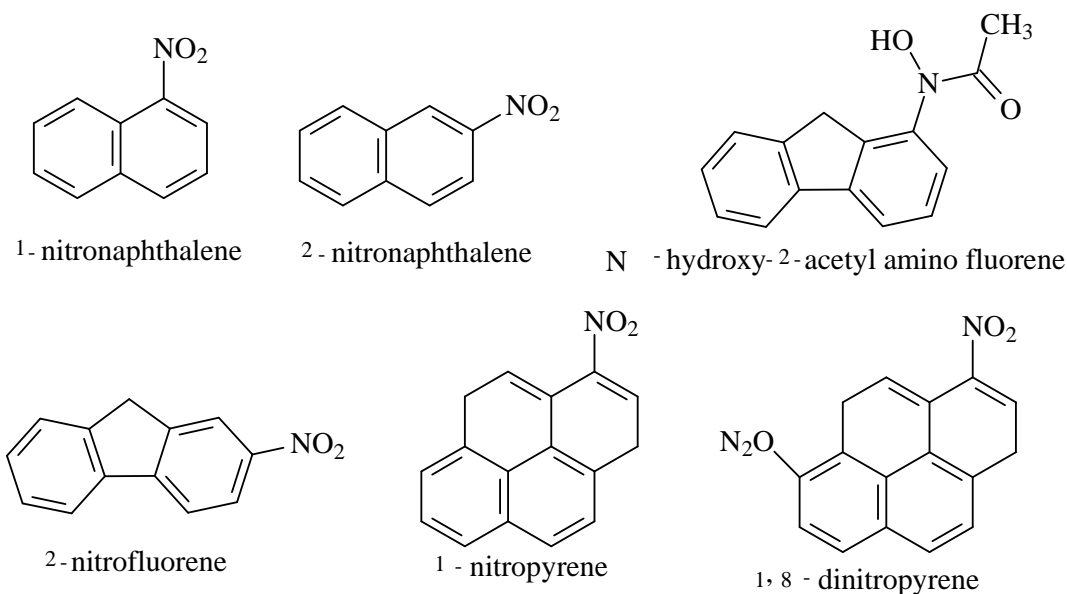
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Nitroarenes are organic compounds consist at least one  $-\text{NO}_2$  group attached to an aromatic ring *e.g.* nitrobenzene, *o*-nitrotoluene, *p*-nitrotoluene, 4-nitrophenol, 2,6-dinitrotoluene, 2,4,6-trinitrotoluene, 1,3,5-trinitrobenzene etc. These compounds are mainly included:

1. One or two nitrated fused ring ( $\text{NO}_2\text{-Ar}$ ) compounds (*e.g.* nitrobenzene)
2. Nitrated polycyclic aromatic hydrocarbons ( $\text{NO}_2\text{-PAH}$ ) (*e.g.* 1-nitropyrene)
3. Nitrated heterocyclic compounds (*e.g.* nitrofurans, nitropyridine etc.)



Nitroarenes are mainly exhausted in the atmosphere from combustion sources by the incomplete combustion of fossil fuels. Nitroarenes have been detected in particulate matter from diesel engine emissions, gasoline engine emissions, kerosene heaters, gas burners, motor oils, coal fly ash, extracts of coke-oven emissions, carbon black, cigarette smoke and grilled chicken. Nitroarenes have also been found in the indoor environment in particulate emissions from kerosene heaters, home heaters, gas burners and wood burning stoves used for cooking. Recent studies showed that several nitrated polycyclic aromatic hydrocarbons causes cancer. 1-nitronaphthalene, 2-nitronaphthalene, *N*-hydroxy-2-acetyl amino fluorene, 2-nitro fluorene, 1-nitropyrene, 1,8-dinitropyrene; nitroarenes have been reported as carcinogens.

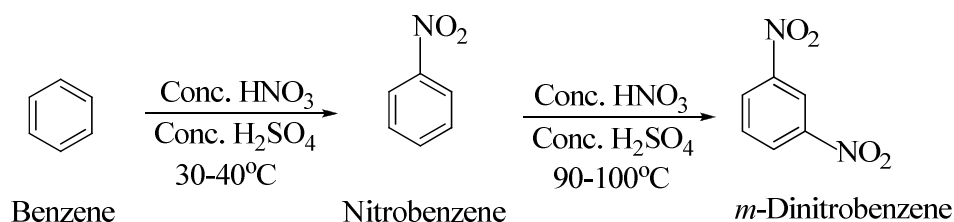




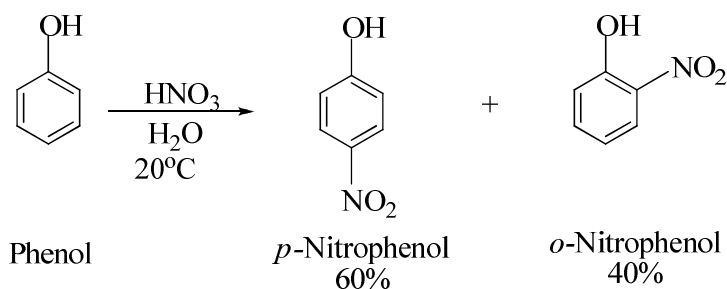
### 8.6 PREPARATION OF NITROARENES

Nitroarenes can be prepared by the following general methods:

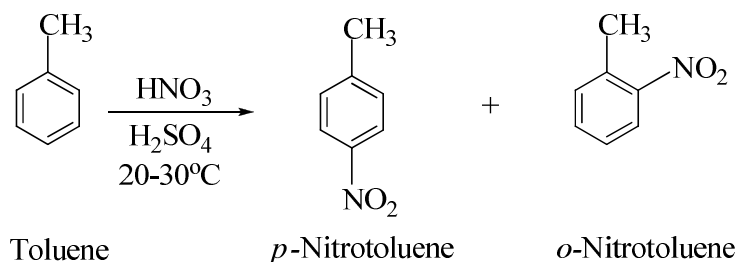
**1. By the nitration of aromatics:** The aromatic nitro compounds can be prepared by the direct nitration of aromatics. The formation of nitroarene depends upon the temperature, nature of the nitrated aromatic compound and nature of reagent used. For example, nitrobenzene is prepared by the direct nitration of benzene using concentrated  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  at about  $30\text{-}40^\circ\text{C}$ .



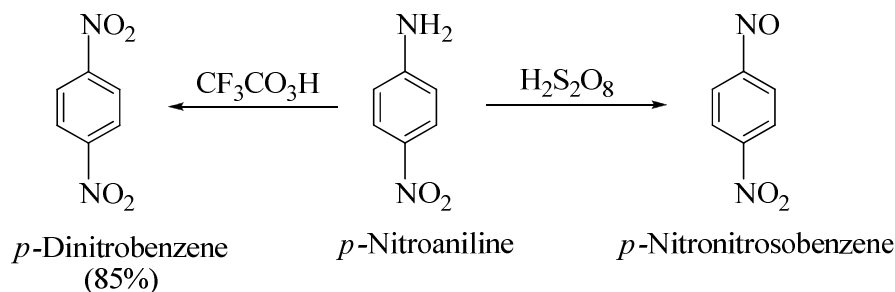
The nitrophenol is prepared by the nitration of phenol in presence of  $\text{HNO}_3$  and  $\text{H}_2\text{O}$  at  $20^\circ\text{C}$ .



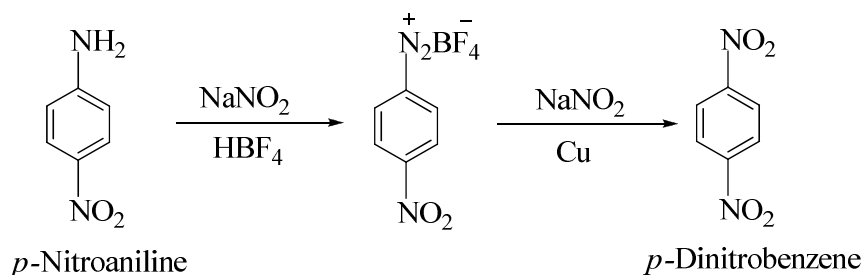
Nitrotoluene can be prepared by the nitration of toluene with concentrated  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  at about  $20\text{-}30^\circ\text{C}$ .



**2. By the oxidation of amino group to nitro group:** *p*-dinitrobenzene can be prepared by the oxidation of amino group into nitro group with per-acids such as persulphuric acid ( $\text{H}_2\text{S}_2\text{O}_8$ ) and peroxy trifluoroacetic acid ( $\text{CF}_3\text{CO}_3\text{H}$ ).



**3. By the replacement of amino group by nitro group:** The  $-\text{NH}_2$  group in aromatic group can be replaced by treating the compound with  $\text{NaNO}_2/\text{HBF}_4$  as follow




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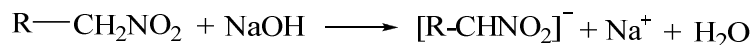
## 8.7 PHYSICAL PROPERTIES OF NITROALKANES

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The nitroalkanes possess following physical properties

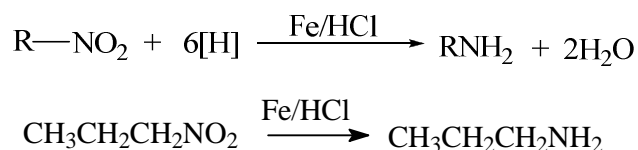
1. Most nitro compounds are yellow crystalline solids; few are pale yellow liquids (*e.g.* nitrobenzene) with strong characteristic odor, whereas nitro-alkanes are colorless oily liquids with pleasant smell.
2. Nitro compounds are insoluble in water but soluble in organic solvents.
3. The density of nitro compounds is greater than 1, therefore they are heavier than water.
4. Nitro compounds have high boiling points than their corresponding hydrocarbons due to high polarity. Their melting and boiling points increase with the number of nitro groups present. For example, the boiling point of nitrobenzene is  $211^\circ\text{C}$  whereas the boiling point of *m*-dinitrobenzene is  $303^\circ\text{C}$ .





**2. Reduction:** Nitro compounds can be reduced to primary amines under a variety of conditions. Various reduction stages of the nitro group are given below: The final product depends upon the pH of the reaction medium and nature of the reducing agent.

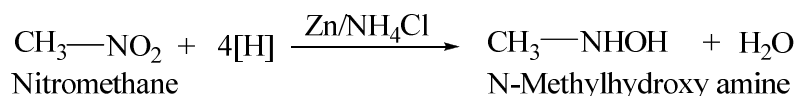
**(i) Reduction in acidic medium:** Nitroalkanes can be reduced to the corresponding primary amines by a combination of active metals (Zn, Fe or Sn) and concentrated hydrochloric acid (HCl).



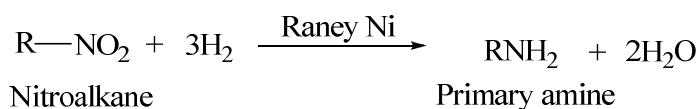
**(ii) Reduction in neutral medium:** Reduction with zinc dust and ammonium chloride solution in neutral medium, nitroalkanes are converted into corresponding *N*-alkyl hydroxyl amines.



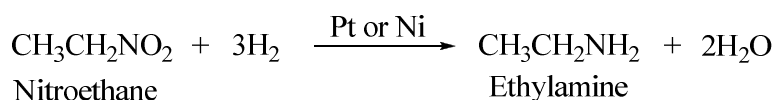
Nitromethane on reduction with zinc dust and ammonium chloride solution in neutral medium converted into *N*-methylhydroxy amine.



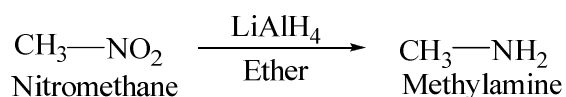
**(iii) Catalytic reduction:** The nitro group of an aliphatic and aromatic nitro compound is easily reduced to corresponding primary amines with hydrogen using raney Ni, Pt or Pd catalyst.



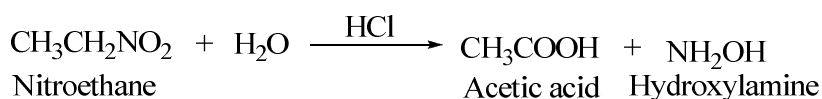
The nitroethane is reduced to ethylamine with Pt or Ni catalyst.



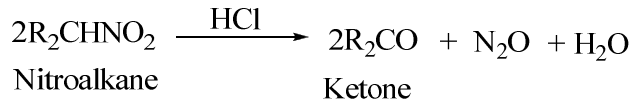
(iv) **Reduction with metal hydrides:** Nitroalkanes are easily reduced to corresponding primary amines with  $\text{LiAlH}_4$ .



**3. Hydrolysis:** When primary nitroalkanes are heated with boiling  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$  undergo hydrolysis to form carboxylic acid and corresponding salt of hydroxyl amine. This reaction is used for the manufacturing of hydroxylamine.

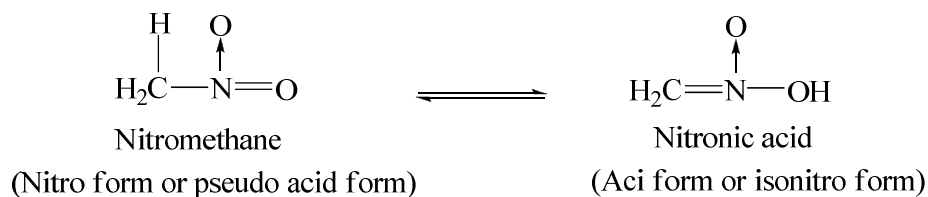


Secondary nitroalkanes hydrolyze with boiling  $\text{HCl}$  to give ketones and nitrous oxide.



Tertiary nitroalkanes, however do not generally undergo hydrolysis with hydrochloric acid.

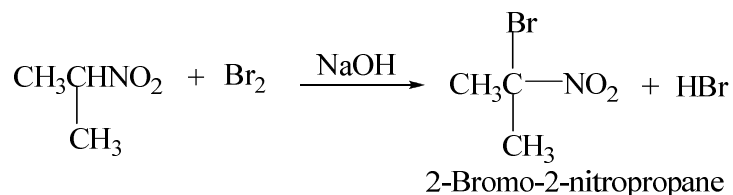
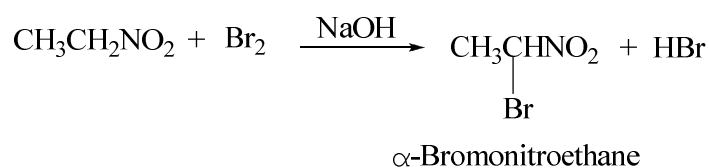
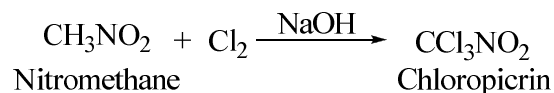
**4. Tautomerism:** Nitroalkanes containing  $\alpha$ -hydrogen atoms, *i.e.*, primary and secondary nitroalkanes, show tautomerism. For example, nitromethane exists in two tautomeric forms, nitro form and isonitro form.



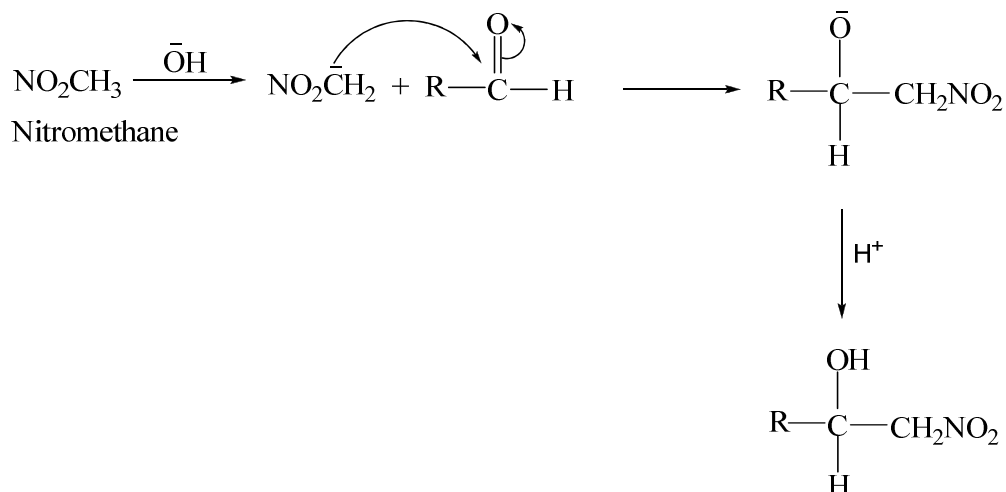
The nitro form is often called *pseudo acid form* whereas the aci-form is called *nitronic acid*. Similarly, nitroethane, 1-nitropropane, 2-nitropropane, show tautomerism whereas

aromatic nitro compounds like nitrobenzene, *m*-dinitrobenzene etc., and tertiary nitro compounds do not show tautomerism due to the absence of  $\alpha$ -hydrogen atom on  $\alpha$ -carbon atom.

**5. Halogenation:** Primary and secondary nitroalkanes on treatment with halogen (chlorine or bromine) in presence of alkali form halonitroalkanes. During this reaction, all three hydrogen atoms of nitroalkanes are replaced by the halogen atoms.

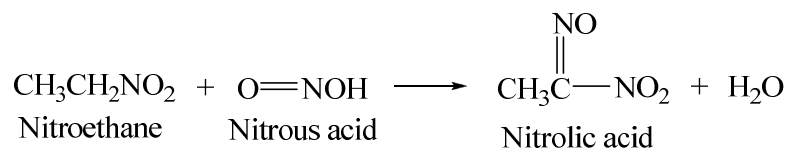


**6. Reaction with aldehydes:** Nitroalkanes having  $\alpha$ -hydrogen can undergo nucleophilic addition reaction with aldehydes similar to aldol type addition reaction.

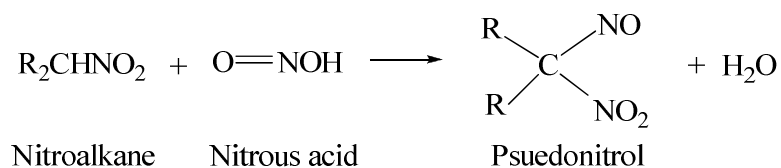


**7. Action with nitrous acid:** Nitroalkanes on reaction with nitrous acid give different products depending upon the type of nitro compound.

Primary nitroalkanes on reaction with nitrous acid give nitrolic acids which dissolve in alkalies to form a red solution.



Whereas, secondary nitroalkanes on reaction with nitrous acid give blue colored pseudonitroles which do not dissolve in alkali.



Tertiary nitroalkanes do not react with nitrous acid since they do not have  $\alpha$ -hydrogen atom.

**Uses of nitro compounds:** Nitroalkanes *e.g.* nitromethane, nitroethane etc. and nitrobenzene are extensively used as solvent in industry.

1. Nitroarenes are important intermediates in the manufacture of polymers detergents, dyes and pharmaceuticals.

- Nitroarenes are also used for the preparation of explosives such as 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitrobenzene (TNB), research and development explosive (RDX).
- Chloropicrin is used as an insecticide.

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### 8.9 MECHANISM OF NUCLEOPHILIC SUBSTITUTION IN NITROARENES

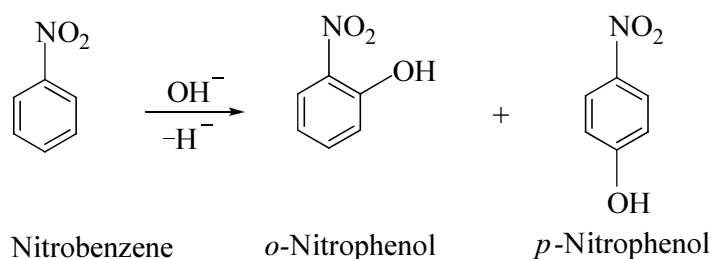
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Nucleophilic aromatic substitution occurs with a variety of strong nucleophiles, including  $\text{-OH}$ ,  $\text{-OR}$ ,  $\text{-NH}_2$ ,  $\text{-SR}$ , and neutral nucleophiles such as  $\text{NH}_3$  and  $\text{RNH}_2$ . The mechanism of nucleophilic aromatic substitution is an addition-elimination type; therefore the mechanism of these reactions has two important steps:

- Addition of the nucleophile to form a resonance-stabilized carbanion
- Elimination of hydrogen or halogen leaving group.

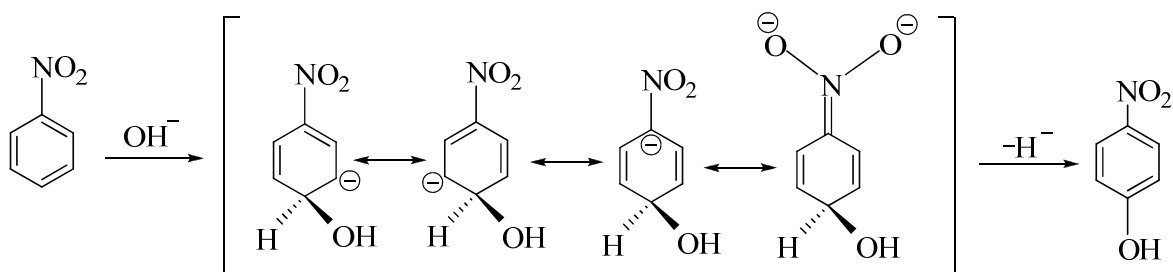
*For example: 1. Nucleophilic aromatic substitution in nitrobenzene*

Nitrobenzene reacts with  $\text{-OH}$  nucleophile to form the *o*-nitrophenol and *p*-nitrophenol.

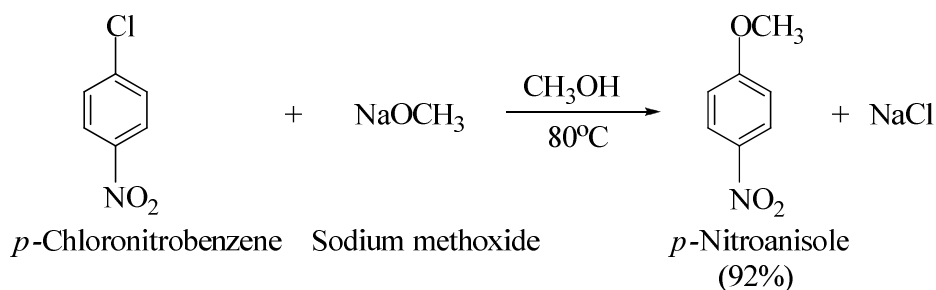


*Mechanism:* The mechanism for the formation of *p*-nitrophenol from nitrobenzene is as follows:

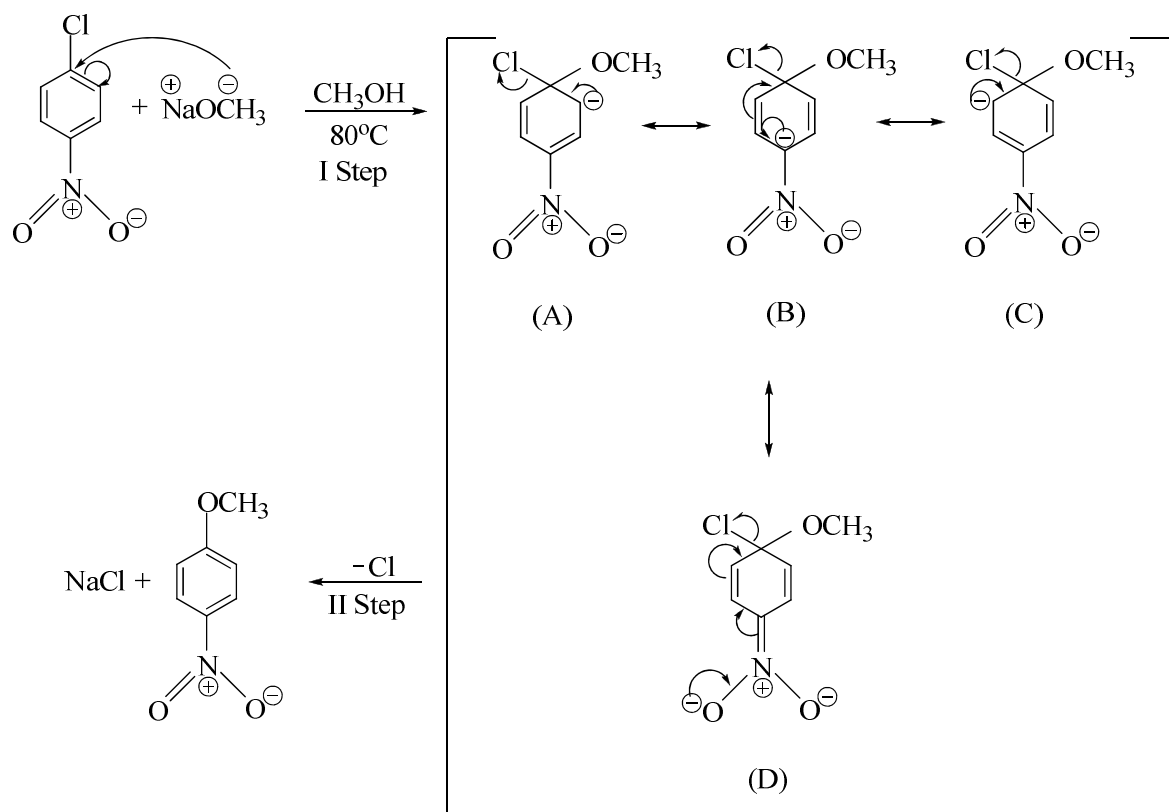




**2. Addition elimination mechanism of nitrochlorobenzene:** The nitro substituted aryl halides undergo reaction with nucleophiles such as ammonia and hydroxide, where the chlorine is eliminated/substituted *e.g.* *p*-chloronitrobenzene reacts with sodium methoxide at 85 °C to form the *p*-nitroanisole.



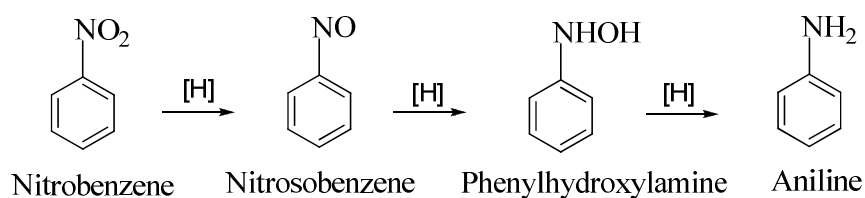
The mechanism of the formation of *p*-nitroanisole from *p*-chloronitrobenzene is as follows:



### 8.10 REDUCTION OF NITROARENES IN DIFFERENT CONDITIONS

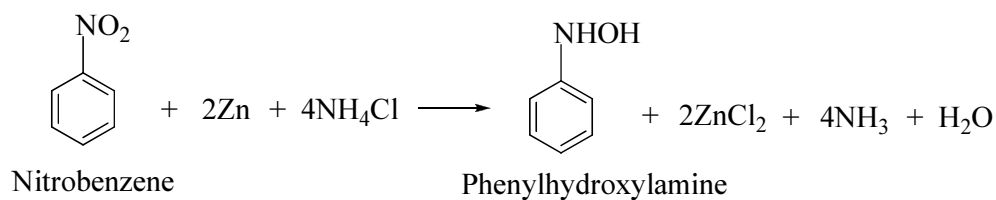
The nitroarenes give different products while reduced in different reaction conditions such as nature of reducing agents and the pH of the reaction medium as follow

**(i) Reduction of nitroarenes in acidic medium:** Nitroarenes can be easily reduced to corresponding primary aryl amines by tin metal and hydrochloric acid. For example, the reduction of nitrobenzene with tin metal and hydrochloric acid gives aniline.

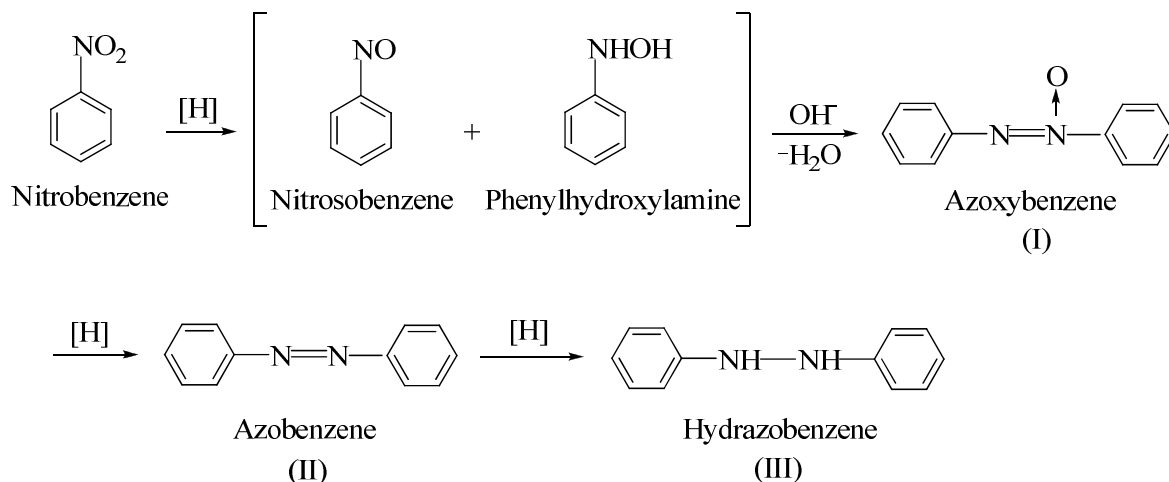


*Mechanism:*





(iii) **Reduction of nitroarenes in alkaline medium:** Whilst acidic and neutral reduction result in the formation of mono-nuclear compounds, reaction in alkaline medium yields a variety of binuclear compounds due to the interaction of nitroso- and hydroxylamine derivatives formed during the reduction. The reduction of nitrobenzene yields different products depending upon the nature of reducing agent used. The scheme of alkaline reduction is given below:

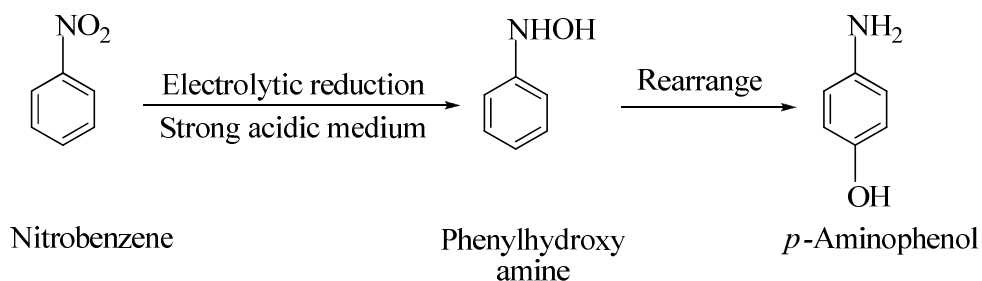
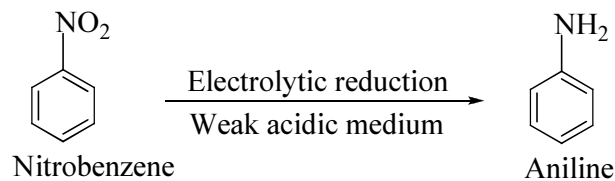


(i) The product-I, azoxybenzene is formed by the reduction of nitrobenzene with alkaline sodium arsenite ( $\text{Na}_3\text{AsO}_3/\text{NaOH}$ ).

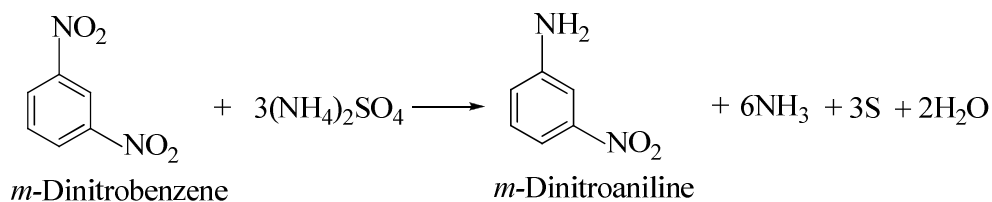
(ii) The product-II, azobenzene is formed, when nitrobenzene is reduced with zinc dust and methanolic caustic soda solution, or by alkaline stannite.

(iii) The product-III, hydrazobenzene is obtained by reduction of nitrobenzene with zinc dust and aqueous sodium hydroxide ( $\text{Zn}/\text{NaOH}$ ).

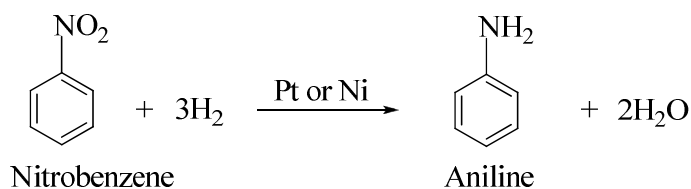
(iv) **Electrolytic reduction:** Electrolytic reduction of nitrobenzene in weakly acidic medium gives aniline but in strongly acidic medium, it gives *p*-aminophenol obviously through the acid catalyzed rearrangement of initially formed phenyl hydroxyl amine.



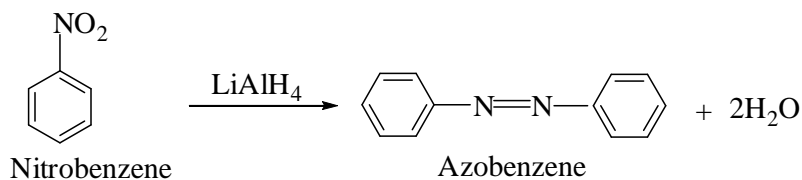
(v) **Selective reduction:** If two or more nitro groups are present in the benzene ring, it is possible to reduce one of them without affecting the others. Such reductions are called selective reductions. For example, reduction of *m*-dinitrobenzene with sodium or ammonium sulphide gives *m*-nitroaniline. This reduction of nitro compounds with sulphides and polysulphides is called **Zinin reduction**.



(vi) **Catalytic reduction:** Nitrobenzene is reduced to aniline with hydrogen using Pt or Ni catalyst.



(vii) **Reduction with metal hydride:** Aromatic nitro compounds on reduction with  $\text{LiAlH}_4$  give azo compounds.

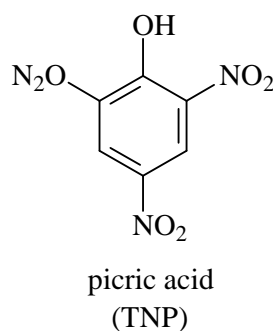



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### 8.11 PICRIC ACID (2, 4, 6-TRINITROPHENOL)

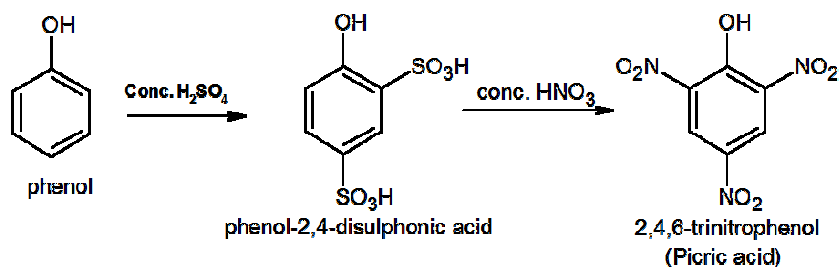
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Picric acid is the chemical compound formally called 2, 4, 6-trinitrophenol (TNP). It has a chemical formula  $\text{C}_6\text{H}_3\text{N}_3\text{O}_7$ . Its name comes from a Greek word *pikros* means "bitter", reflecting the bitter taste of picric acid.

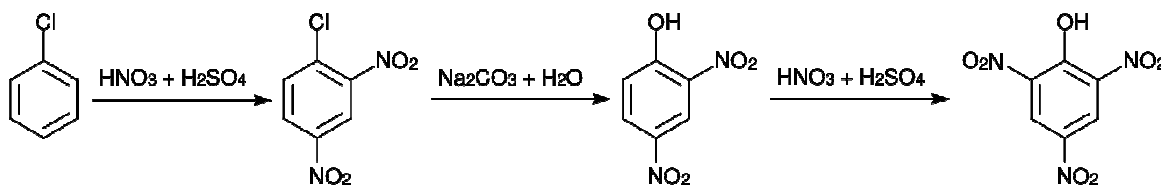


**Preparation of picric acid:** TNP can be synthesized by various methods as:

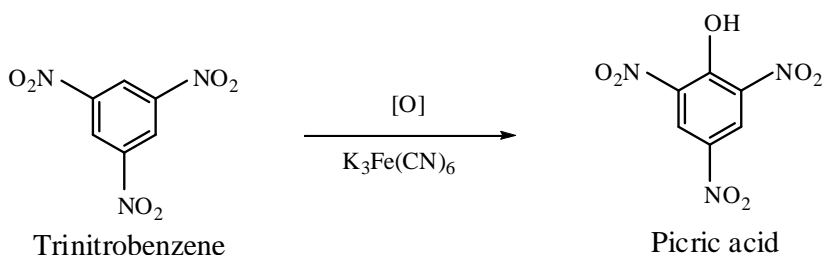
**1. From phenol:** Picric acid can be prepared from phenol by sulphonation followed by the nitration.



2. **From chlorobenzene:** Picric acid can be obtained by the reaction of nitric acid followed by hydrolysis and followed by nitration.



3. **From trinitro benzene:** Picric acid can be prepared by the oxidation of sym-trinitrobenzene with potassium ferricyanide.




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## 8.12 PHYSICAL PROPERTIES OF PICRIC ACID

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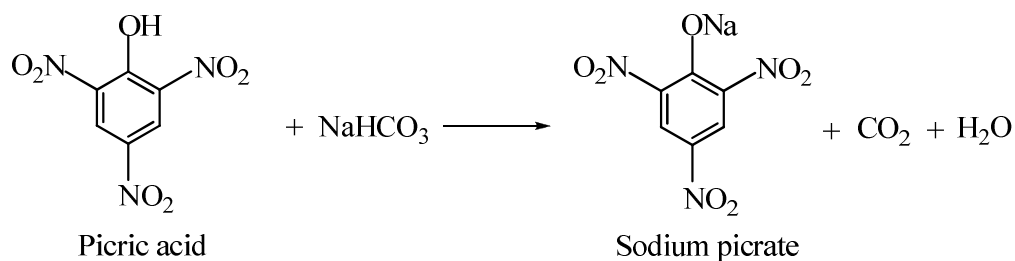
Picric acid is a yellow crystalline solid and one of the most acidic phenols. It is volatile, flammable, highly toxic and bitter in taste. Its melting point is 122°C. It is sparingly soluble in water, but soluble in hot water, alcohols and ethers. It is explosive when dry and forms picrates when exposed with metals. Picric acid is especially hazardous because it is volatile and slowly sublimates even at room temperature.

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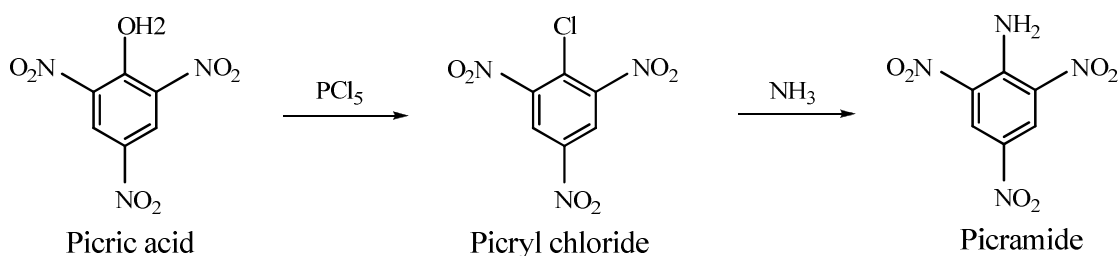
## 8.13 CHEMICAL PROPERTIES OF PICRIC ACID:

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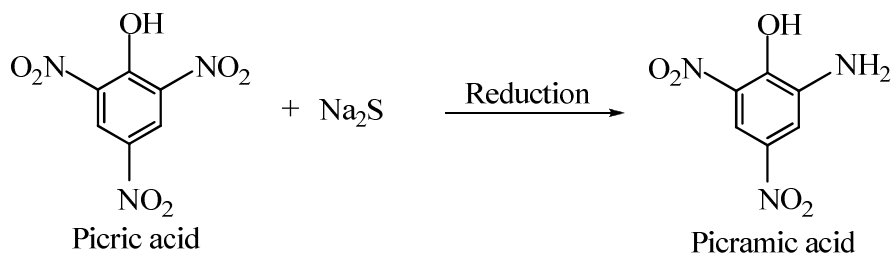
1. Picric acid is much stronger acidic than phenol due to  $-\text{NO}_2$  functional group. Picric acid reacts with  $\text{NaHCO}_3$  to liberate  $\text{CO}_2$ .



2. Picric acid on reaction with phosphorus pentachloride forms picryl chloride.



3. On reduction with sodium sulphide (Na<sub>2</sub>S) in presence of water, picric acid gives picramic acid.



**Uses:** Picric acid is used in electric batteries, leather industry, dyes, pigments, inks, paints, manufacture of colored glass, textile mordents, as a laboratory reagent, in matches and explosives.



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### 8.14 SUMMARY

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This unit reveals the knowledge of organic compounds in which nitrogen is covalently attached with carbon like alkyl or aryl groups. Emphasis has been given particularly to aware the readers about organic compounds which contain at least one nitro functional group in the molecule generally known as nitro-compounds. These compounds may be aliphatic or aromatic according to the nitro group attached to alkyl or aryl group. Aromatic nitro compounds, also called nitroarenes, having  $-\text{NO}_2$  group on *o*, *m* or *p* position of a benzene ring *e.g.* nitrobenzene, *o*-nitrotoluene, *p*-nitrotoluene, 4-nitrophenol, 2,6- dinitrotoluene, 2,4,6-trinitrotoluene, 1,3,5-trinitrobenzene etc. These compounds can be prepared by the direct nitration of aromatic compounds, by the oxidation of amino group to nitro, by the replacement of amino group by nitro etc. The aliphatic nitro compounds can be primary, secondary or tertiary types depending upon the nature of carbon with which  $-\text{NO}_2$  group is attached. The primary and secondary aliphatic nitro compounds  $\alpha$ -hydrogen containing are acidic due to electron withdrawing nature of nitro group. The nitro compounds are easily reduced with various reducing agents in different mediums. The final product formed depends on the nature of reducing agent and the pH of the medium. This unit also describes the individual nitro compound picric acid (2, 4, 6-trinitrophenol) which can be obtained by the sulphonation of phenol followed by the nitration, by the reaction of nitric acid followed by hydrolysis and followed by nitration, by the oxidation of trinitrobenzene with potassium ferricyanide. The physical, chemical properties alongwith the uses of picric acid has also been described in this unit.

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### 8.15 TERMINAL QUESTIONS

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#### Section-A

#### Long answered questions

1. What are nitro compounds? Describe the nomenclature and general methods of preparation of nitroarenes.
2. Describe the chemical properties of nitroalkanes.

3. How can you prepare nitroarenes from: (i) the nitration of aromatics (ii) from *p*-nitrobenzene (iii) from *p*-nitroaniline?
4. Describe the mechanism of
- Nucleophilic aromatic substitution in nitroarenes.
  - Reduction of nitrobenzene in acidic medium.
5. Describe the general methods of preparation, chemical properties and uses of picric acid.

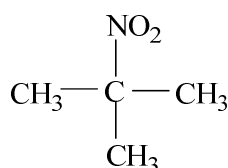
**Section-B****Short answered questions**

- What are nitro compounds? Explain the structure of nitro compounds.
- How can you distinguish between alkyl and aryl nitro compounds?
- Write a short note on nitroarenes.
- Write the physical properties of nitro compounds.
- Describe the reduction of nitrobenzene in acidic, neutral and alkaline medium.
- Give the mechanism of nucleophilic substitution in nitroarenes.
- Explain the followings:
  - Acidic character of nitroalkanes
  - Halogenation of nitroalkanes
- How can you convert?
  - Primary nitroalkanes into carboxylic acids
  - Secondary nitroalkanes into ketones
  - Nitroalkane into primary amine
  - Nitromethane to chloropicrin
- How will you obtain:
  - Nitrobenzene from benzene
  - p*-Nitronitrosobenzene from *p*-dinitrobenzene
  - Picric acid from chlorobenzene
  - Picramide from picric acid

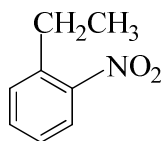
## Section-C

## Multiple choice questions (MCQ)

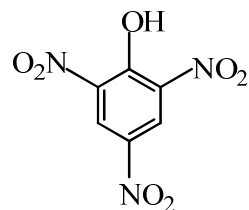
- Which functional group is present in a nitro compounds?  
(a) -COOH (b) -NO<sub>2</sub>  
(c) C-O-C (d) -SH
- Which one of the followings is a nitroalkane?  
(a) CH<sub>3</sub>SH (b) CH<sub>3</sub>OH  
(c) CH<sub>3</sub>CH<sub>2</sub>NO<sub>2</sub> (d) CH<sub>3</sub>SCH<sub>3</sub>
- What is the IUPAC name of the given compound?



- (a) 2-Methyl-2-nitropropane (b) Ethanethiol  
(c) Triethyl nitro (d) Ethyl hydrogen sulphide
- What is the IUPAC name of the given nitroarene?



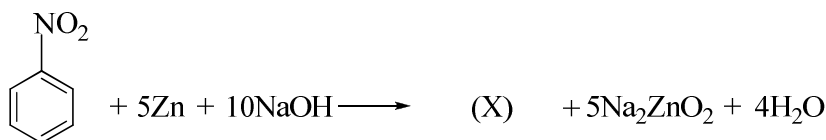
- (a) 2-Methyl-2-nitropropane (b) 2-Nitroethyl benzene  
(c) *p*-Nitrotoluene (d) 2-Nitroethyl toluene
- The given structure is for



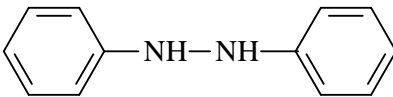
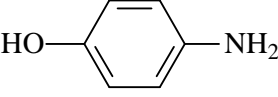
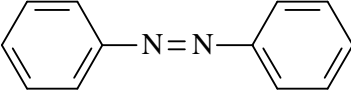
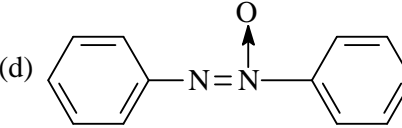
- (a) Aspirin (b) RDX  
(c) Picric acid (d) Trinitrotoluene

6. Nitroarenes can be obtained
- (a) By heating haloalkanes with potassium sulphide.
  - (b) By the oxidation of alcohols with  $\text{KMnO}_4$ .
  - (c) By heating alkyl halide with alcoholic  $\text{AgNO}_2$ .
  - (d) By the nitration of benzene.
7. Nitroalkanes are more acidic than corresponding hydrocarbons
- (a) Because their boiling points are higher.
  - (b) Because they are heavier than water.
  - (c) Because they have a pleasant odor.
  - (d) Due to the electron withdrawing nature of nitro group.
8. The reduction nitroalkanes with Fe and concentrated HCl give
- (a) Hydroazobenzene
  - (b) Primary amines
  - (c) Hydroxylamine
  - (d) Azobenzene
9. Secondary nitroalkanes undergo hydrolysis with boiling HCl give
- (a) Ketones
  - (b) Carboxylic acids
  - (c) Thioethers
  - (d) Alcohols
10. Reduction in which the nitroalkanes are reduced to corresponding N-alkyl hydroxyl amines with zinc dust and ammonium chloride solution is conducted in
- (a) Acidic medium
  - (b) Alkaline medium
  - (c) Neutral medium
  - (d) None of these
11. Nitrobenzene is converted into azobenzene by reduction with
- (a) Alkaline sodium stannite
  - (b) Alkaline sodium arsenite
  - (c) Zinc and ammonium chloride
  - (d) Zinc metal and aqueous sodium hydroxide
12. Reduction of nitrobenzene with  $\text{LiAlH}_4$  will produce
- (a) Azoxybenzene
  - (b) p-Aminophenol
  - (c) m-Dinitrobenzene
  - (d) Aniline
13. Nitroethane reacts with nitrous acid ( $\text{HNO}_2$ ) to form
- (a) Nitrolic acid
  - (b) Nitrous oxide
  - (c) Hydroxylamine
  - (d) Ethanamide
14. Tertiary nitroalkanes cannot tautomerise because they

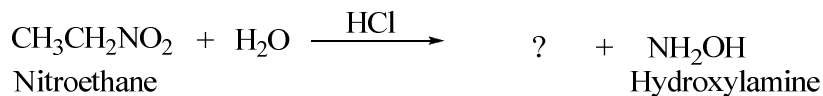
- (a) Are stable (b) Are not stable  
 (c) Are saturated hydrocarbons (d) Do not contain  $\alpha$ -hydrogen
15. Which of the following gives a ketone when boiled with concentrated HCl?  
 (a) Primary nitroalkanes (b) Secondary nitroalkanes  
 (c) Tertiary nitroalkanes (d) All of the above
16. The major product (X) of the reaction is:



Nitrobenzene

- (a)  hydrazobenzene
- (b)  p-aminophenol
- (c)  azobenzene
- (d)  azoxybenzene

17. Nitromethane on reduction with Zn and  $\text{NH}_4\text{Cl}$  gives:  
 (a) Methanamide (b) Ethylamine  
 (c) *N*-Methylhydroxy amine (d) Methylamine
18. Which compound is obtained at the end of the following reaction?



- (a) Acetic acid (b) Formaldehyde  
 (c) Methanethiol (d) Methyl chloride
19. Chloropicrin is formed by the halogenation of nitromethane with  
 (a) Bromine (b) Chlorobenzene  
 (c) Chlorine (d) Toluene
20. The reduction of nitrobenzene with zinc and sodium hydroxide gives  
 (a) Azobenzene (b) Azoxybenzene  
 (c) Nitrosobenzene (d) Hydrazobenzene
21. Picric acid can be obtained from

- (a) Hydrolysis of picryl chloride  
 (b) Phenol by sulphonation followed by the nitration  
 (c) Nitration of benzoic acid  
 (d) Nitration of toluene
22. On reduction with  $\text{NaHCO}_3$ , picric acid gives  
 (a) Picramide (b) *m*-Dinitrobenzene  
 (c) Sodium picrate (d) Picramic acid
23. The reduction of picric acid with sodium sulphide ( $\text{Na}_2\text{S}$ ) in presence of water gives  
 (a) Picramic acid (b) Picramide  
 (c) Sodium picrate (d) Trichlorobenzene
24. The reduction of nitrobenzene with Sn and HCl gives  
 (a) Azoxybenzene (b) Hydroazobenzene  
 (c) Primary aryl amines (d) *p*-Aminophenol
25. Primary nitroalkanes are upon hydrolysis with concentrated hydrochloric acid gives  
 (a) Primary amines (b) Ketones  
 (c) Alcohols (d) Carboxylic acids

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### 8. 16 ANSWER (MCQs)

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1. (b)	2. (c)	3. (a)	4. (b)	5. (c)
6. (d)	7. (d)	8. (b)	9. (a)	10. (c)
11. (a)	12. (d)	13. (a)	14. (d)	15. (b)
16. (a)	17. (c)	18. (a)	19. (c)	20. (d)
21. (b)	22. (c)	23. (a)	24. (c)	25. (d)

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### 8. 17 REFERENCES

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**UNIT-9 AMINO COMPOUNDS**

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**CONTENTS:**

- 9.1 Objectives
- 9.2 Introduction
- 9.3 Structure of amino compounds
- 9.4 IUPAC nomenclature of aliphatic amines
- 9.5 IUPAC nomenclature of aromatic amines
- 9.6 Physical properties of amines
- 9.7 Stereochemistry of amines
- 9.8 Separation of a mixture of primary, secondary and tertiary amines
- 9.9 Structural features effecting basicity of amines
- 9.10 Preparation of alkyl and aryl amines
- 9.11 Reductive amination of aldehydic and ketonic compounds
- 9.12 Important reactions of amines
- 9.13 Summary
- 9.14 Terminal questions
- 9.15 Answers (MCQ)
- 9.16 References



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## 9.1 OBJECTIVES

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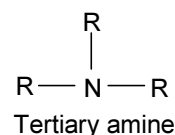
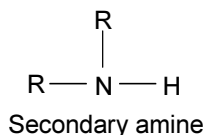
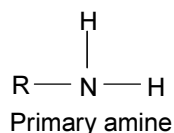
In continuation to unit 8 (organic compounds containing nitrogen) the aim of this unit is to describe amines as derivatives of ammonia having a pyramidal structure, classify them as primary, secondary and tertiary amines, describe their common and IUPAC names. To explain that how we can distinguish between primary, secondary and tertiary amines? To describe some of the important methods of preparation of amines, to explain their physical and chemical properties and to study the mechanism of the reductive amination of aldehydes and ketonic compounds, Gabriel's phthalimide synthesis and Hofmann's bromamide reaction etc.

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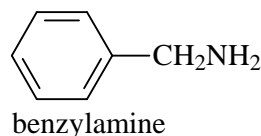
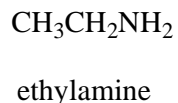
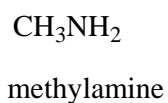
## 9.2 INTRODUCTION

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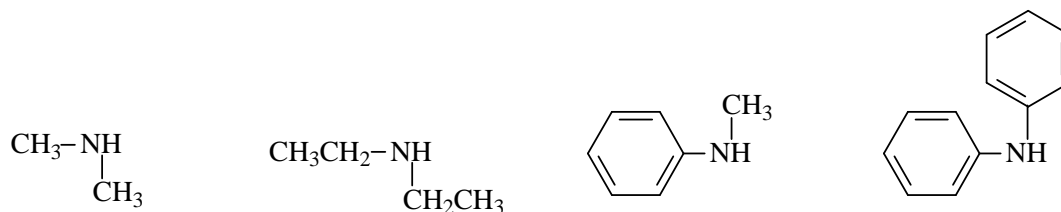
Amines are aliphatic and aromatic derivatives of ammonia which are obtained by the replacement of one, two or all three hydrogen atoms of ammonia by alkyl or aryl groups. Amines are described as primary ( $1^\circ$ ), secondary ( $2^\circ$ ) or tertiary ( $3^\circ$ ) depending on how many alkyl or aryl substituents are attached to the nitrogen atom. The tetra alkyl derivatives of ammonium salts are known as quaternary ammonium salts e.g., tetramethyl ammonium chloride,  $(\text{CH}_3)_4\text{N}^+\text{Cl}^-$ .



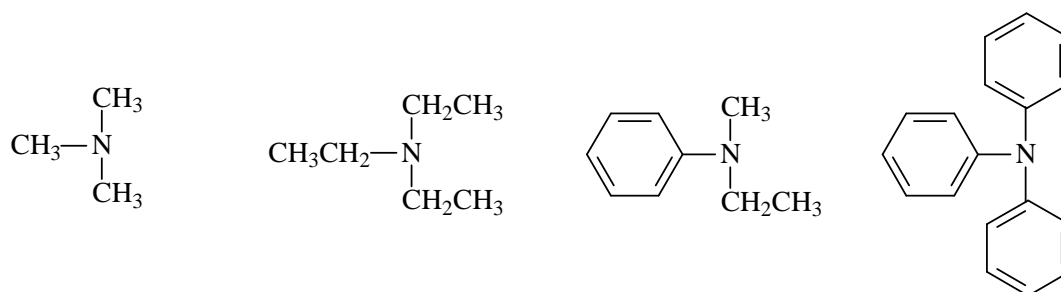
**Primary amines:** Primary amines are obtained by the replacement of one hydrogen atom of ammonia by an alkyl or aryl group. For example: Methyl amine, ethyl amine, phenyl amine etc.



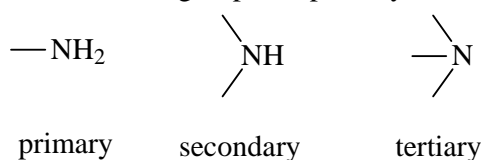
**Secondary amines:** Secondary amines are obtained by the replacement of two hydrogen atoms of ammonia by the two alkyl or aryl groups. For example: Dimethyl amine, ethyl methyl amine, methyl phenyl amine, diphenyl amine etc.



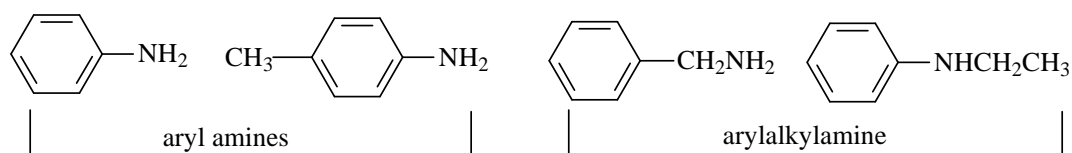
**Tertiary amines:** Tertiary amines are obtained by the replacement of all three hydrogen atoms of ammonia by the three alkyl or aryl groups. For example: Trimethyl amine, triethyl amine, ethyl methyl phenyl amine, triphenyl amine etc.



The characteristic functional groups for primary, secondary and tertiary amines are:



Aromatic amino compounds are of two types, aryl amines and arylalkyl amines. Aryl amines are those compounds in which the  $\text{—NH}_2$  group is directly attached to the nucleus *e.g.*, aniline, *p*-tolidine etc. whereas in arylalkyl amines the  $\text{—NH}_2$  group is attached to a carbon atom of the side chain *e.g.*, benzylamine,  $\beta$ -phenylethylamine etc.



### 9.3 STRUCTURE OF AMINO COMPOUNDS

Amines are ammonia derivatives; the shape of amine functional group is similar to its parent molecule ammonia. The nitrogen in ammonia forms three  $\sigma$  bonds and also carries one lone pair of electrons. The nitrogen in ammonia as well as aliphatic amines is  $sp^3$  hybridized. Therefore the shape of ammonia is trigonal pyramidal which can be represented as



The amino compounds are obtained by replacing hydrogen atom by alkyl or aryl groups, their shape can be represented as:

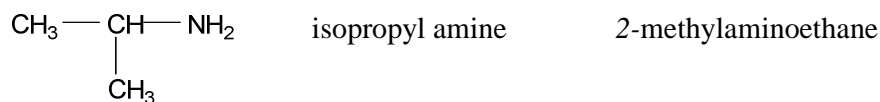
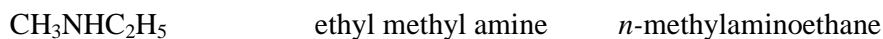
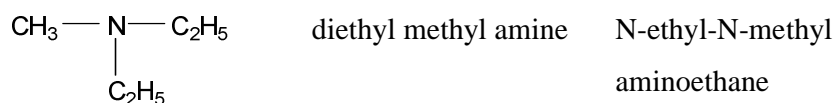
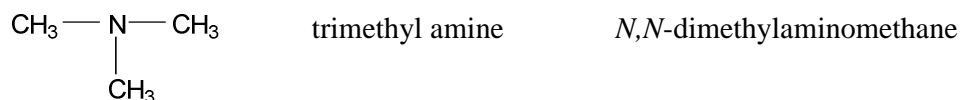


The bond angle between H-N-H in ammonia is  $107^\circ$ , the bond angle in amine is assumed almost same as in ammonia.

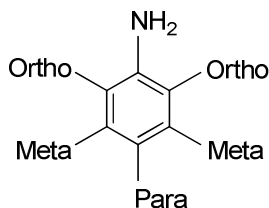
### 9.4 IUPAC NOMENCLATURE OF ALIPHATIC AMINES

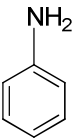
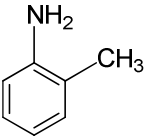
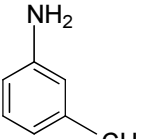
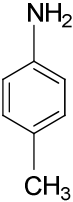
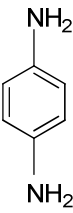
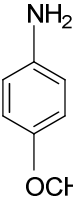
Usually amines are named after the alkyl group attached to the nitrogen atom. In IUPAC nomenclature, the primary amines are named as aminoalkanes; secondary amines are named as *N*-alkylaminoalkanes and tertiary as dialkylaminoalkanes.

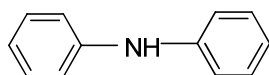
Compound	Common name	IUPAC name
<b>Primary amines</b>		
$\text{CH}_3\text{NH}_2$	methyl amine	aminomethane
$\text{CH}_3\text{CH}_2\text{NH}_2$	ethyl amine	aminoethane
$\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$	propyl amine	aminopropane

**Secondary amines****Tertiary amines****9.5: IUPAC NOMENCLATURE OF AROMATIC AMINES:**

The simplest member of aromatic amines is aminobenzene (aniline). Amines containing a  $-\text{NH}_2$  group, firstly identified the position of the amino group and count this position as position-1 of the ring. Then give numbers to all positions (as 2, 3, 4, 5, 6 etc.) in clockwise direction. They are named as *o*, *m* or *p* substituted. The next position to the amino group is *ortho* (*o*), the third position to the amino group is *meta* (*m*) and the vertically opposite position to the amino group is *para* (*p*).



Compound	Common name	IUPAC name
	aniline	aminobenzene
	<i>o</i> -toluidine	2-methyl aniline
	<i>m</i> -toluidine	3-methyl aniline
	<i>p</i> -toluidine	4-methyl aniline
	<i>p</i> -phenylene diamine	<i>p</i> -iaminobenzene
	anisidine	<i>p</i> -methoxy aniline



diphenyl amine

*N*-phenyl amine

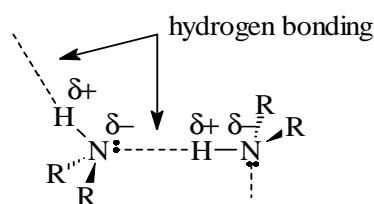
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## 9.6 PHYSICAL PROPERTIES OF AMINES

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**1. Physical state:** Lower amines are combustible gases at room temperature, C<sub>3</sub>-C<sub>11</sub> members of amines are volatile liquids, while the higher amines are solids. The lower members of amines have fishy ammoniacal odour,

**2. Hydrogen bonding:** Amines are polar compounds and both primary and secondary amines form intermolecular hydrogen bonds. The boiling points and solubility of amines are associated with the intermolecular hydrogen bonding involved in these molecules.

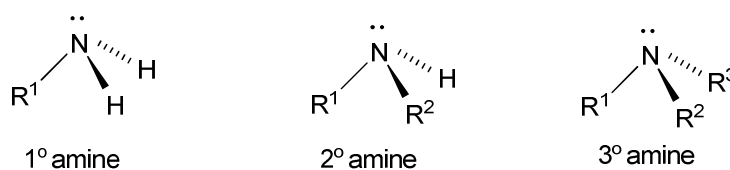


**3. Boiling points:** An N-H---N hydrogen bond is weaker than O-H---O hydrogen bond because the electronegativity difference between nitrogen and hydrogen (0.9) is less than between oxygen and hydrogen (1.4). Therefore amines have lower boiling points than the corresponding alcohols. Tertiary amines cannot form hydrogen bond because they have no hydrogen therefore the boiling point of tertiary amines will be even lower than primary or secondary amines.

**4. Solubility of amines:** Primary and secondary amines form hydrogen bonds with water and are more soluble in water than hydrocarbons of comparable molecular weight. Low molecular weight amines are completely soluble in water while higher molecular weight amines are moderately soluble or insoluble in water.

### 9.7 STEREOCHEMISTRY OF AMINES

Amines are classified into primary, secondary and tertiary based on the number of hydrogen atom (s) are replaced by the alkyl or aryl groups. Tertiary amines have three different groups *i.e.*  $R^1$ ,  $R^2$ , and  $R^3$  attached to the nitrogen atom, they are asymmetric or chiral, and therefore they do not form superimposable mirror image. Tertiary amines exist in two enantiomeric forms. This is due to the inability of unshared pair of electrons present in fourth  $sp^3$  orbital of nitrogen to serves as a fourth group to keep configuration.



In contrast, quaternary ammonium salts, in which the nitrogen atom is attached to four different groups. In quaternary ammonium salts, the groups may also be chiral and able to show enatiomerism as well as optical activity. This is because the nitrogen in these salts is tetrahedral and all its  $sp^3$  orbitals are involved in the bond formation.

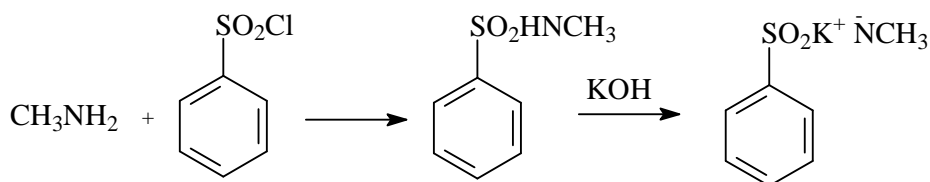
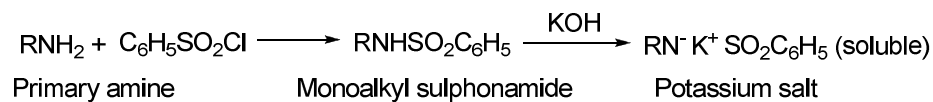
Amines display different characteristic infrared absorption peaks based on the degree of amines.

- a) Primary amines contain two N-H bonds which display two peaks around  $3300\text{ cm}^{-1}$   
The shape of IR peak is similar to the molar teeth, hence also known as “ molar peak”
- b) Secondary amines contain one N-H bond which displays a single peak around  $3300\text{ cm}^{-1}$
- c) Tertiary amines contain no N-H bonds and do not show up in infrared spectroscopy.

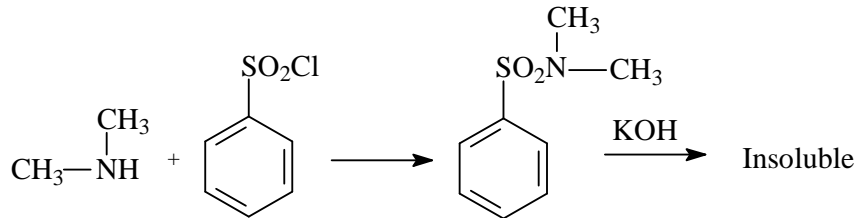
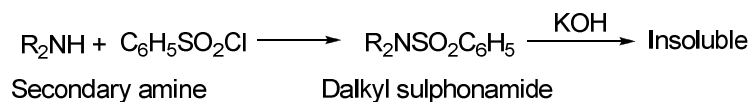
### 9.8 SEPARATION OF A MIXTURE OF PRIMARY, SECONDARY AND TERTIARY AMINES

There are two methods which are used to distinguished the primary, secondary and tertiary amines *i.e.* Hinsberg,s method and Hofmann's method.

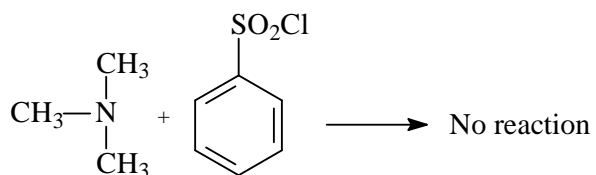
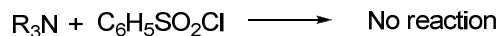
**1. Hinsberg's method:** The Hinsberg's reagent is benzene sulphonyl chloride ( $C_6H_5SO_2Cl$ ). The primary, secondary and tertiary amines can be separated by Hinsberg's reagent test. Primary amine reacts with Hinsberg's reagent to form a precipitate of *N*-alkyl benzene sulphonamide which is soluble in strong alkali like KOH.



Secondary amine reacts with Hinsberg's reagent to form a precipitate of *N,N*-dialkyl benzene sulphonamide which is insoluble in alkali.

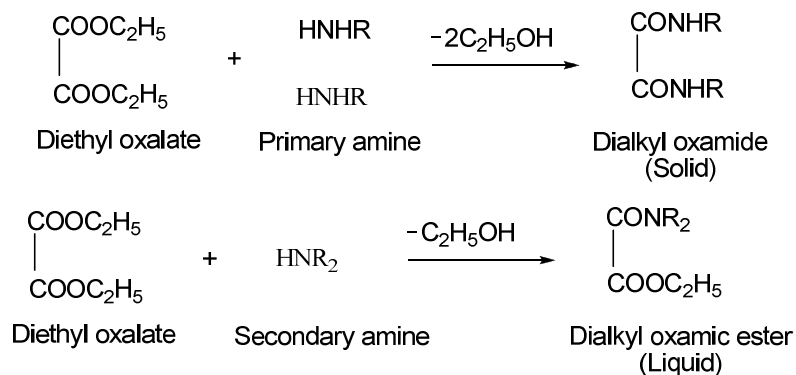


Tertiary amines do not react with Hinsberg's reagent.

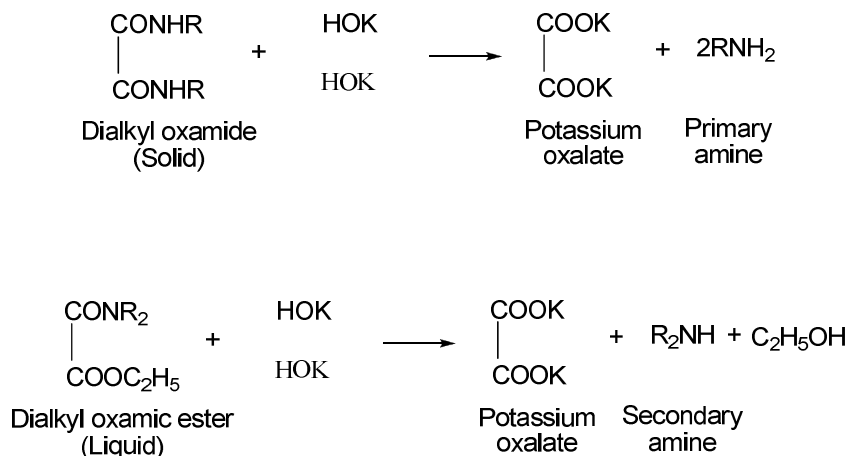




**2. Hofmann's method:** The mixture of three amines is treated with diethyl oxalate. The primary amine forms a solid oxamide; a secondary amine gives a liquid oxamic ester while tertiary amine does not react.

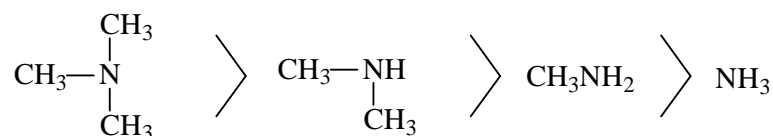


Now, the mixture containing primary, secondary and tertiary amines is subjected to fractional distillation, when tertiary amine, which is highly volatile, distils over. The remaining residue mixture containing solid oxamide and liquid oxamic ester are separated by the simple filtration. Both solid oxamide and liquid oxamic ester are separately treated with a strong alkali like KOH to recover and purified by the distillation.

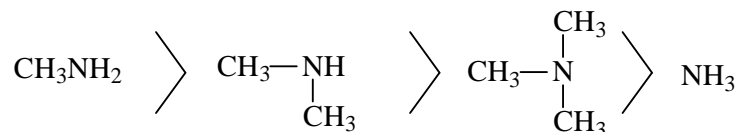


### 9.9 STRUCTURAL FEATURES EFFECTING BASICITY OF AMINES

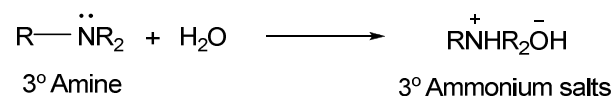
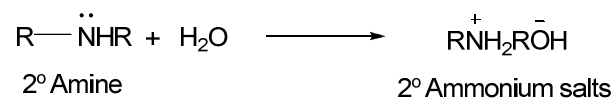
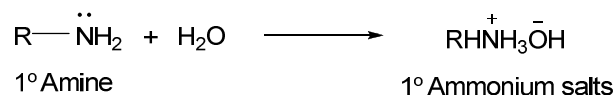
Amines, like ammonia are weak bases ( $K_b = 10^{-4}$  to  $10^{-6}$ ). The basicity of amines is due to the presence of unshared pair of electrons on nitrogen atom which can share with other atoms. This unshared pair of electrons creates an electron density around the nitrogen atom. The greater the electron density, the more basic is the amine. Electron releasing groups (e.g., methyl, ethyl, and other alkyl groups) increase the basicity of aromatic amines whereas electron withdrawing groups (e.g., halogen, nitro, carbonyl groups) decrease the basicity of aromatic amines. Thus, the basicity of aliphatic amines increases with increases alkyl substitutions as given below:



However, in aqueous solutions, the order of basicity changes.



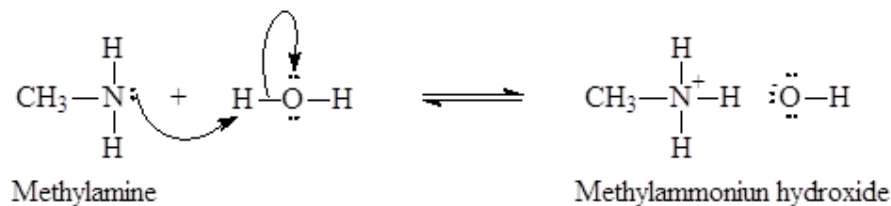
The differences in the basicity order in the gas phase and aqueous solutions are the result of solvation effects. Amines in water solution exist as ammonium ions.



In water, the ammonium salts of primary and secondary amines undergo solvation effects (due to hydrogen bonding) to a much greater degree than ammonium salts of

tertiary amines. These solvation effects increase the electron density on the amine nitrogen to a greater degree than the inductive effect of alkyl groups.

Amines act as nucleophiles in most circumstances; the unshared pair of electrons on nitrogen forms a new covalent bond with hydrogen and displaces hydroxide ion.



The equilibrium constant for this reaction is as follows:

$$K_{\text{eq}} = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2][\text{H}_2\text{O}]}$$

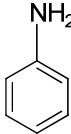
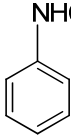
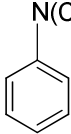
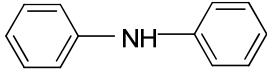

The base ionization constant  $K_b = K_{\text{eq}} [\text{H}_2\text{O}]$ . The value of  $K_b$  for methylamine is  $4.37 \times 10^{-4}$  ( $\text{p}K_b = 3.36$ ).


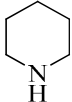
$$K_b = K_{\text{eq}} [\text{H}_2\text{O}] = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]}$$

Amines are basic in nature (Lewis base) the basic strength in term of their  $\text{p}K_b$  values are being given in table 1. The smaller the  $\text{p}K_b$  value stronger is the base.

Table -1: Basic strength of amines ( $\text{p}K_b$ ):

Compound	Structure	$\text{p}K_b$
ammonia	$\text{NH}_3$	4.74
<b>Primary amines</b>		
methylamine	$\text{CH}_3\text{NH}_2$	3.36
ethylamine	$\text{CH}_3\text{CH}_2\text{NH}_2$	3.34

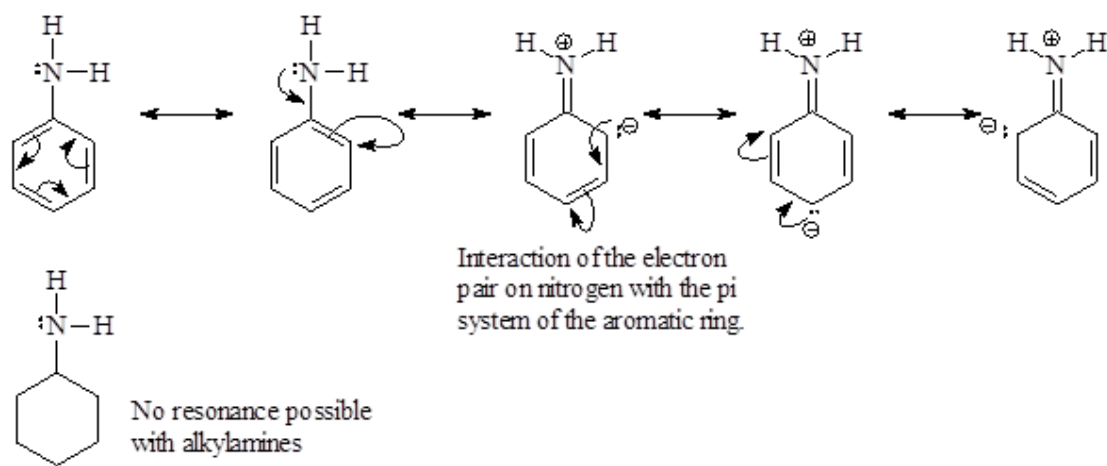
<i>n</i> -propyl amine	$\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$	3.42
<b>Secondary amines</b>		
dimethylamine	$(\text{CH}_3)_2\text{NH}$	3.29
diethylamine	$(\text{CH}_3\text{CH}_2)_2\text{NH}$	3.02
dipropylamine	$(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{NH}$	3.1
<b>Tertiary amines</b>		
triethylamine	$(\text{CH}_3)_3\text{N}$	4.3
triethylamine	$(\text{CH}_3\text{CH}_2)_3\text{N}$	3.26
<b>Aromatic amines</b>		
aniline		9.38
<i>N</i> -methylaniline		9.15
<i>N,N</i> -dimethylaniline		8.95
diphenyl aniline		13.15
<b>Heterocyclic aromatic amines</b>		
pyrrole		~14

pyridine		~8.7
piperidine		2.7

All aliphatic amines have about the same base strength,  $pK_b$  3.0 - 4.0 and are slightly stronger bases than ammonia. The increase in basicity compared with ammonia can be attributed to the greater stability of an alkyl ammonium ion, as for example,  $RCH_2NH_3^+$ , compared with the ammonium ion,  $NH_4^+$ . This greater stability arises from the electron releasing effect of alkyl groups and the resulting partial delocalization of the positive charge from nitrogen onto carbon in the alkyl ammonium ion.

Aromatic amines are weaker bases than ammonia and aliphatic amine. The less basic character of anilines can be explained on the following bases:

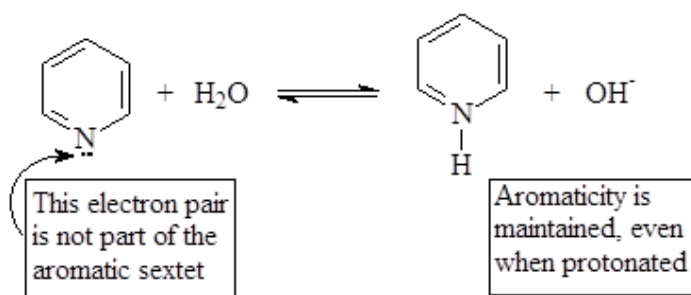
**1. Delocalization of the unshared electron pair on nitrogen atom:** The resonance stabilization of the free base form of aromatic amines. For aniline and other aryl amines, this resonance stabilization is a result of interaction of the unshared pair on nitrogen with the  $\pi$ - system of the aromatic ring. Due to this interaction the electron pair on nitrogen is less available for reaction with acid. No such resonance stabilization is possible for alkyl amines and therefore the electron pair on the nitrogen of an alkyl amine is more available for reaction with acid; alkyl amines are stronger bases than aryl amines.



**2. Substituent effect:** The second factor contributing to the decreased basicity of aromatic amines is the electron withdrawing effect of the  $sp^2$ -hybridized carbons of the aromatic ring compared with the  $sp^3$ -hybridized carbons of aliphatic amines. The unshared pair of electrons on nitrogen in an aromatic amine is pulled toward the ring and, therefore, less available for protonation to form the conjugate acid of the amine.

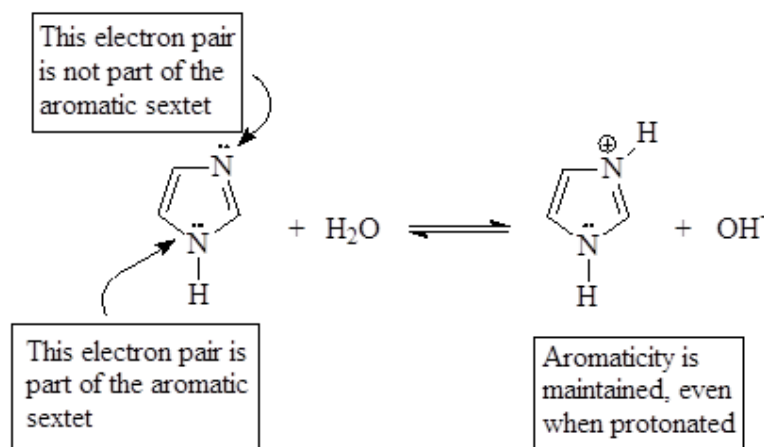
*Electron releasing groups (e.g., methyl, ethyl, and other alkyl groups) increase the basicity of aromatic amines whereas electron withdrawing groups (e.g., halogen, nitro, carbonyl groups) decrease the basicity of aromatic amines.*

The decrease in basicity on halogen substitution is due to the electron withdrawing inductive effect of the electronegative halogen. The decrease in basicity on nitro substitution is due to a combination of inductive and resonance effects, as can be seen by comparing the base ionization constants of 3-nitroaniline ( $pK_b$  11.53) and 4-nitroaniline ( $pK_b$  13.0). Note that the conjugate acid of 4-nitroaniline ( $pK_a$  1.0) is a stronger acid than phosphorous acid ( $pK_a$  2.0). Heterocyclic aromatic amines are weaker bases than aliphatic amines. When a nitrogen atom is incorporated directly into an aromatic ring, its basicity depends on the bonding context. For example, In pyridine ring, the nitrogen lone pair occupies an  $sp^2$  orbital which is not a part of the aromatic sextet.



Proton transfer from water or other acid to pyridine does not involve the electrons of the aromatic sextet. Pyridine is a weaker base than aliphatic amines because the unshared pair of electrons of the pyridine nitrogen lies in  $sp^2$  hybrid orbital, whereas in aliphatic amine, the unshared pair lies in  $sp^3$  orbital. Electrons in  $sp^2$  hybrid orbital (33% s character) are held more tightly by the nucleus than electrons in  $sp^3$  hybrid orbital (25%

s character). It is this effect that decreases the basicity of the electron pair on  $sp^2$  hybridized nitrogen compared with that on  $sp^3$  hybridized nitrogen.



There are two nitrogen atoms in imidazole, each with an unshared pair of electrons. One shared pair lies in a  $2p$  orbital and is an integral part of the  $(4n+2)$  pi electrons of the aromatic system. The other unshared pair lies in an  $sp^2$  hybrid orbital and is not part of the aromatic sextet. It is the pair of electrons not part of the pi system that functions as the proton acceptor.

In pyridine the unshared pair of electrons functioning as the proton acceptor and in imidazole lies in  $sp^2$  hybrid orbital and has decreased basicity compared with an unshared pair of electron in  $sp^3$  hybrid orbital. The positive charge on the imidazolium ion is delocalized on both nitrogen atoms of the ring and, therefore, imidazole is a stronger base than pyridine.

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## 9.10 PREPARATION OF ALKYL AND ARYL AMINES

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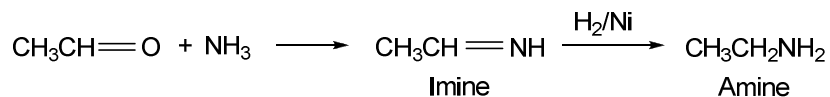
The alkylation of ammonia, Gabriel's phthalimide synthesis, Hofmann's bromamide synthesis, reduction of nitriles, reduction of oximes and acid amides, reduction of nitroarenes, and reductive amination of aldehydes and ketones are methods commonly used for preparing amines.

**A. Methods for the preparation of all three types of amine along with quaternary ammonium salts.**

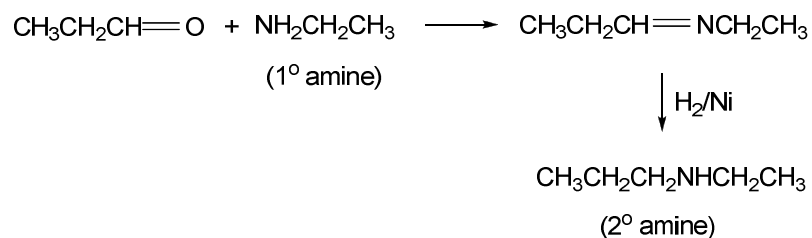




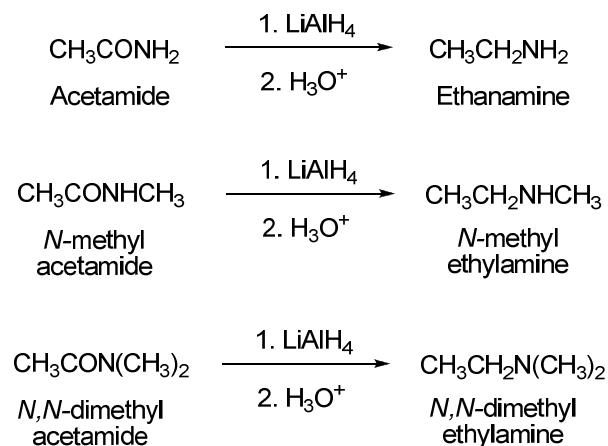
**3. From carbonyl compounds:** On heating with an acidic solution of ammonia or amine, carbonyl compounds are converted into amines.



This reaction is called the *reductive amination of aldehydes*. Using this reductive amination the 1° amine to 2° amines can be formed.



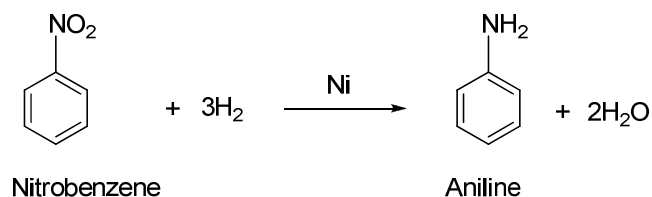
**4. By the reduction of amides:** Amides yield primary amines on reduction by lithium aluminum hydride, while *N*-substituted and *N,N*-disubstituted amides produce secondary and tertiary amines, respectively.



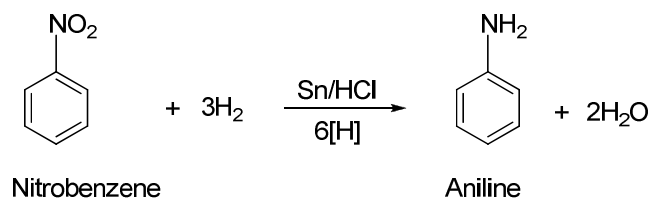
#### B. Additional methods for the preparation of primary amines:

**1. By the reduction of nitroarenes:** Aromatic amines are normally prepared by the reduction of corresponding nitroarenes in presence of hydrogen and Raney nickel, tin and hydrochloric acid, iron and hydrochloric acid, zinc and acetic acid, or ammonium hydrogen sulphide.

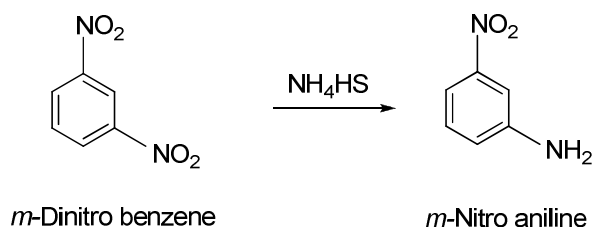
(i) **Catalytic reduction:** Nitro compounds are reduced to amines with hydrogen gas in presence of powdered nickel.



(ii) **Reduction with Sn/HCl, or Fe/HCl, or Zn/CH<sub>3</sub>COOH:** Nitro compounds are also reduced with metal and concentrated hydrochloric acid like Sn/HCl, Fe/HCl, or Zn/CH<sub>3</sub>COOH into amines.

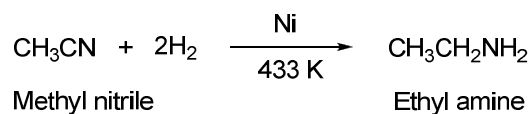


(iii) **Partial reduction with NH<sub>4</sub>HS :** By partial reduction, one of two nitro groups in a dinitro compound is reduced into amino group by using ammonium hydrogen sulphide as reducing agent.

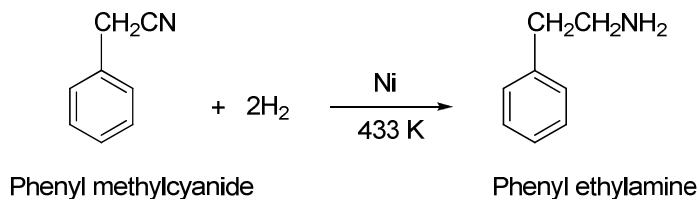


**2. By the reduction of nitriles or cyanides:** The carbon-nitrogen triple bond in a nitrile or cyanide can be reduced by the reaction of hydrogen gas in presence of a metal catalyst like nickel, palladium or lithium aluminium hydroxide.

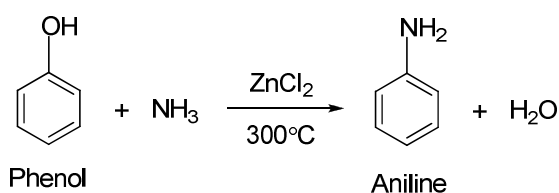
For example, methyl nitrile is reduced by hydrogen and nickel to ethyl amine.



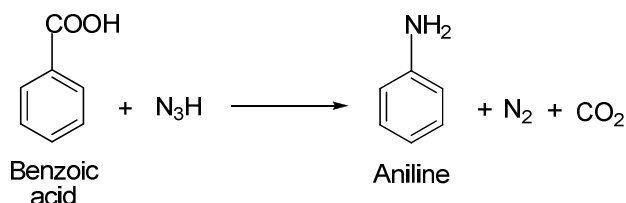
Phenyl methyl cyanide is reduced by hydrogen and nickel or by lithium aluminium hydroxide to phenyl ethyl amine.



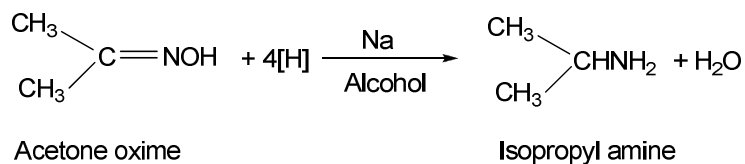
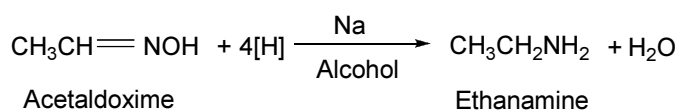
**3. By the action of ammonia on phenol:** Mono aryl amines are prepared by the reaction of ammonia on phenols in presence of zinc chloride at 300 °C.



**4. By Schmidt reaction:** Aromatic amines can be obtained by the treatment of aromatic carboxylic acid in concentrated sulphuric acid with chloroform solution of hydrazoic acid.

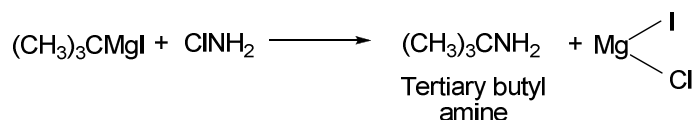
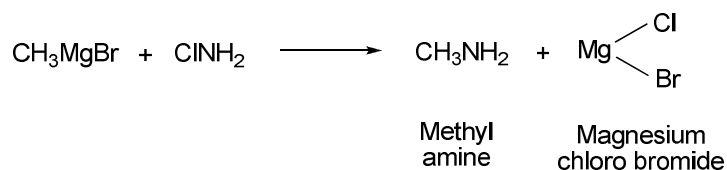


**5. By the reduction of oximes :** Oximes yield primary amines on reduction by sodium and ethanol or by lithium aluminium hydroxide (LiAlH<sub>4</sub>).

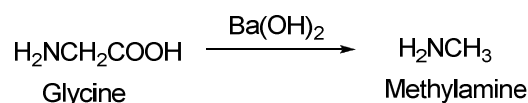


**6. By the action of chloramine with Grignard's reagent:** The primary amines can be obtained by the action of chloramines on Grignard's reagent.

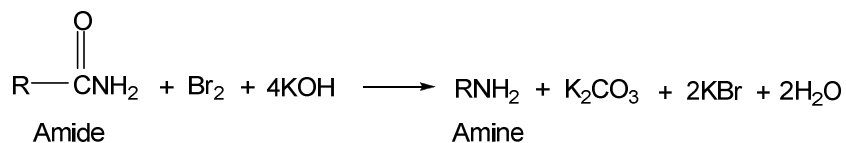
For example, methyl amine is prepared by the action of chloramines on methyl magnesium bromide.



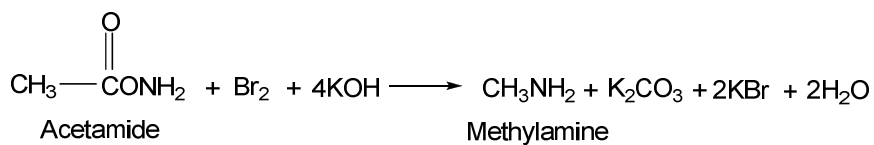
**7. By the decarboxylation of amino acids:** When an amino acid is heated with  $\text{Ba}(\text{OH})_2$ , it loses  $\text{CO}_2$  to form a primary amine. For example:



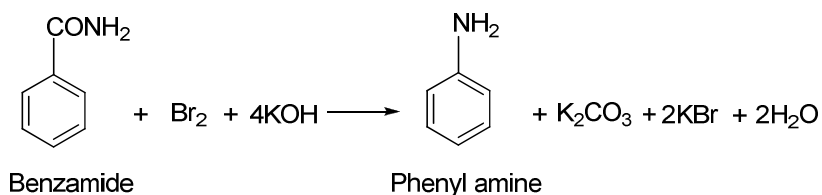
**8. By Hofmann's bromamide synthesis:** Hofmann bromination reaction is an organic reaction used to convert a primary amide to a primary amine using bromine in an aqueous or ethanolic solution of sodium hydroxide. This reaction is as:



For example, acetamide reacts with bromine and potassium hydroxide to form methyl amine.

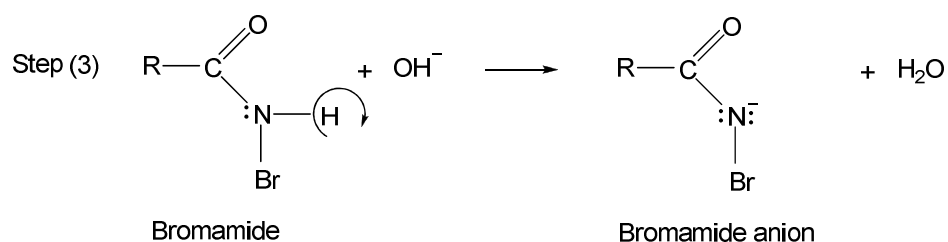
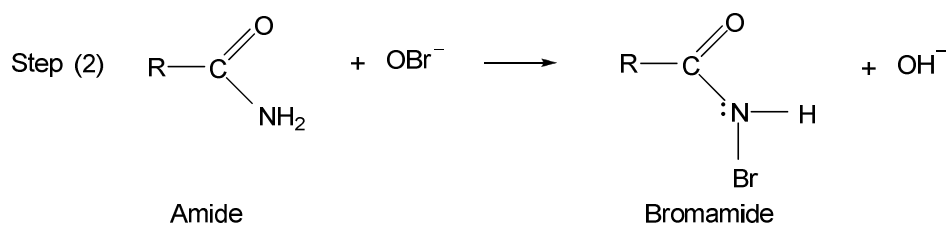
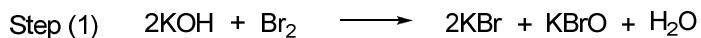


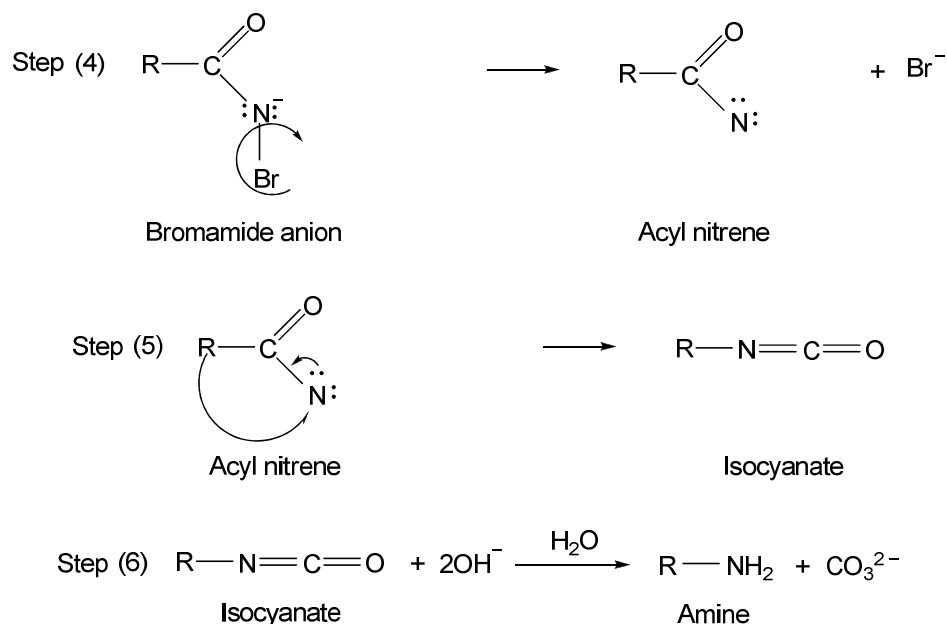
Similarly,



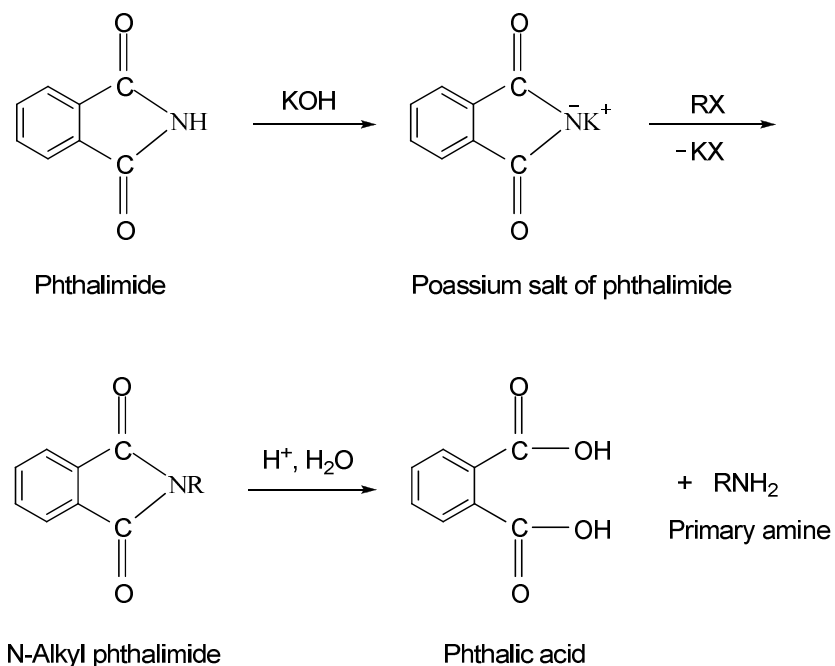
**Mechanism:** The reaction mechanism involves several steps:

1. The hypobromite ion  $\text{OBr}^-$  anion is produced by the reaction of alkali with bromine.
2. The anion reacts with amide to give bromamide.
3. Base abstraction of the remaining amide proton gives a bromamide anion.
4. The bromamide anion rearranges as the R group attached to the carbonyl carbon migrates to nitrogen at the same time the bromide ion leaves, giving an isocyanate (step 4 and 5).
5. The isocyanate adds water in a nucleophilic addition step to yield a carbamic acid after that carbamic acid spontaneously loses  $\text{CO}_2$  to yield amine.



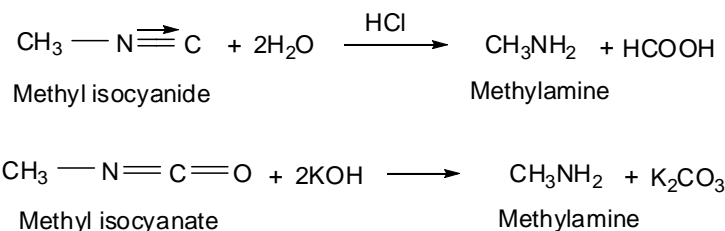


**9. By Gabriel's phthalimide reaction:** This method is used for the preparation of primary amines. Phthalimide on reaction with ethanolic potassium hydroxide gives potassium salt of phthalimide, which on heating with alkyl halide followed by alkaline hydrolysis forms the corresponding primary amine.

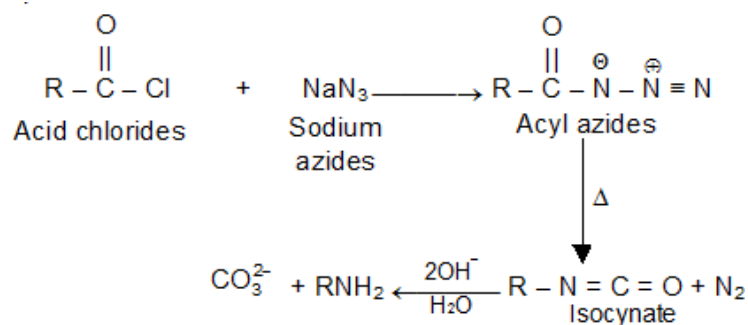


Aromatic primary amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

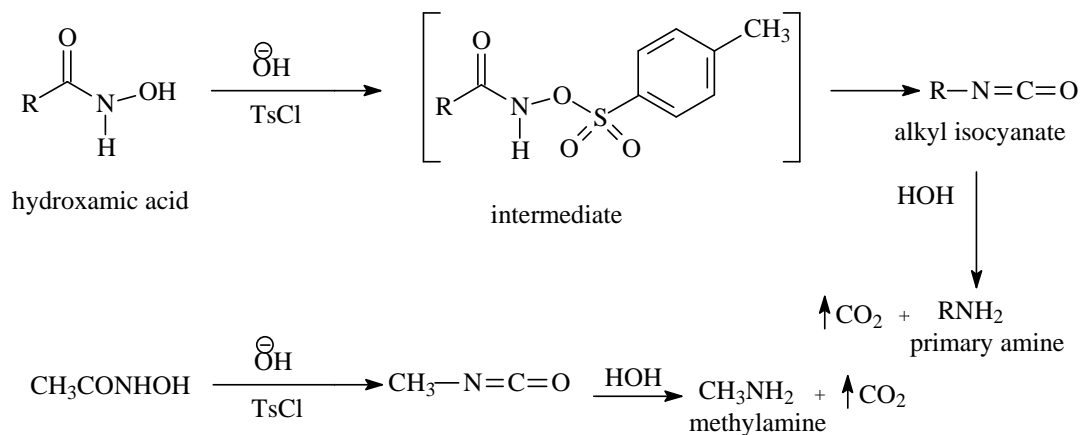
**10. By Wurtz reaction:** Primary amines can be obtained by the hydrolysis of isocyanide or isocyanate.



**11. By Curtius reaction:** Acid chlorides on reaction with sodium azides give isocyanate which is decomposed with water into amines.

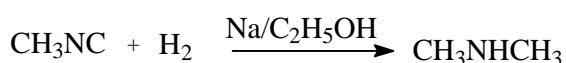
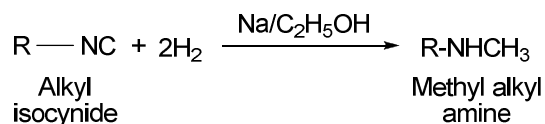


**12. Lossen reaction:** Lossen rearrangement is a conversion of hydroxamic acid to isocyanate through the formation of O- acyl sulphonyl or phosphoryl intermediate hydroxamic acid O-derivative. This rearrangement is used for the synthesis of primary amines from hydroxamic acid.

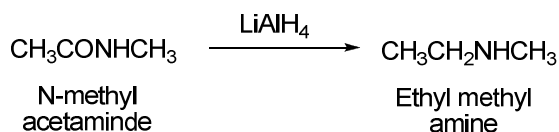


**C. Additional methods for the preparation of secondary amines**

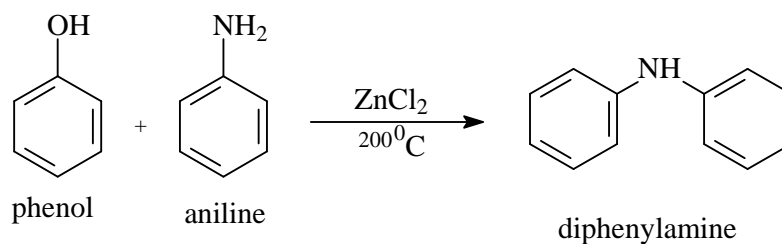
**1. By reduction of alkyl isocyanide or isocyanates:** Isocyanide or isocyanates are reduced to secondary amines with hydrogen gas in presence of Na/C<sub>2</sub>H<sub>5</sub>OH.



**2. By reduction of *N*-substituted amides:** Secondary amides can be reduced to amines by a strong oxidizing agent like lithium aluminium hydroxide by the conversion of C=O group to -CH<sub>2</sub>. Amides cannot be reduced by the less reactive NaBH<sub>4</sub>.

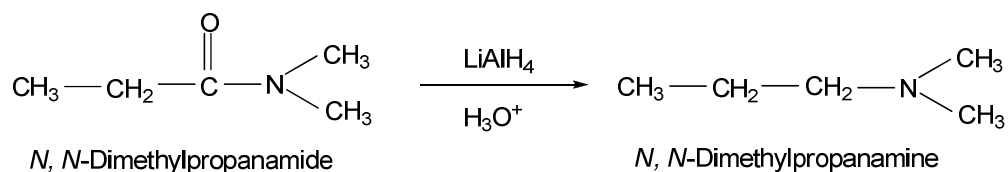


**3. By heating phenol with aniline:** Secondary aromatic amines are prepared by heating phenol with aniline in presence of anhydrous zinc chloride at 200 °C.

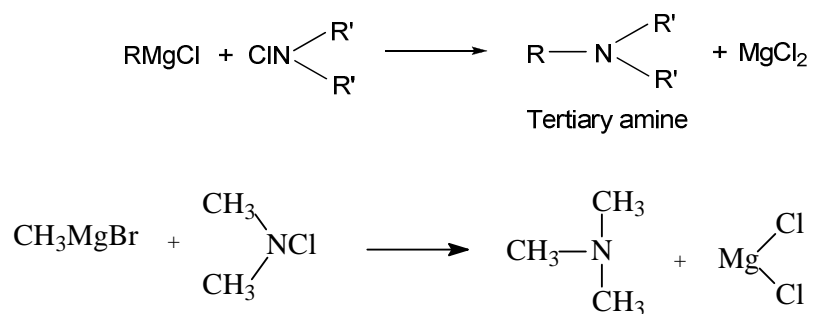
**D. Additional methods for the preparation of tertiary amines**

**1. By reduction of *N,N*-disubstituted amides:** *N,N*-disubstituted amides yield tertiary amines on reduction by lithium aluminum hydride.

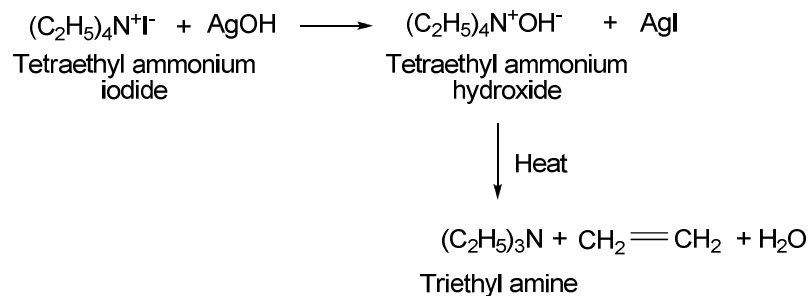




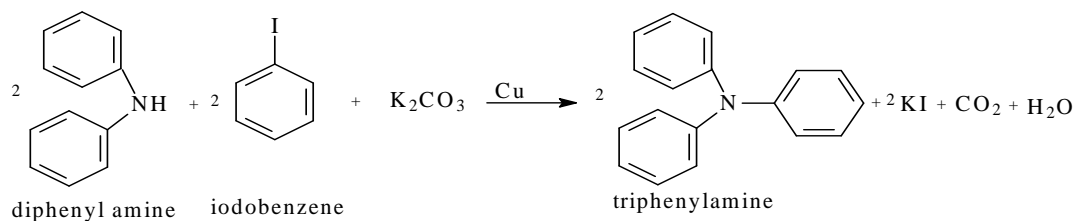
**2. From Grignard's reagent:** Grignard reaction can be used to synthesise tertiary amines as follow



**3. By the decomposition of tetra alkyl ammonium hydroxide:** A quaternary ammonium salt is hydrolyzed with moist silver oxide into quaternary ammonium hydroxide which on strong heating gives tertiary amine.

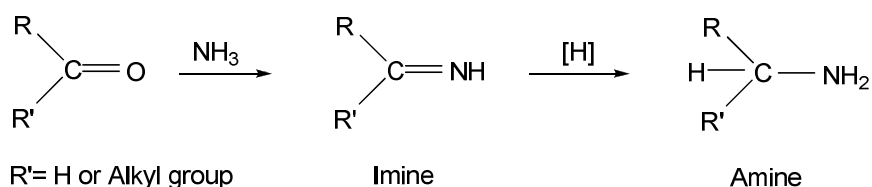


**4. By Ullmann's reaction:** Tertiary aromatic amines are obtained by heating diphenyl amine with iodobenzene, potassium carbonate and a small amount of copper as catalyst in nitrobenzene solution.

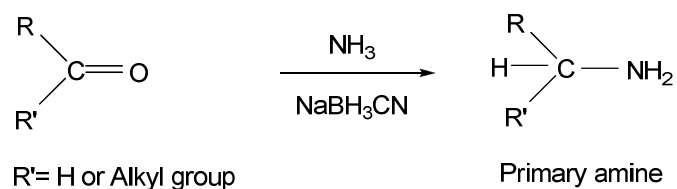


### 9.11 REDUCTIVE AMINATION OF ALDEHYDIC AND KETONIC COMPOUNDS

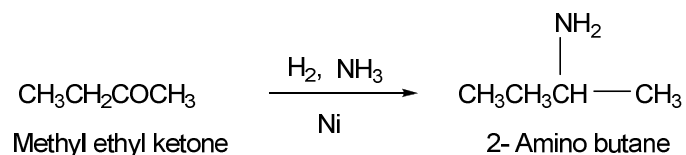
Aldehydes and ketones can be converted into primary, secondary and tertiary amines using reductive amination in presence of ammonia or amine. The reaction is completed in two steps. The first step is the nucleophilic addition of the carbonyl group to form an imine. The second step is the reduction of the imine to an amine using a reducing agent. A reducing agent employed commonly includes hydrogen and a catalyst such as Ni, NaBH<sub>3</sub>CN (sodium cyanoborohydride), LiBH<sub>3</sub>CN (lithium cyanoborohydride) etc. The general reductive reactions of aldehydes and ketones are as:



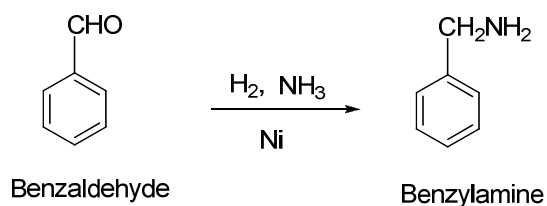
Conversion of aldehyde or ketone into primary amine:



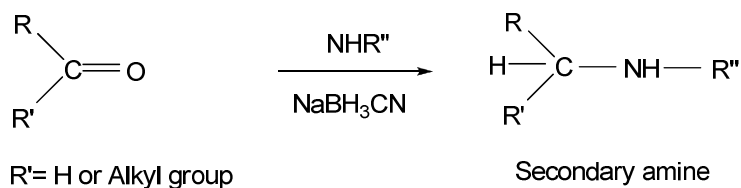
For example, methyl ethyl ketone is reduced by ammonia in presence of nickel into 2-amino butane.



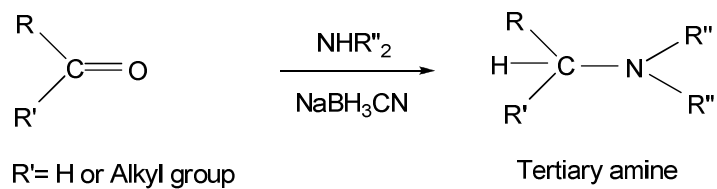
Similarly, benzaldehyde is reduced with ammonia in presence of hydrogen and nickel into benzylamine.



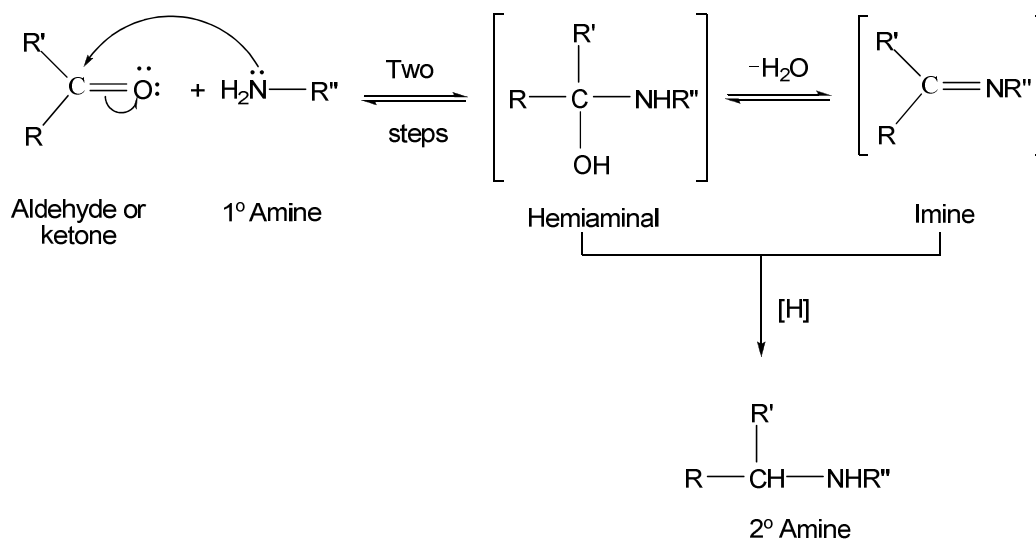
Conversion of aldehyde or ketone into secondary amine:



Conversion of aldehyde or ketone into tertiary amine:



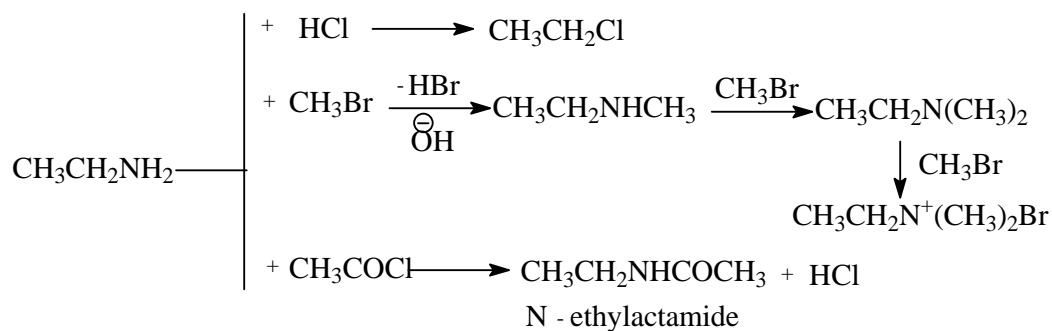
**Mechanism:** The sequential mechanism is as follow:

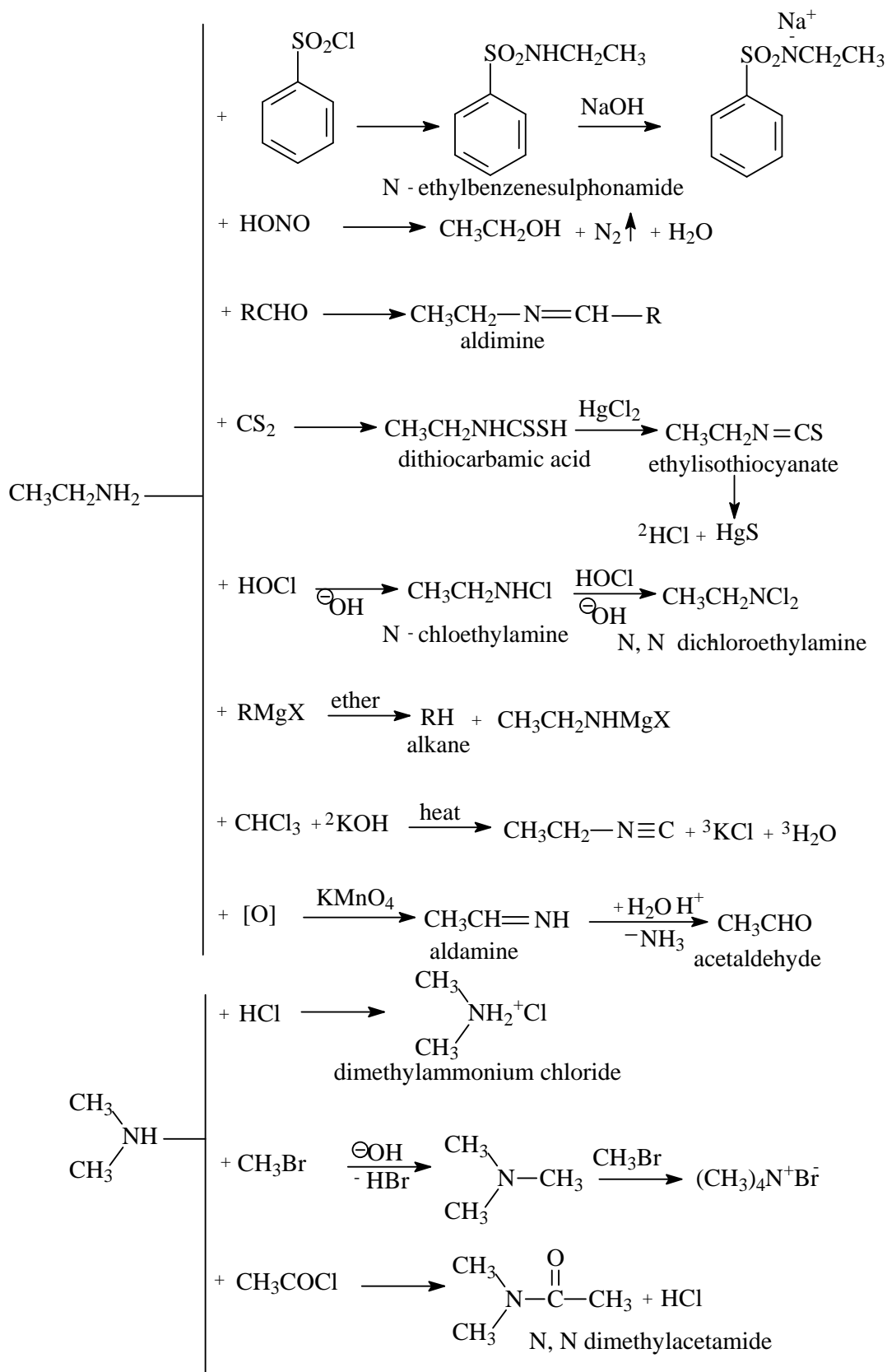


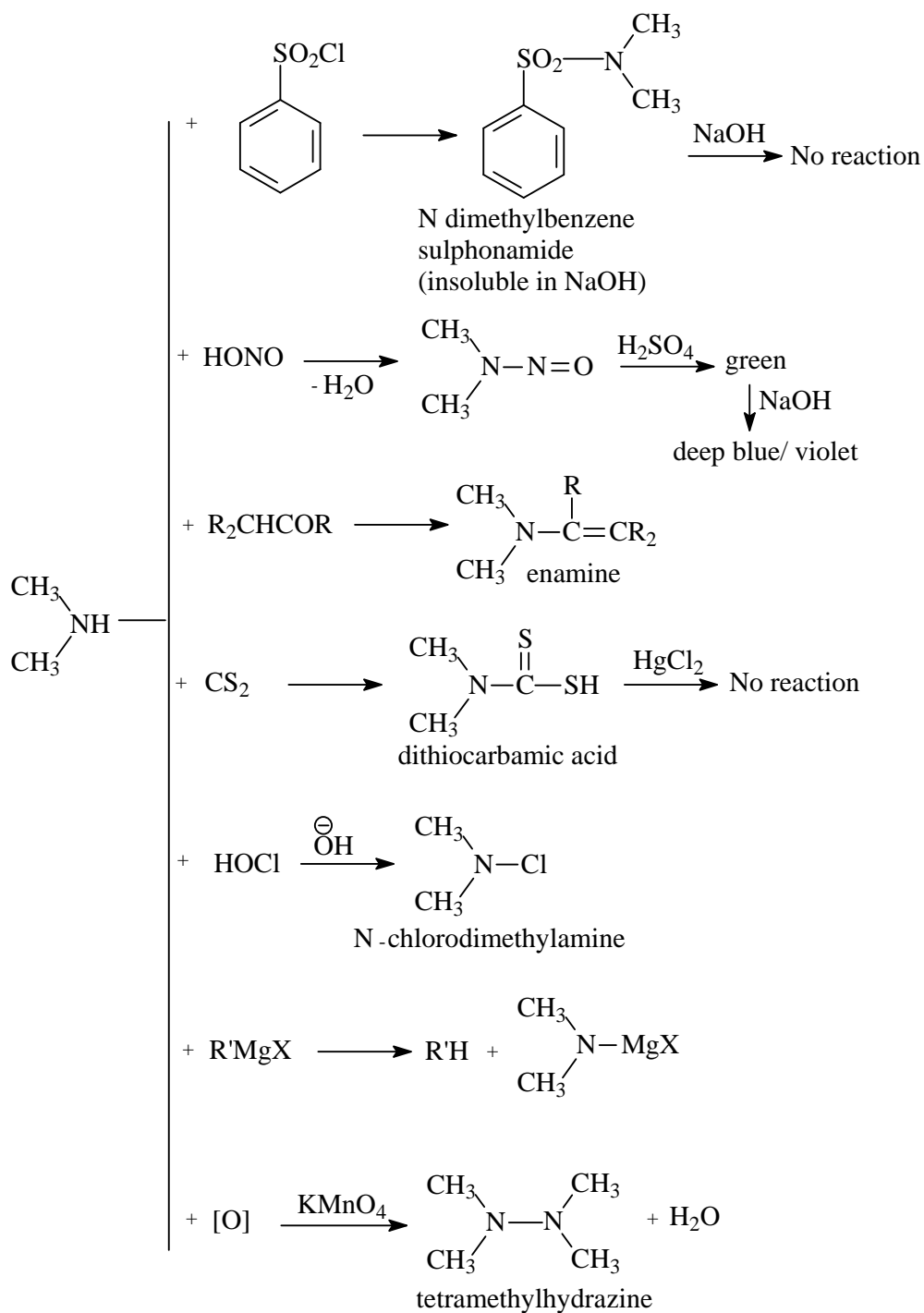
### ***9.12 IMPORTANT REACTIONS OF AMINES***

As we know that amines are important class of organic compounds containing nitrogen as one of the element in their composition. The amines are synthesized in pilot scale in industries for many purposes i.e. as starting material for synthesis of other molecules, synthesis of drug molecules, textile dyes, solvents etc. Both aliphatic and aromatic amines undergo variety of chemical reactions. Though some has been described in above, however some of the important reactions as being consolidately presented as follow.

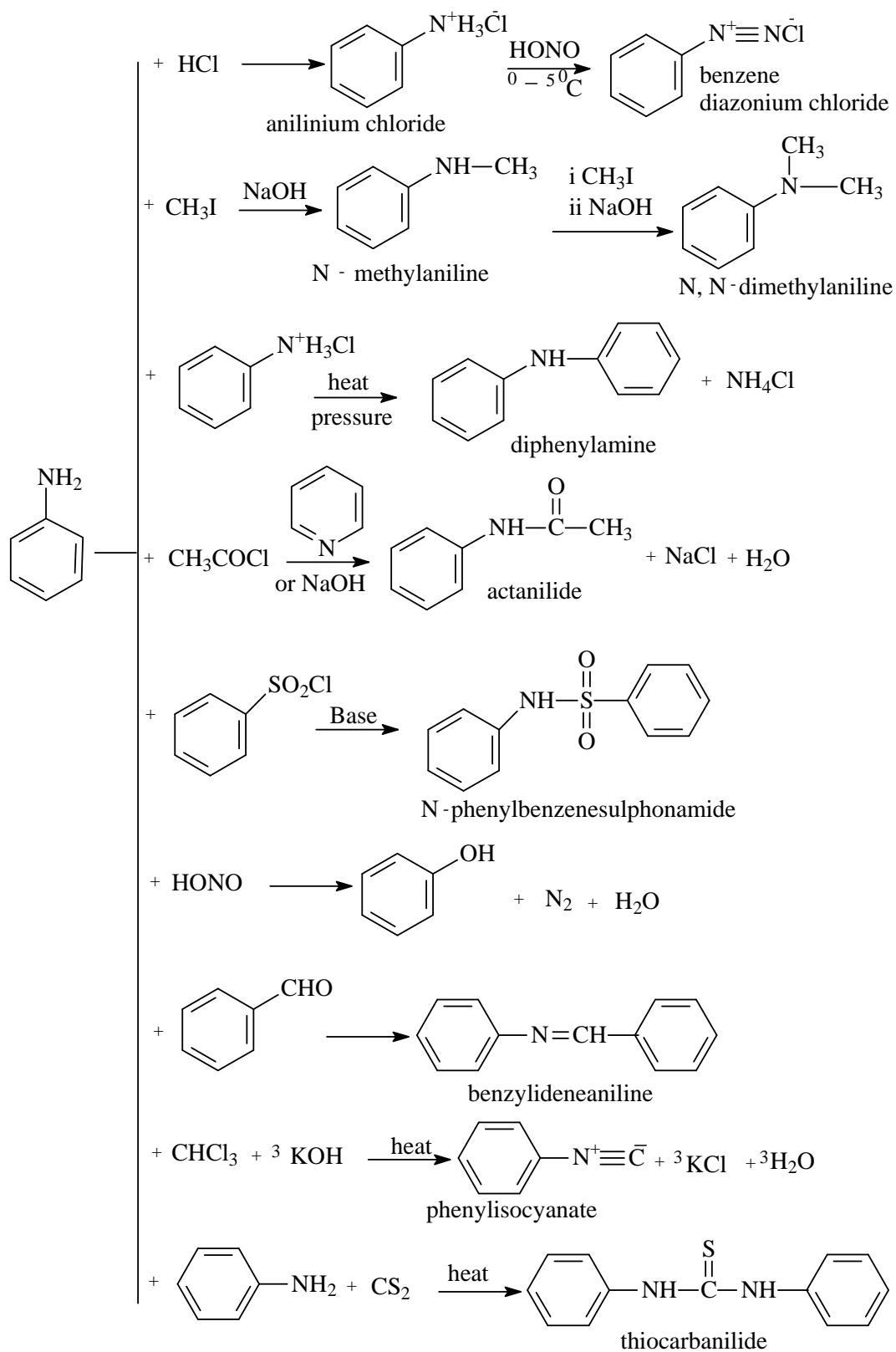
*Reactions of aliphatic amines:* Some of the important reactions of primary and secondary amines like acylation, alkylation, formation of salts, sulphonation, reaction with nitrous acid, reaction with carbondisulphide, reaction with Grignard reagent, reaction with HOCl, oxidation reactions is being given as follow:

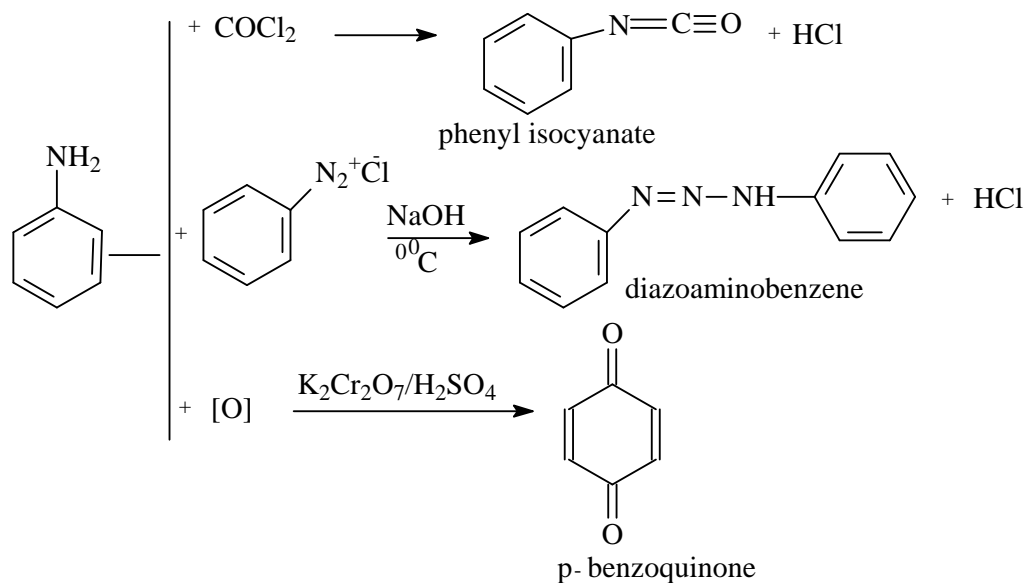




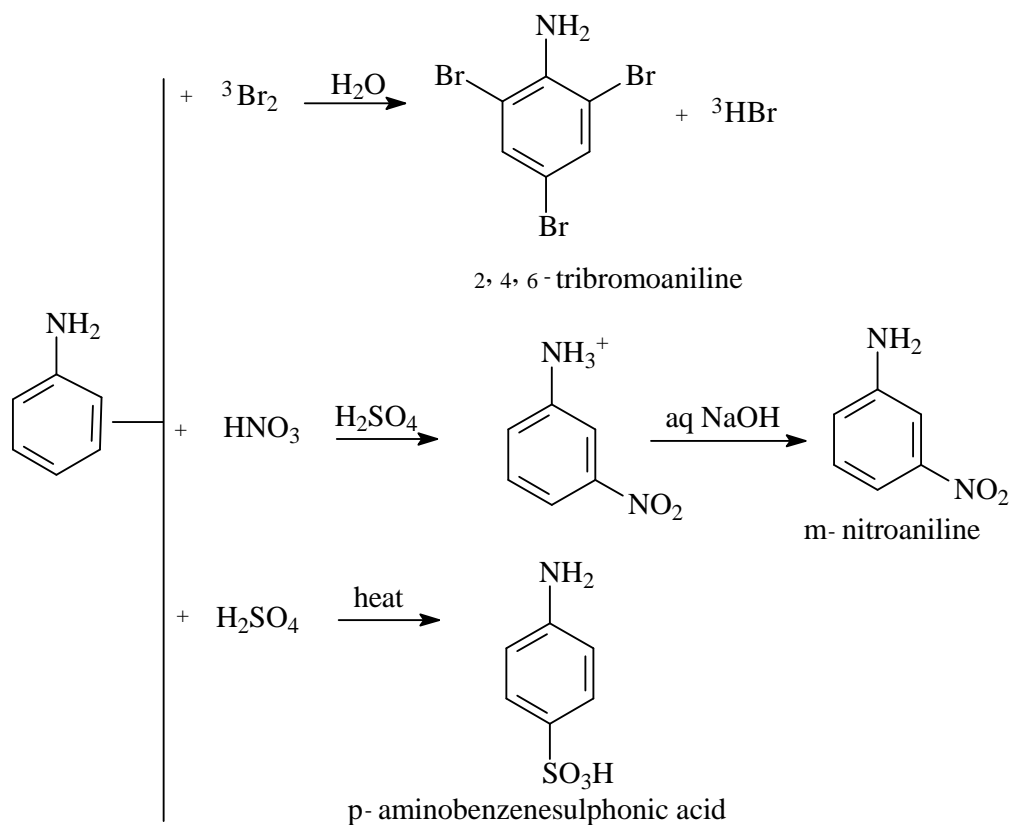


**Reactions of aromatic amines:** aromatic amines undergo two types of reactions namely reactions due to amine group and reactions due to aromatic ring. The important reactions due to both group are given below by taking the example of aniline



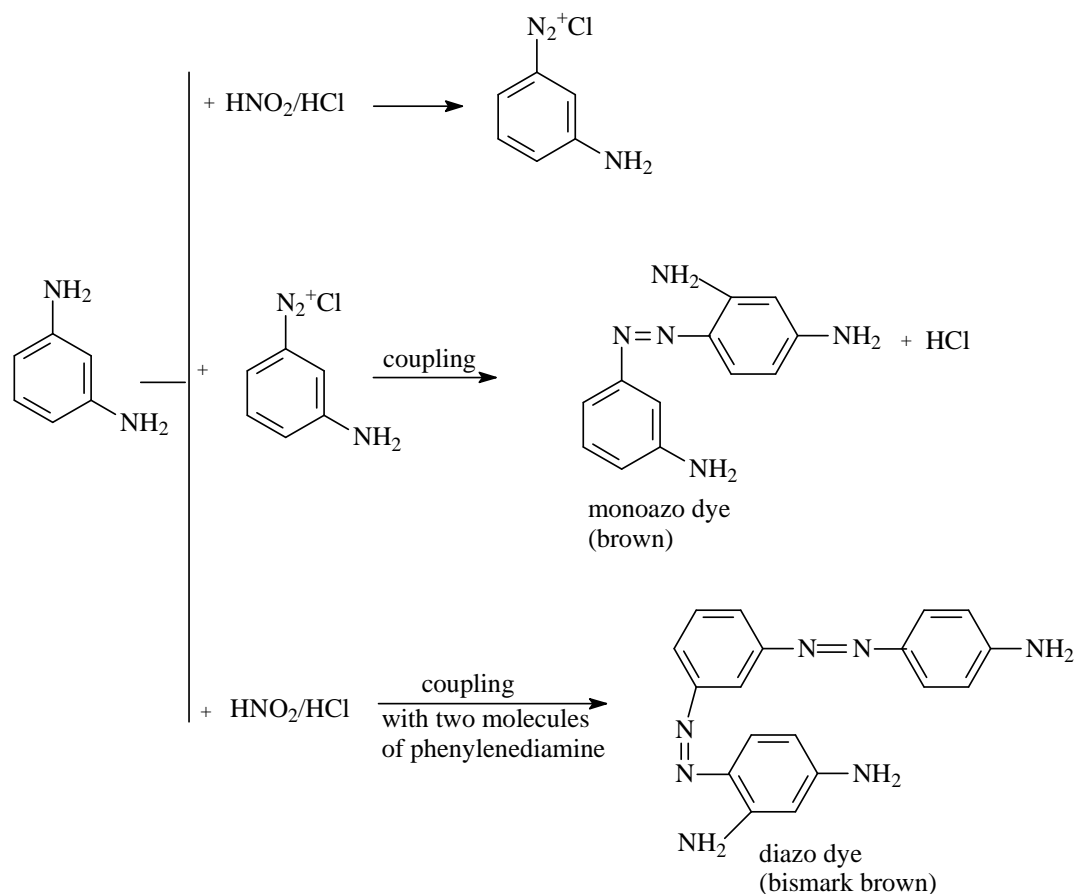
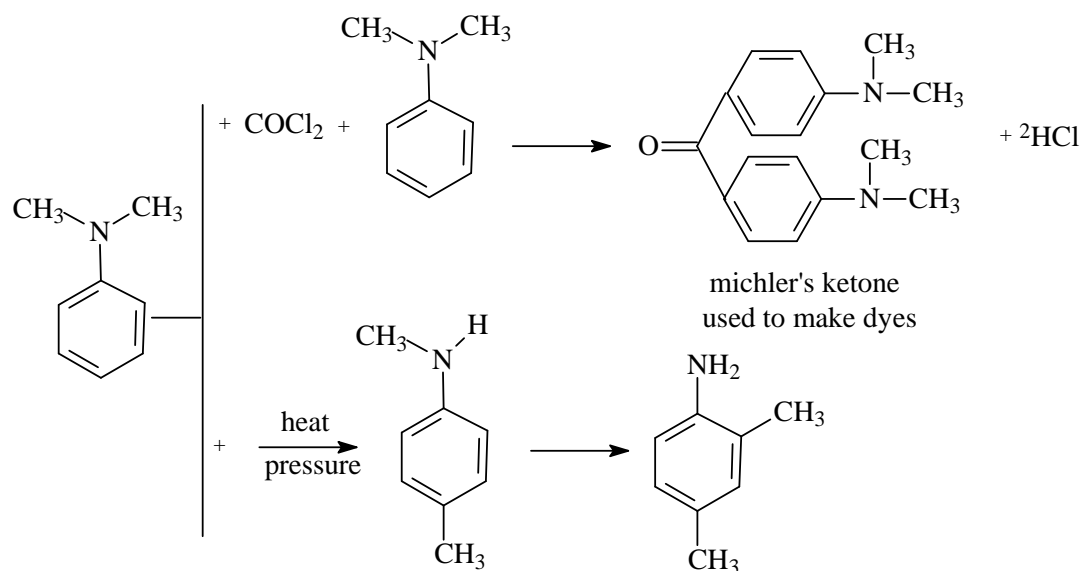


**Reaction in aromatic amines due to benzene ring:** The aromatic amines undergo substitution reactions in its ring part





The tertiary and aromatic diamines give some of the important reactions as:



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### 9.13 SUMMARY

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After studying this unit it can be summarized that this unit educate us about aliphatic and aromatic derivatives of ammonia known as amines and are obtained by the replacement of one, two or all three hydrogen atoms of ammonia by alkyl or aryl groups. Classification of amines as primary, secondary and tertiary amines based on the number of hydrogens replaced by alkyl or aryl groups. We learned about aromatic amino compounds their types as aryl amines and arylalkyl amines. Aryl amines are those compounds in which the  $\text{-NH}_2$  group is directly attached to the nucleus e.g., aniline, p-tolidine etc. whereas in arylalkyl amines the  $\text{-NH}_2$  group is attached to a carbon atom of the side chain e.g., benzylamine,  $\beta$ -phenylethylamine etc. We studied IUPAC nomenclature of amines, physical and chemical properties of aliphatic and aromatic amines in detail. As amines possess basic character, this unit also tells us about basic characters  $\text{pK}_b$  values indicating the basic strength and stereochemistry of amines. We also studied various methods of preparation of primary, secondary and tertiary amines. The consolidated chemical reactions of aliphatic and aromatic reactions have also been described in this unit.

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### 9.14 TERMINAL QUESTIONS

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#### Section -A

#### Q.1 Long answered questions:

5. What are amines? Describe the general methods of preparation of alkyl and aryl amines.
6. Give the preparation, physical and chemical properties of acid anhydrides.
7. How can you prepared primary amines from: (i) Gabriel's phthalimide reaction (ii) Wurtz reaction (iii) Hofmann's bromamide method (iv) Curtius reaction.
8. Describe the general methods of preparation, physical and chemical properties of amides.
9. Describe the mechanism of the acid and alkaline hydrolysis of esters.

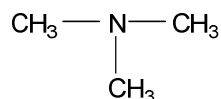
**Section -B****Q.2 Sort answered questions**

10. How can you distinguish between primary, secondary and tertiary amines?
11. Why amines are basic in nature? Explain the role of substituents on the basicity of amines.
12. Compare the reactivity of carboxylic acid derivatives towards nucleophilic substitution.
13. How can you prepare secondary amines from isocyanides?
14. How can you prepare tertiary amines from tetra alkyl ammonium hydroxide?
15. How can you synthesize primary and secondary amines by reductive amination of aldehydes?
16. Give the mechanism of reductive amination of aldehyde and ketones.
17. Explain the followings:
  - (c) Acetyl chloride has lower boiling point than acetic acid
  - (d) Acetyl chloride is more reactive than acetic anhydride
18. How can you convert?
  - (e) Acyl chlorides into esters
  - (f) Esters into amides
  - (g) Amides into amines
  - (h) Amides into carboxylic acids
19. How will you obtain:
  - (e) Primary amine from primary amide
  - (f) Primary amine from phthalimide
  - (g) Benzylamine from benzaldehyde
  - (h) Methylamine from methylisocyanate

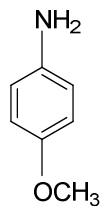
## Section -C

## Q.3 Multiple choice questions (MCQs)

26. Which functional group is present in a primary amine?  
 (a) -COOH (b) -NH<sub>2</sub>  
 (c) C-O-C (d) -SH
27. Which one of the followings is an amino compound?  
 (a) CH<sub>3</sub>SH (b) CH<sub>3</sub>NHC<sub>2</sub>H<sub>5</sub>  
 (c) CH<sub>3</sub>CH<sub>2</sub>NO<sub>2</sub> (d) CH<sub>3</sub>SCH<sub>3</sub>
28. What is the IUPAC name of the given compound?



- (a) *N, N*-Dimethylaminomethane (b) *N*-ethyl-*N*-methyl aminoethane  
 (c) Triethyl nitro (d) *N*-methylaminopropane
29. The given structure is for

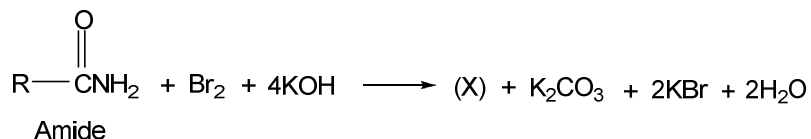


- (a) *p*-Toluidine (b) *o*-Toluidine  
 (c) *p*-Methoxyaniline (d) *p*-Diaminobenzene
30. All three amines can be obtained  
 (a) By Hofmann's bromamide method.  
 (b) By Curtius reaction.  
 (c) By the decarboxylation of amines.  
 (d) By reductive amination of aldehydes and ketones.
31. Amines are weak bases  
 (a) Because their boiling points are higher.  
 (b) Because lower members are water soluble.

- (c) Because they are volatile.  
(d) Due to the presence of unshared pair of electrons on nitrogen atom.
32. The reduction of nitroalkane with Sn/HCl gives  
(a) Tertiary amines (b) Primary amines  
(c) Secondary amines (d) All of these
33. All three amines can be prepared by the reductive amination of  
(a) Aldehydes and ketones (b) Carboxylic acids  
(c) Ethers and thioethers (d) Alcohols and thiols
34. Aromatic amines are less basic than ammonia and aliphatic amines because  
(a) They have  $(4n+2) \pi$  electrons.  
(b) They are more reactive.  
(c) The lone pair of electrons on nitrogen is partially shared with benzene ring.  
(d) Nitrogen does not have lone pair of electrons in aromatic amines.
35. Aromatic primary amines cannot be prepared by Gabriel's phthalimide synthesis because  
(a) Aryl halides do not undergo nucleophilic substitution with anion formed by phthalimide.  
(b) Aromatic amines are less basic than aliphatic amines.  
(c) Aryl halides are decomposed with phthalimide.  
(d) None of the above.
36. Reduction of nitrobenzene with Ni will produce  
(a) Azoxybenzene (b) p-Aminophenol  
(c) *m*-Dinitrobenzene (d) Aniline
37. Hofmann's bromamide reaction is used to convert  
(a) Primary amide to primary amines  
(b) Alkyl halide to primary amine  
(c) Aldehyde to primary amines  
(d) Glycine to primary amines
38. Tertiary amines cannot form hydrogen bonding because they  
(a) Are stable (b) Are unstable  
(c) Are saturated hydrocarbons (d) Do not have hydrogen
39. Which of the following gives a tertiary amine when treated with AgOH?

- (a) N-Methyl acetamide  
 (c) Acetone oxime
- (b) Tetraethyl ammonium iodide  
 (d) Phenyl methylcyanide

40. The major product (X) of the reaction is:



- (a)  $\text{RNH}_2$   
 (c) 
- (b)   
 (d)  $(\text{CH}_3)_4\text{N}^+\text{Cl}^-$

16. Methanol has the higher boiling point than methylamine because

- (a) Methylamine is more basic than methanol.  
 (b) Methylamine does not show hydrogen bonding.  
 (c) Hydrogen bonding is stronger in methanol than in methylamine.  
 (d) An unshared pair of electrons is present on nitrogen atom in amines.

17. Amines which are bonded in one alkyl group are

- (a) Primary amine  
 (c) Tertiary amine
- (b) Secondary amine  
 (d) Quaternary amines

18. Aniline reacts with phenol in presence with zinc chloride at 200°C to form

- (a) Primary amine  
 (c) Tertiary amine
- (b) Secondary amine  
 (d) Quaternary amines

19. Chloramine reacts with methyl magnesium bromide to form

- (a) Tertiary butyl amine  
 (c) Acyl amides
- (b) Ethyl methyl amine  
 (d) Methyl amine

20. Quaternary ammonium salts on hydrolysis with most silver produce

- (a) Primary amine  
 (c) Tertiary amine
- (b) Secondary amine  
 (d) Azo compounds

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**9.15 ANSWERS (MCQs)**

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26. (b)	27. (b)	28. (a)	29. (c)	30. (d)
31. (d)	32. (b)	33. (a)	34. (c)	35. (a)
36. (d)	37. (a)	38. (d)	39. (b)	40. (a)
41. (c)	42. (a)	43. (b)	44. (d)	45. (c)

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**9.16 REFERENCES**

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**UNIT-10 ORGANOSULPHUR AND  
ORGANOPHOSPHORUS COMPOUNDS**

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**CONTENTS:**

- 10.1 Objectives
- 10.2 Introduction
- 10.3 Preparation of organosulphur compounds
- 10.4 Thiols and thioethers
- 10.5 Preparation of thiols and thioethers
- 10.6 Physical properties of thiols and thioethers
- 10.7 Chemical properties of thiols and thioethers
- 10.8 Biological role of organosulphur compounds
- 10.9 Preparation of organophosphorus compounds
- 10.10 Nomenclature of organophosphorus compounds
- 10.11 Physical properties of organophosphorus compounds
- 10.12 Chemical properties of organophosphorus compounds
- 10.13 Pentavalent organophosphorus compounds
- 10.14 Organophosphoranes, phosphoylids: Wittig reagent
- 10.15 Biological role of organophosphorus compounds
- 10.16 Summary
- 10.17 Terminal questions
- 10.18 Answers(MCQs)
- 10.19 Reference

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***10.1 OBJECTIVES***

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The learning objective of this important unit are to study the organosulphur compounds like thiols/mercaptans, thioethers and organophosphorus compounds like phosphine, phosphorane, phosphine oxides, their preparation, physical properties and chemical reactions. Because of the importance of sulphur and phosphorus for living system, the aim of this unit is also to study the biological role of organosulphur and organophosphorus compounds.



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## 10.2 INTRODUCTION

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The organosulphur and organophosphorus compounds are very important class of organic compounds. These compounds are found in many living things in the form of amino acids, nucleotides, co-enzymes etc. These classes of compounds can be introduced separately as follow:

**A. Organosulphur compounds:** Organosulfur compounds are organic compounds that contain sulphur. They are found in all living systems in the form of certain essential amino acids (*e.g.*, cystine, methionine), peptides (*e.g.*, glutathione), coenzymes (*e.g.*, coenzyme-A, lipoic acid), vitamins (*e.g.*, thiamine, biotin), and hormones. They also include various bioactive synthetic compounds such as sulpha drugs, antibiotics (penicillin's, cephalosporins, bacitracin, gliotoxin etc.), alkaloids, insecticides, fungicides, poisons (sulphur mustard) and various classes of dyes. Fossil fuels like coal, crude oil and natural gas contain organosulphur compounds. Organosulphur compounds may have a sulphur-hydrogen, sulphur-oxygen, sulphur-nitrogen, or a sulphur-halogen bond. The sulphur atom in these compounds may be in  $-2$ ,  $+4$ , and  $+6$  oxidation states.

There are three main classes of organosulphur compounds:

1. The first class of organosulphur compounds contains sulphur atom in the  $-2$  oxidation state. They include mercaptans (thiols,  $R-SH$ ), thioethers ( $R-S-R'$ ), thiophenols ( $Ar-SH$ ), thioaldehydes ( $R-CH=S$ ), and thioketones ( $R-CS-R'$ ), disulphides and polysulphides ( $R-S_x-R'$ ), and sulphonium salts ( $RR'S^+X^-$ , where  $X$  is a halogen ion).
2. The second class of organosulphur compounds contains sulphur atom in  $+4$  oxidation state *e.g.*, sulphinic acids ( $R-SO_2H$ , or  $R-SO(OH)$ ) and sulphoxides ( $R-SOR'$ ).
3. The third class of organosulphur compounds contains sulfur atom in the  $+6$  oxidation state *e.g.*, sulphonic acids ( $R-SO_3H$ ) and sulphones ( $R-SO_2-R'$ ).

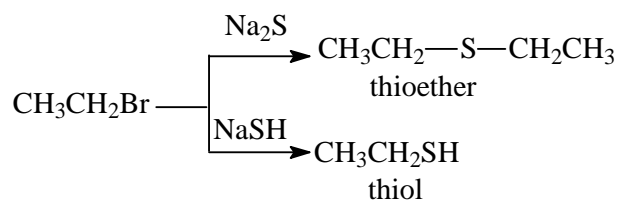
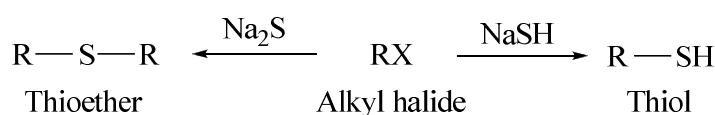
**B. Organophosphorus compounds:** Organophosphorus compounds are organic derivatives of phosphorus which usually contain a phosphoryl ( $P=O$ ) or a thiophosphoryl ( $P=S$ ) bond. These compounds are usually esters, amides, or thiol derivatives of phosphoric, phosphonic, phosphinic, or thiophosphoric acids. These

compounds are potentially toxic and commonly used as pesticides *e.g.*, parathion is highly toxic to mammals and birds used in agriculture and in residential areas to control pests and mosquitoes. Generally, organophosphorus compounds are classified into three main classes according to the number of P-C bonds: alkyl phosphines ( $R-P-H_2$ ), dialkyl phosphines ( $R_2-P-H$ ) and trialkyl phosphines ( $R_3-P$ ). Organophosphorus compounds can also be classified according to the nature of phosphorus as phosphines, phosphine oxide ( $R_3PO$ ), phosphine sulphides ( $R_3-P-S$ ), phosphine imines ( $R_3PNR'$ ), methylene phosphenes ( $R_3P=CR'R''$ ) and phosphonium compounds ( $R_4P^+X^-$ ). Organophosphorus acids containing oxygen are phosphonous acid ( $RPO_2H_2$ ), phosphinous acid ( $R_2POH$ ), phosphonic acid ( $RPO_3H_2$ ), and phosphinic acid ( $R_2PO_2H$ ), and various organic derivatives such as hypophosphorous acid ( $H_3PO_2$ ), phosphorous acid ( $H_3PO_3$ ), phosphoric acid ( $H_3PO_4$ ) etc.

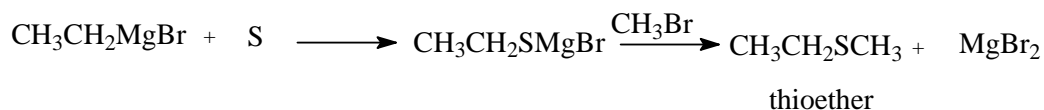
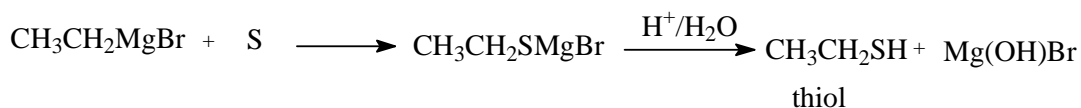
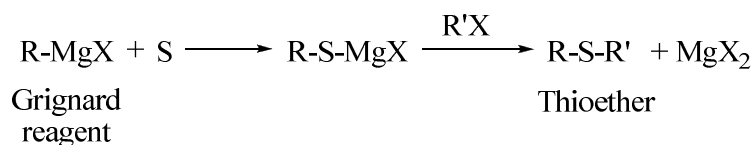
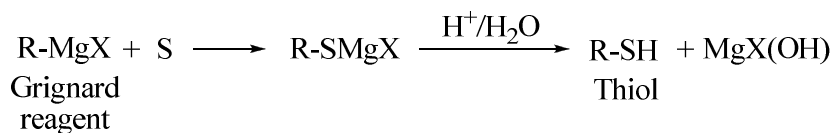
### 10.3 PREPARATION OF ORGANOSULPHUR COMPOUNDS

The organosulphur compounds can be synthesized by the treatment of elemental sulphur or inorganic sulphur compounds like  $Na_2S$  or  $K_2S$ ,  $KSH$  or  $NaSH$ ,  $SCl_2$ ,  $SO_2$ ,  $SO_3$  and  $H_2SO_4$  with organic compounds.

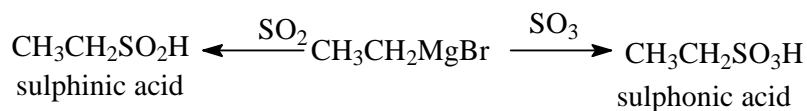
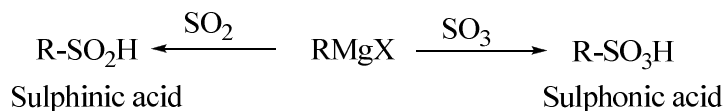
**1. From alkyl halides:** Alkyl halides on reaction with  $KSH$  or  $NaSH$  give thiols ( $R-SH$ ), while on heating with potassium sulphide or sodium sulphide, they produce thioethers ( $R-S-R$ ).



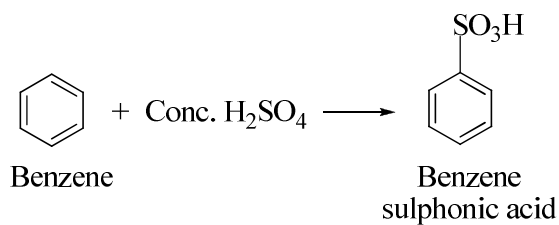
**2. From Grignard's reagent:** Grignard's reagent on treatment with elemental sulphur and followed by the hydrolysis in presence of an acid gives the corresponding thiols (R-SH), whereas on reaction with sulphur and followed by the reaction with haloalkanes, it produces thioethers (R-S-R'). The reactions are as follows:



The sulphinic (R-SO<sub>2</sub>H) and sulphonic acids (R-SO<sub>3</sub>H) can be obtained by the reaction of SO<sub>2</sub> or SO<sub>3</sub> on Grignard reagent, respectively.



**3. From the sulphonization of benzene:** The simple aromatic sulphur compound is obtained by the reaction of concentrated sulphuric acid on benzene.




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### 10.4 THIOLS AND THIOETHERS

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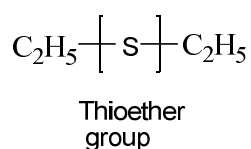
**A. Thiols:** Thiols are the sulfur analogue of alcohols which are formed by the replacement of oxygen by sulphur atom from alcohols. The  $-\text{SH}$  functional group itself is referred to as either a thiol group or a sulphhydryl group. Thiols are sometimes referred to as mercaptans. The term mercaptan was introduced in 1832 by William Christopher Zeise and is derived from the Latin mercurium captans (meaning mercury capturing) because the thiolate group bonds very strongly with mercury compounds. Thiols react with mercury to form mercaptides. **Nomenclature**

In IUPAC system, thiols are named by adding the suffix *-thiol* after the name of parent alkane. Therefore, the name becomes alkanethiol (*Table-10.1*)

Table-10.1: IUPAC nomenclature of thiols

Compound	Common name	IUPAC name
$\text{CH}_3\text{SH}$	methyl mercaptan	methanethiol
$\text{CH}_3\text{CH}_2\text{SH}$	ethyl mercaptan	ethanethiol
$\text{CH}_3\text{CH}_2\text{CH}_2\text{SH}$	<i>n</i> -propyl mercaptan	propane-1-thiol
$\text{CH}_3\text{CH}(\text{SH})\text{CH}_3$	isopropyl mercaptan	propane-2-thiol
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{SH}$	<i>n</i> -butyl mercaptan	1-butanethiol

**B. Thioethers:** Thioethers, also called sulphides are the sulphur analogues of ethers. They have the general formula  $\text{R-S-R}'$ , where R and R' are alkyl groups. These alkyl groups may be identical or different. The functional group in thioether is  $-\text{S}-$ .



Thioethers are colorless oily liquids having unpleasant smell. Mustard gas is a thioether which is prepared by the ethane.

**Nomenclature:** In IUPAC system, symmetrical thioethers are named as dialkyl sulphides (*Table-10.2, below*).

*Table 10.2 Symmetrical thioethers*

Compound	Common name	IUPAC name
CH <sub>3</sub> -S-CH <sub>3</sub>	dimethyl sulphide	methyl thiomethane
CH <sub>3</sub> CH <sub>2</sub> -S-CH <sub>2</sub> CH <sub>3</sub>	diethyl sulphide	ethyl thioethane

Similarly the un-symmetrical thioethers, both alkyl groups should be written before the suffix sulphide (*Table-10.3, below*).

*Table 10.3 Symmetrical thioethers*

Compound	Common name	IUPAC name
CH <sub>3</sub> CH <sub>2</sub> -S-CH <sub>3</sub>	ethyl methyl sulphide	methyl thioethane
CH <sub>3</sub> -S-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	methyl-n-propyl sulphide	1-methyl thiopropane
C <sub>6</sub> H <sub>5</sub> -S-CH <sub>3</sub>	methyl phenyl sulphide	thioanisole

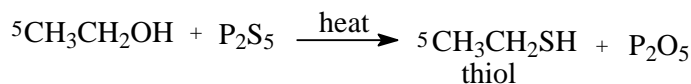
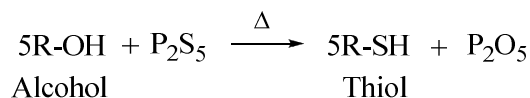
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## ***10.5 PREPARATION OF THIOLS AND THIOETHERS***

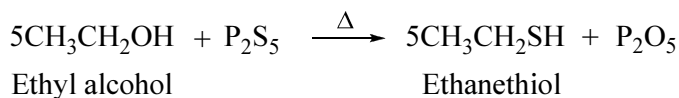
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**A. General methods for preparation of thiols:** Thiols can be obtained by the following general methods:

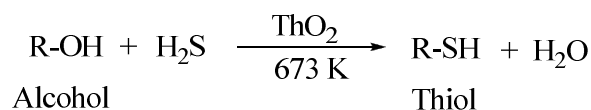
**1. From alcohols:** Thiols can be prepared by heating alcohols with phosphorous pentasulphide. The general reaction is as follows:



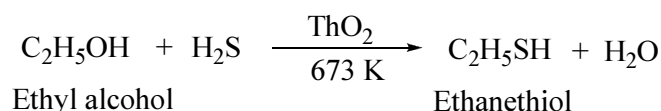
For example, when ethyl alcohol is heated with phosphorous pentasulphide, the ethanethiol is obtained.



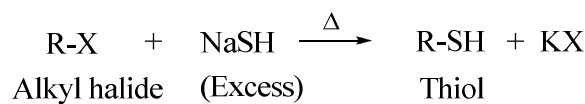
Thiols can also be prepared by heating alcohols with hydrogen sulphide in the presence of ThO<sub>2</sub> (thoria) catalyst.



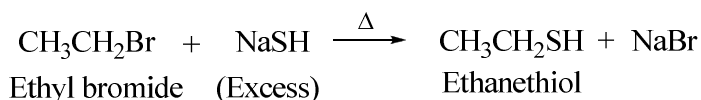
For example,



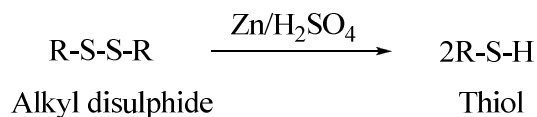
**2. From alkyl halides:** Thiols are prepared by using S<sub>N</sub>2 reactions of KSH or NaSH with primary or secondary alkyl halides.



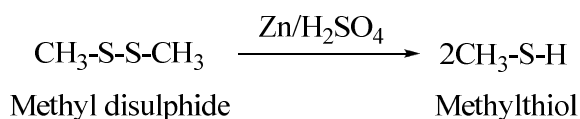
For example, ethyl bromide reacts with the excess amount of sodium hydrosulphide in alcoholic medium undergoes nucleophilic substitution to produce ethanethiol.



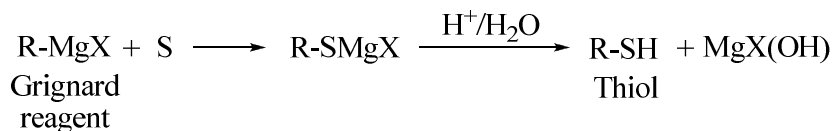
**3. From alkyl disulphides:** Alkyl disulphides with zinc in the presence of acid reduced into thiols.



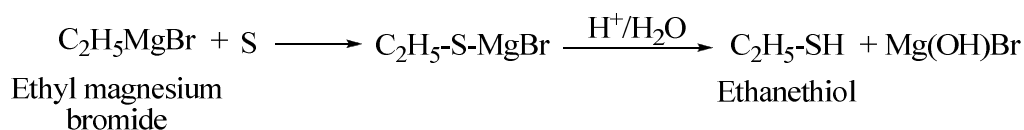
For example, dimethyl disulphide with zinc dust and acid reduced into methanethiol.



**4. From Grignard's reagents:** Grignard's reagent on treatment with sulphur and followed by the hydrolysis in presence of an acid gives the corresponding thiols. The general equation is as:

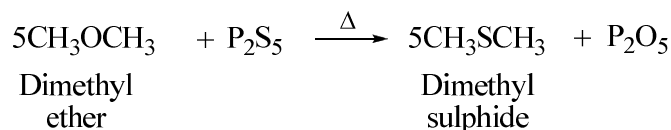


For example, ethyl magnesium bromide on treatment with sulphur and followed by the hydrolysis in presence of an acid gives ethanethiol.

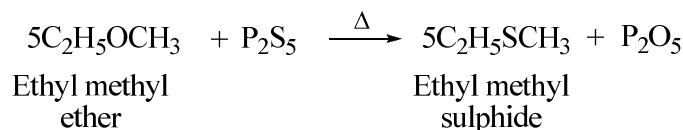


**B. General methods for preparation of thioethers:** Thioethers can be prepared by the following general methods.

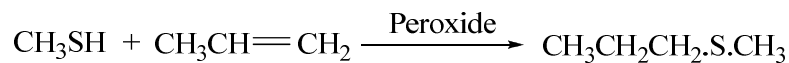
**1. From ethers:** Thioethers can be prepared by heating ethers with phosphorous pentasulphide. For example, dimethyl ether on heating with phosphorous pentasulphide forms dimethyl sulphide.



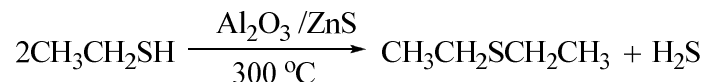
Similarly, ethyl methyl ether on heating with phosphorous pentasulphide produces ethyl methyl sulphide.



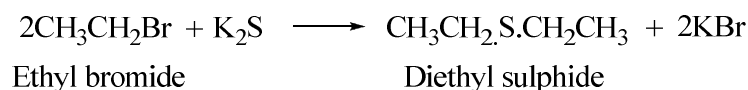
**2. From thiols:** Thioethers can be obtained by the treatment of thiols with olefins in the presence of peroxides. For example, methanethiol on reaction with propylene in presence of peroxide forms methyl-n-propyl sulphide.



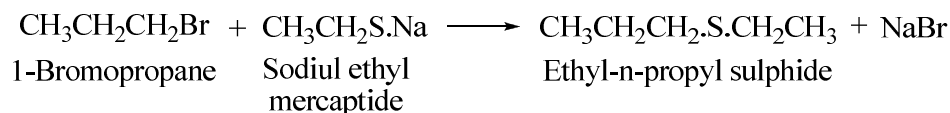
Thioethers can also be prepared by passing of a thiol over a mixture of alumina and zinc chloride at 300 °C. For example, when ethanethiol is passed over a mixture of alumina and zinc chloride at 300 °C, diethyl sulphide is obtained.



**3. From alkyl halides:** Alkyl halides on heating with potassium sulphide or sodium mercaptide produce thioethers. For example, ethyl bromide on heating with potassium sulphide forms diethyl sulphide.



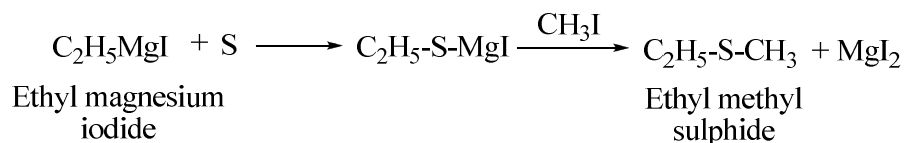
Similarly, 1-bromopropane on reaction with sodium ethyl mercaptide produces ethyl-n-propyl sulphide.



**4. From Grignard's reagent:** Grignard's reagent on reaction with sulphur and followed by the reaction with haloalkanes results the formation of thioethers. The general reaction is as:

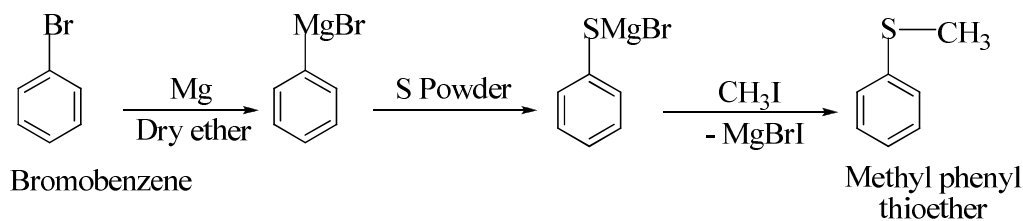


For example, the reaction of sulphur with ethyl magnesium iodide (Grignard's reagent) followed by the reaction with methyl iodide results the formation of ethyl methyl sulphide.



Similarly, methyl phenyl thioether is obtained by the reaction of sulphur with Phenylmagnesium bromide (Grignard's reagent) in the presence of methyl iodide.





## 10.6 PHYSICAL PROPERTIES OF THIOLS AND THIOETHERS

**A. Physical properties of thiols:** Except methanethiol which is a gas, the higher thiols are volatile liquids having extremely unpleasant odors, as garlic and rotten eggs. Methanethiol or ethanethiol is purposely added to LPG cylinders and natural gas in order to reveal leaks. Thiols, unlike alcohols, do not form hydrogen bonds (S-H bonds are less polar than O-H bonds), therefore they have lower boiling points than to corresponding alcohols (*Table-10.4*). Thiols are insoluble in water due to the absence of hydrogen bonding with water, but readily soluble in organic solvents like ether and alcohol. They are more easily oxidized than alcohols; oxidation takes place at sulphur. Thiols ( $pK_a = 7$ ) are more acidic than alcohols ( $pK_a = 16$ ), and their proton can be removed by the reaction with base.

**Table 10.4: Boiling points of thiols and corresponding alcohols**

Thiols / alcohols	Boiling points (°C)
CH <sub>3</sub> SH	6
CH <sub>3</sub> OH	56
C <sub>2</sub> H <sub>5</sub> SH	35
C <sub>2</sub> H <sub>5</sub> OH	78
C <sub>3</sub> H <sub>7</sub> SH	68
C <sub>3</sub> H <sub>7</sub> OH	98

**B. Physical properties of thioethers:** Thioethers are colourless, oily liquids having an unpleasant order. The boiling points of thioethers are more than those of corresponding ethers. The boiling point of dimethyl thioether is 38°C, whereas the boiling point of

diethyl thioether is 92°C. Thioethers are insoluble in water, but soluble in organic solvents like ether and alcohol.

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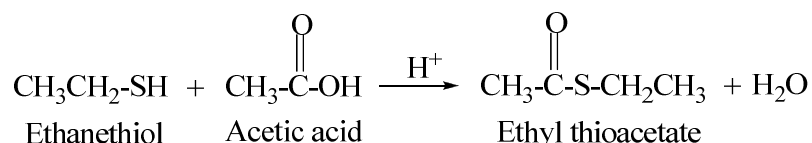
## *10.7 CHEMICAL PROPERTIES OF THIOLS AND THIOETHERS*

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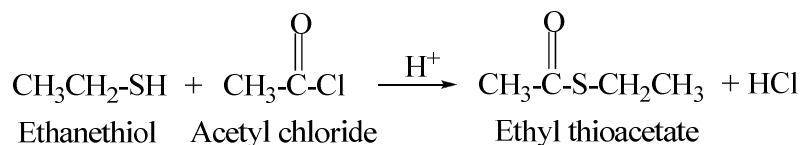
Both thiols (mercaptans) and thioethers undergo various types of chemical reactions. Some of the important reactions of thiols and thioether are being discussed as follow

### A. Chemical properties of thiols

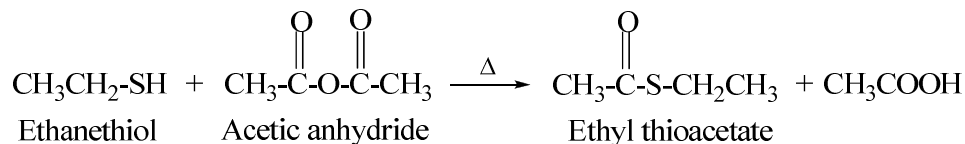
**1. Reaction with acids and acid anhydride:** Thiols on reaction with acids, acid chlorides or acid anhydrides give thioesters. For example, ethanethiol on reaction with acetic acid gives ethyl thioacetate.



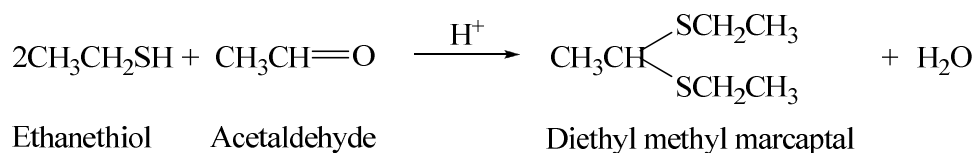
Ethanethiol on reaction with acetyl chloride gives ethyl thioacetate.



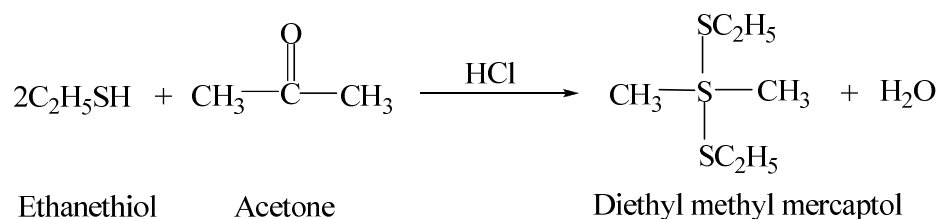
Similarly, ethanethiol on reaction with acetic anhydride produce ethyl thioacetate.



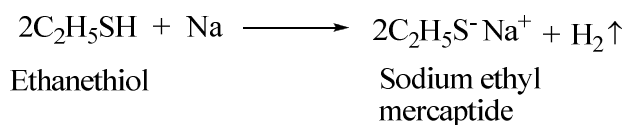
**2. Reaction with aldehydes and ketones:** On reaction with aldehyde or ketones in the presence of an acid, thiols form mercaptals and mercaptols respectively. For examples, ethanethiol on treatment with acetaldehyde in presence of hydrochloric acid produces diethyl methyl mercaptal.



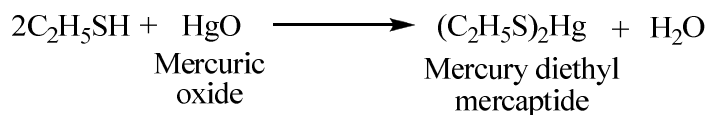
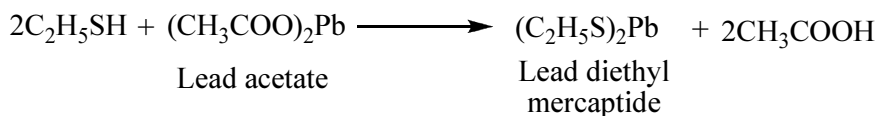
Similarly, reaction of ethanethiol with acetone in presence of hydrochloric acid results the formation of diethyl methyl mercaptol.



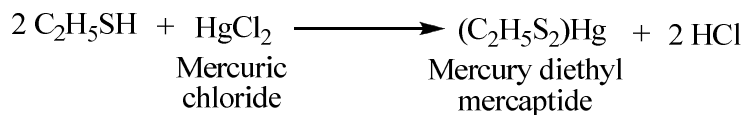
**3. Reactions with alkali metals and alkali:** On reaction with alkali metals, thiols form mercaptides with the evolution of hydrogen gas.



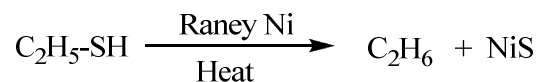
**4. Reactions with metal salts and metallic oxides:** Thiols on reaction with metal oxides and other metal salts form the following salts:



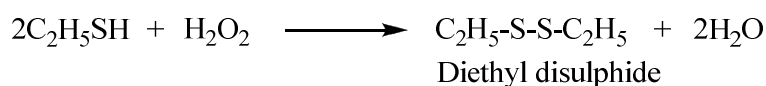
Ethanethiol reacts with mercuric chloride to form a precipitate of mercury diethyl mercaptide. This reaction is used to distinguish between ethane thiol and ethyl alcohol, ethyl alcohol does not give this reaction.



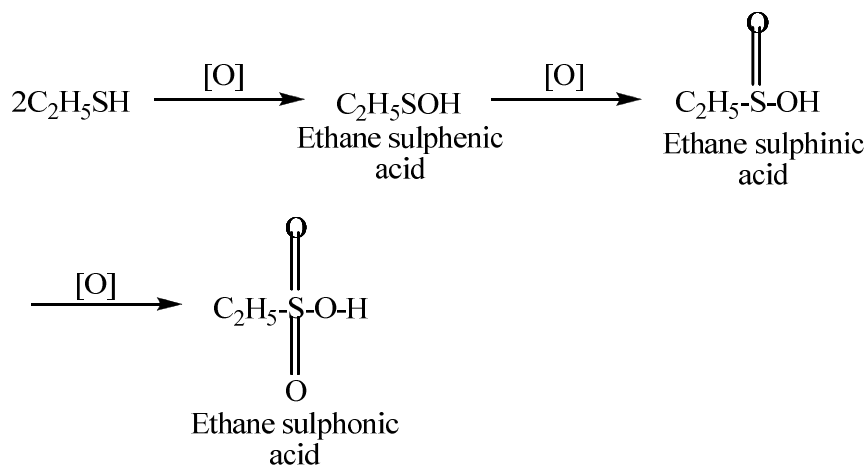
**5. Desulphurization:** Thiols undergo desulphurization with Raney nickel to form ethane.



**6. Oxidation with mild oxidizing agents:** With mild oxidizing agents like hydrogen peroxide, cupric chloride or iodine sodium hypochlorite results in the formation of disulphides. For example, ethanethiol on oxidation with  $\text{H}_2\text{O}_2$  forms diethyl disulphide.

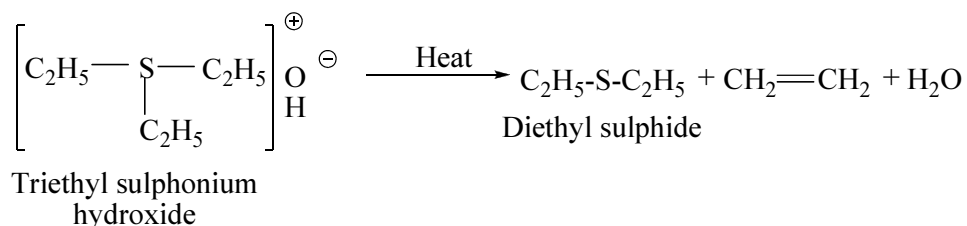
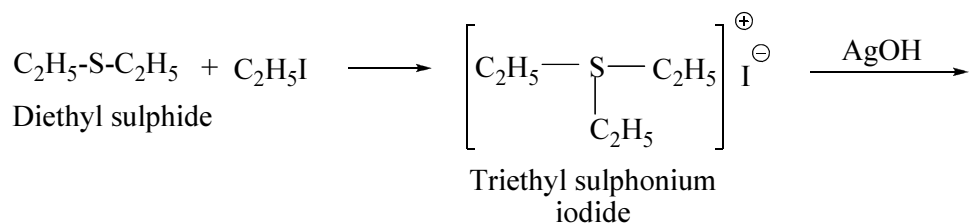


**7. Oxidation with strong oxidizing agents:** When oxidized with strong oxidizing agents, like concentrated nitric acid or potassium permanganate, thiols can be oxidized to corresponding sulphonic acids.

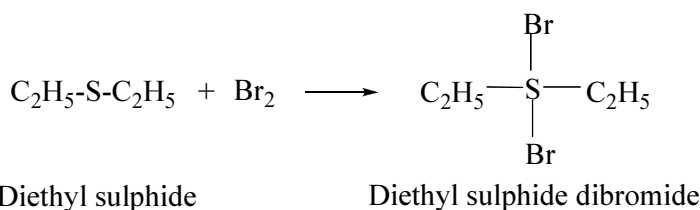


## B. Chemical properties of thioethers

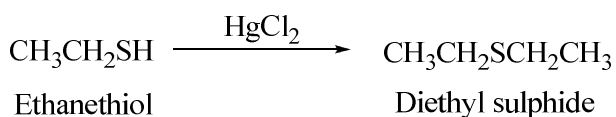
**1. Reaction with alkyl halides:** Alkyl halides on reaction with thioethers results the formation of sulphonium salts. These sulphonium halides on reaction with moist silver oxide form sulphonium hydroxides which on heating decomposed into thioethers and alkenes.



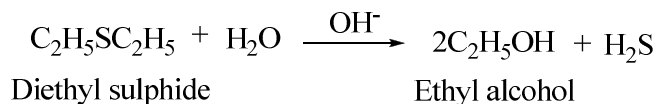
**2. Reaction with halogens:** Thioethers on treatment with halogens form corresponding thioether dihalides. For example, diethyl sulphide on reaction with bromine gives diethyl sulphide dibromide.



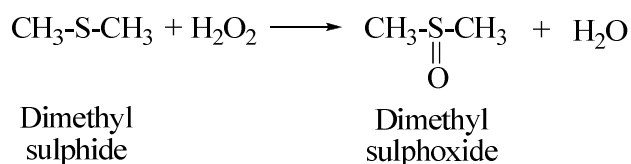
**3. Reaction with metal salts:** Thioethers on reaction with metal salts form insoluble coordination compounds.



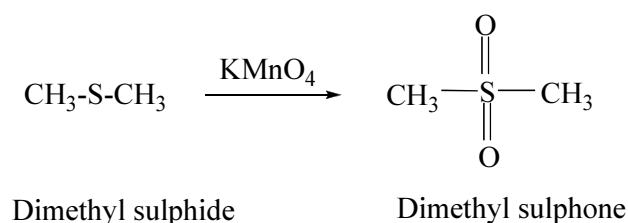
**4. Hydrolysis:** Thioethers on boiling with alkali undergo hydrolysis to produce alcohols. For example, ethyl methylsulphide is hydrolyzed with sodium hydroxide to ethyl alcohol.



**5. Oxidation with mild oxidizing agents:** With mild oxidizing agents like chlorine, hydrogen peroxides, the thioethers are oxidized into sulphoxides. For example, the dimethyl sulphide oxidized with hydrogen peroxide into dimethyl sulphoxide.



**6. Oxidation with strong oxidizing agents:** When oxidized with strong oxidizing agents, like concentrated nitric or potassium permanganate, thioethers are converted into sulphones. For example, dimethyl sulphide is oxidized by the  $\text{KMnO}_4$  into dimethyl sulphone.

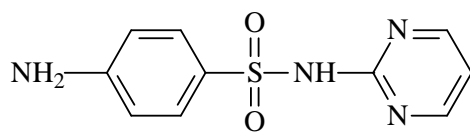



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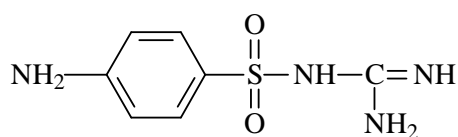
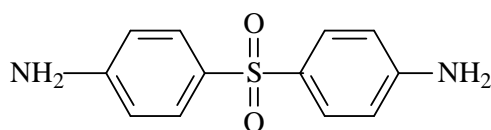
### ***10.8 BIOLOGICAL ROLE OF SULPHUR COMPOUNDS***

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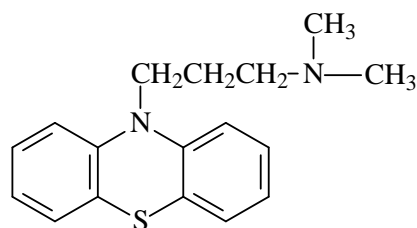
Organosulphur compounds such as diallyl disulfide, diallyl trisulfide and S-ally cysteine are used as therapeutics. They can be used as inhibitors of polymerization and oxidation, stabilizers of polymer materials, and as solvents. The sulphonic acids and their salts are used as intermediates in heavy organic synthesis and as surfactants. Most organosulphur compounds are highly toxic and are used as insecticides, fungicides and poisons. Vitamin B<sub>1</sub> plays an important role, as a co-enzyme in the decarboxylation of pyruvate and also in the formation of another co-enzyme the co-enzyme A which is a key enzyme for the degradation of glucose. Besides this many drugs contain sulphur as one of the element in their structure. The sulpha drugs are widely used as anti-bacterial agents by mimicking p-aminobenzoic acid. The common drugs in use are as follow. Penicillin is also a sulphur containing drug.



sulphadiazine

sulphaguanidine  
(used in dysentery)

p p-diaminodiphenylsulphone

Chlorpromazine  
(tranquilizer)

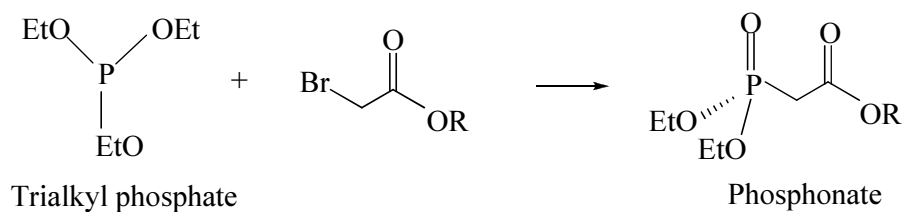
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### 10.9 PREPARATION OF ORGANOPHOSPHORUS COMPOUNDS

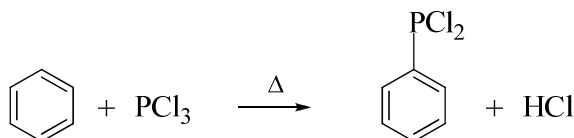
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The Organo phosphorus compounds can be prepared by the following general methods:

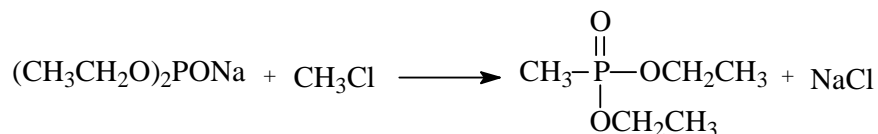
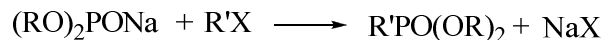
**1. By Arbuzov reaction:** Arbuzov reaction is a chemical reaction of a trialkyl phosphate and an alkyl halide to form a phosphonate.



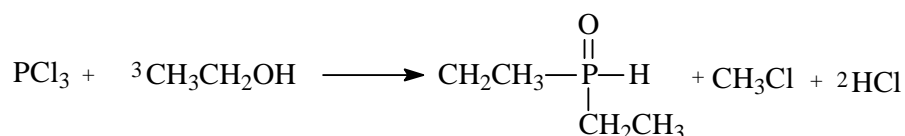
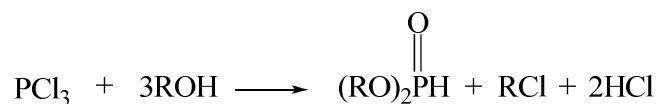
**2. By the reaction of phosphorous trichloride with benzene:**  
Dichlorophenylphosphin is obtained by heating phosphorous trichloride with benzene.



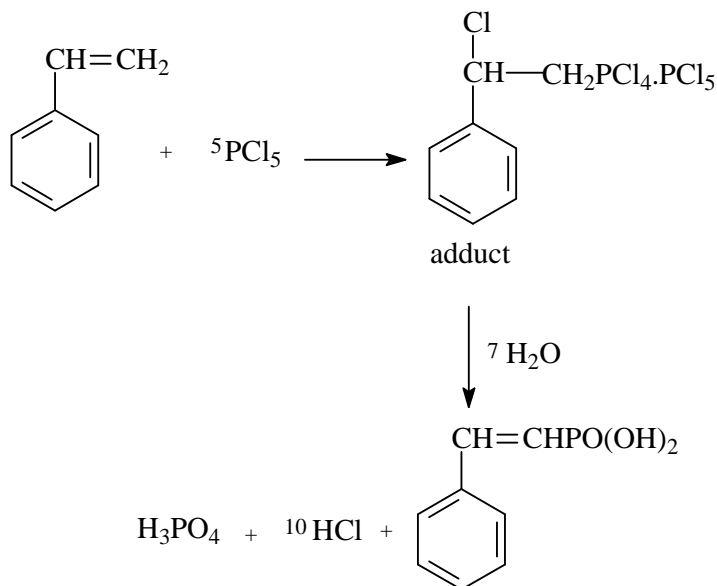
**3. By Michaelis Becker reaction:** Michaelis Becker reaction is the reaction of a hydrogen phosphonate with a base, followed by a nucleophilic substitution of phosphorus on an haloalkane, to produce an alkyl phosphonate.



**4. By the reaction of phosphorous trichloride with alcohols:** Phosphorous trichloride directly reacts with alcohols to form dialkyl phosphonates.

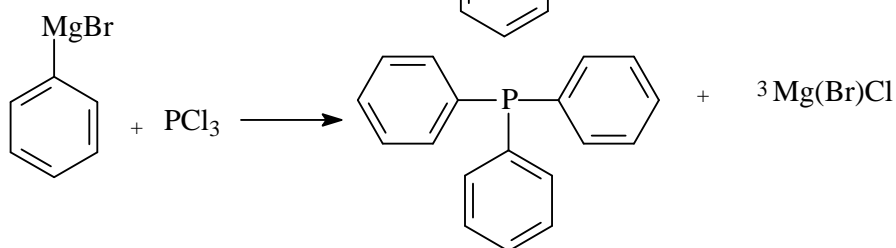
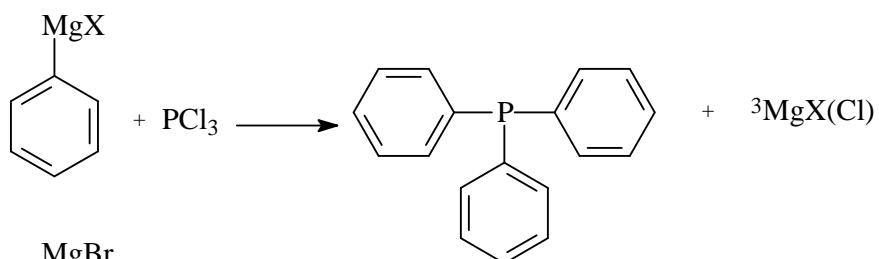
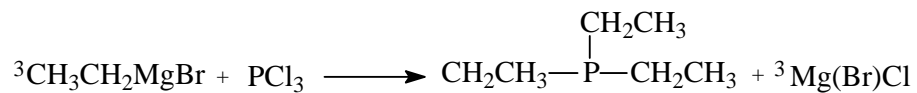
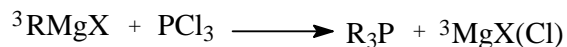


**5. By the reaction of phosphorus pentachloride with styrene:**  $\beta$ -Styrylphosphonic acid can be obtained by the addition of phosphorous pentachloride to styrene followed by the hydrolysis.

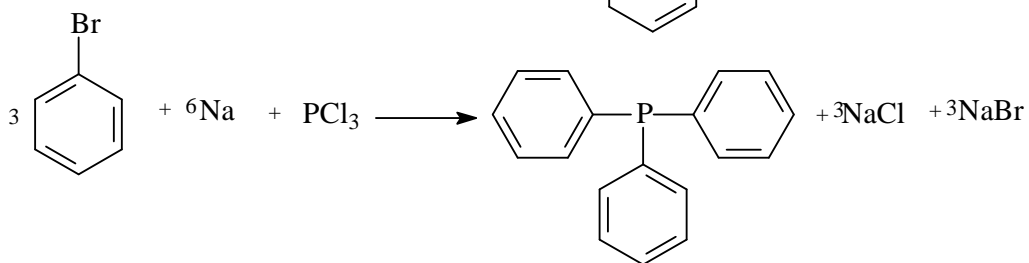
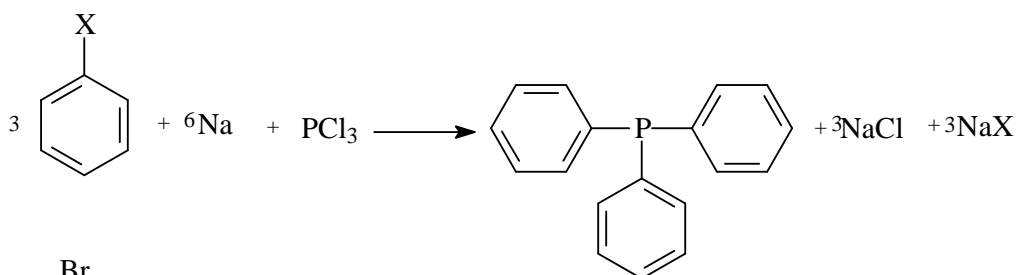




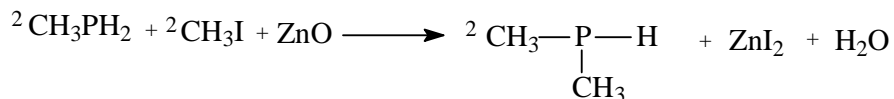
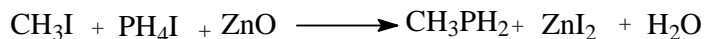
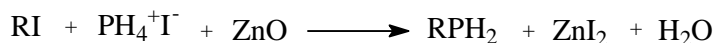
**6. From phosphorus halides:** Phosphorus halides when treated with an excess of Grignard reagent as follows:-



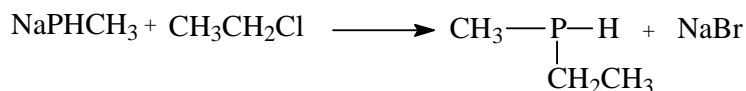
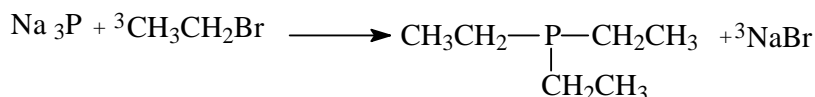
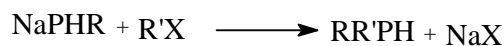
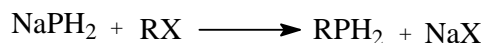
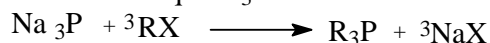
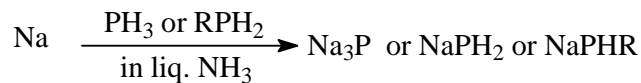
Alternatively, triarylphosphines can be prepared by treating a mixture of halobenzene and  $\text{PCl}_3$  with sodium metal.



**7. From phosphonium salt:** The organophosphorus compounds can be synthesized from phosphonium salt as follow.

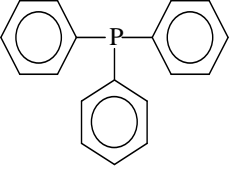
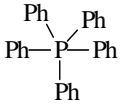
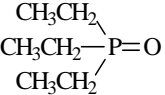


**8. From metal phosphides:** Metal phosphides obtained by treating  $PH_3$  or  $RPH_2$ , when reacted with alkyl halides results in the formation of primary, secondary and tertiary phosphines.



## **10.10 NOMENCLATURE OF ORGANOPHOSPHORUS COMPOUNDS**

The trivalent phosphorous trihydrides are called phosphine, pentahydride are known as phosphorane and oxygen derivatives are called phosphine oxide. Compounds having P-X and P-N bonds are named as acid halides and acid amides when all the OH groups are replaced. The suffix acid is retained even if one -OH is still present as follow:-

Structure and name of the parent compound	Structure and name of the compounds derived from this
$\begin{array}{c} \text{H}-\text{P}-\text{H} \\   \\ \text{H} \end{array}$ phosphine	$\begin{array}{c} \text{CH}_3-\text{P}-\text{H} \\   \\ \text{H} \end{array}$ methyl phosphine
$\begin{array}{c} \text{H} & \text{H} \\ & \diagdown \quad / \\ & \text{P} \\ & / \quad \diagdown \\ \text{H} & \text{H} \end{array}$ phosphorane	 triphenyl phosphine
$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{P}=\text{O} \\   \\ \text{H} \end{array}$ phosphine oxide	$\begin{array}{c} \text{CH}_2\text{CH}_3 \\   \\ \text{CH}_3-\text{P}^+-\text{HBr}^- \\   \\ \text{H} \end{array}$ methylethylphosphonium bromide
$\begin{array}{c} \text{OH} \\   \\ \text{H}-\text{P}-\text{OH} \end{array}$ phosphorus acid	 pentaphenylphosphorane
$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{P}-\text{OH} \end{array}$ phosphinous acid	$(\text{C}_6\text{H}_5)_3\text{P}=\text{CH}_2$ methylenetriphenylphosphorane
$\begin{array}{c} \text{O} \\    \\ \text{H}-\text{P}-\text{OH} \\   \\ \text{OH} \end{array}$ phosphonic acid	 triethylphosphine oxide
$\begin{array}{c} \text{O} \\    \\ \text{H}-\text{P}-\text{OH} \\   \\ \text{H} \end{array}$ phosphinic acid	$\begin{array}{c} \text{Cl} \\   \\ \text{CH}_3-\text{P}-\text{Cl} \end{array}$ methyl phosphorus chloride
$\begin{array}{c} \text{O} \\    \\ \text{H}-\text{P}-\text{OH} \\   \\ \text{H} \end{array}$ phosphonic acid	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{P}-\text{Cl} \end{array}$ dimethylphosphinous chloride
$\begin{array}{c} \text{NH} \\   \\ \text{H}-\text{P}-\text{NH}-\text{C}_6\text{H}_5 \\   \\ \text{C}_6\text{H}_5 \end{array}$ NN diphenylmethyl phosphonic diamide	$\begin{array}{c} \text{O} \\    \\ \text{CH}_2\text{CH}_3-\text{P}-\text{CH}_2\text{CH}_3 \\   \\ \text{H} \end{array}$ diethyl phosphonate
$\begin{array}{c} \text{O} \\    \\ \text{CH}_3-\text{P}-\text{Cl} \\   \\ \text{CH}_3 \end{array}$ dimethylphosphinic chloride	

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**10.11 PHYSICAL PROPERTIES OF ORGANOPHOSPHORUS  
COMPOUNDS**

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Alkyl phosphines, except CH<sub>3</sub>PH (methyl phosphine) which is a gas, mostly colourless bad smelling liquids. Few alkylphosphines are low melting solids.

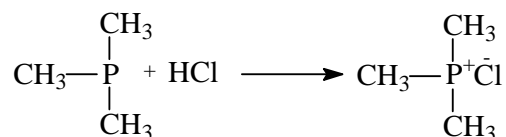
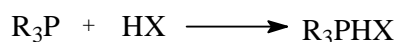
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**10.12 CHEMICAL PROPERTIES OF ORGANOPHOSPHORUS  
COMPOUNDS**

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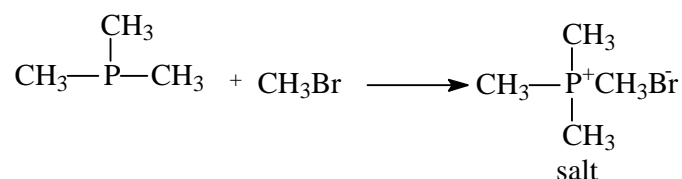
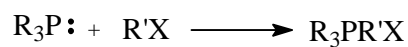
The organophosphorus possesses following chemical properties.

1. **Basic character:** Like amines, the alkyl and aryl phosphines are weaker bases and form adduct while treated with acids.



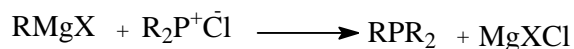
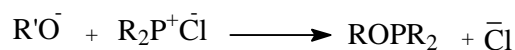
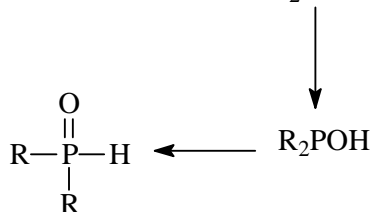
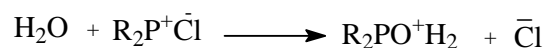
Phosphines are weaker base than amines, however the order is: 3<sup>0</sup> > 2<sup>0</sup> > 1<sup>0</sup>

2. **Nucleophilicity:** Though phosphines are weaker base than amines. They are better nucleophile viz;



The greater nucleophilicity of phosphines is due to the fact that the lone pair of electron in the outer shell of phosphorus is less firmly held and is more polarizable than that of nitrogen.

3. **Electrophilicity:** Trivalent phosphorous compounds having electronegative atoms like halogen or oxygen with phosphorous are attacked by nucleophiles, this is because of positive charge on phosphorous which makes it electrophilic in nature.

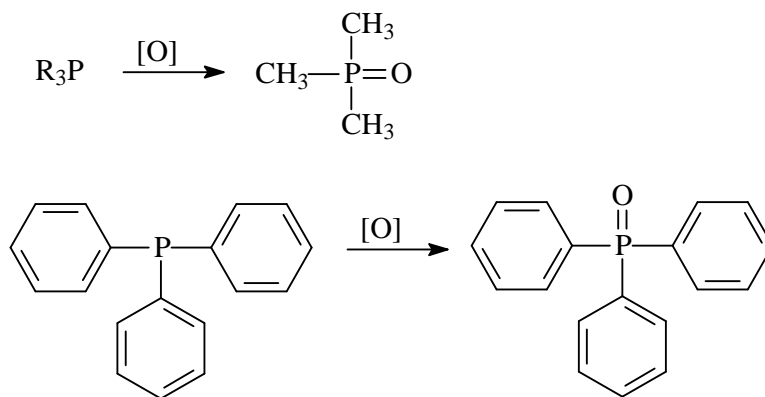



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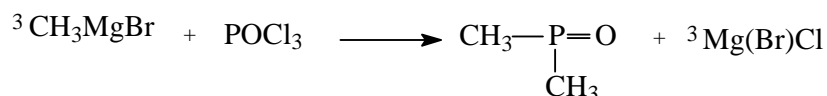
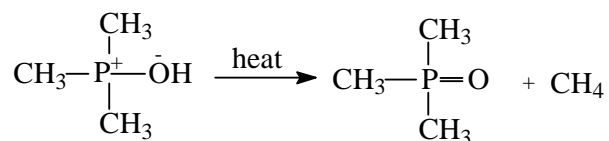
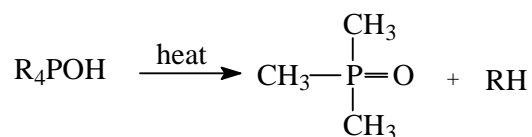
### 10.13 PENTAVALENT PHOSPHORUS COMPOUNDS

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**Phosphine oxide:** These compounds are prepared by the oxidation of trialkyl or triarylphosphines by nitric acid or  $\text{H}_2\text{O}_2$



Alternatively they can be synthesized by heating tetraalkylphosphonium hydroxide or by the action of Grignard reagent on  $\text{POCl}_3$



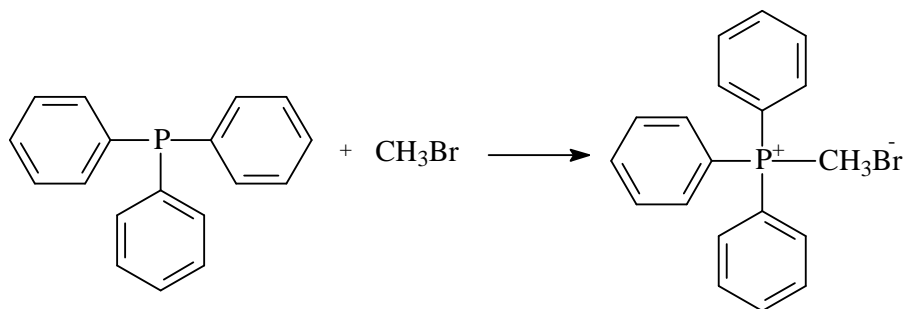
These are most stable organo phosphorous compounds

### 10.14 ORGANOPHOSPHORANE, PHOSPHORUS YLIDS:

#### WITTIG REAGENT

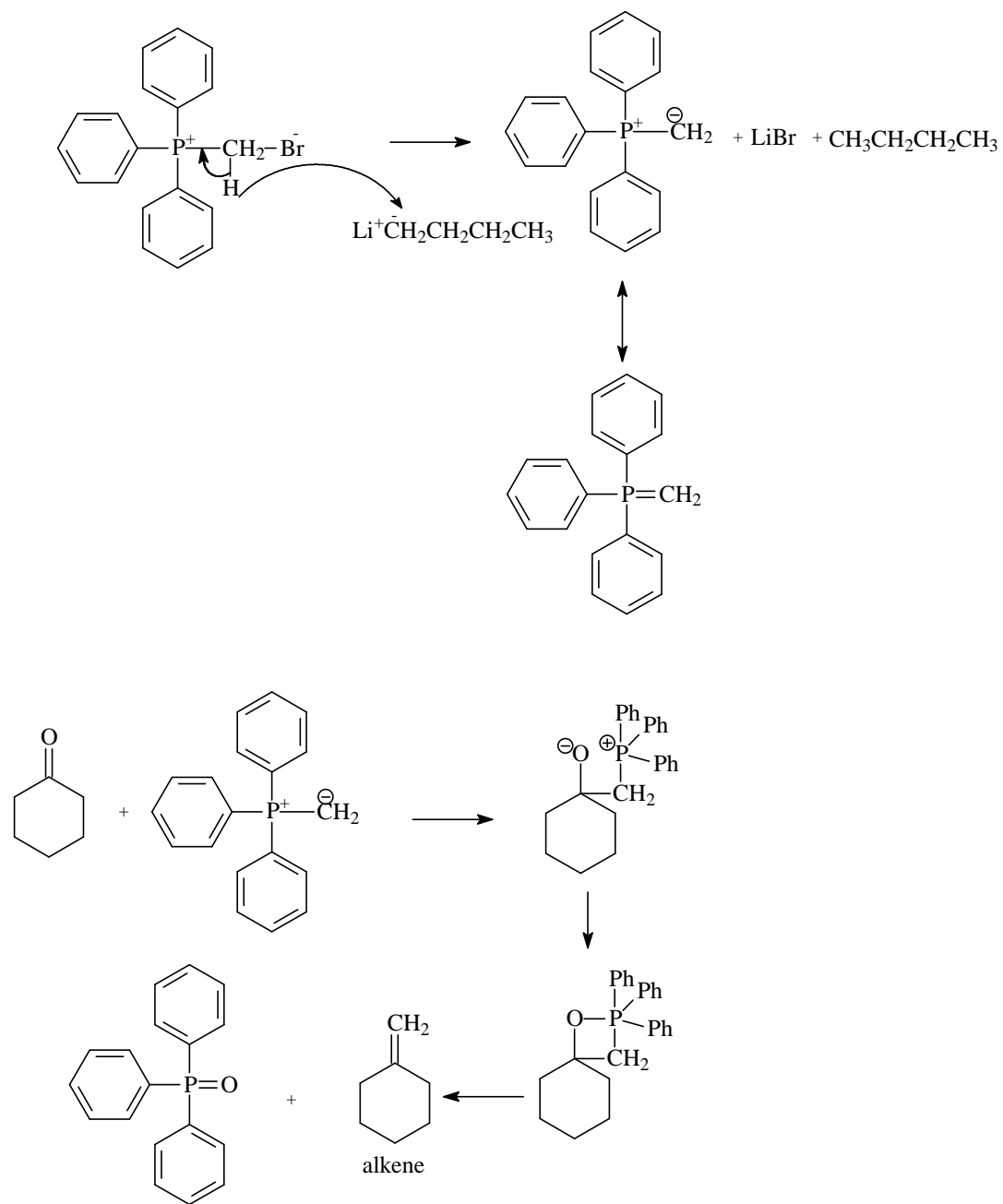
These compounds are prepared in two steps as:

**A.** The nucleophilic triphenylphosphine is treated with primary or secondary alkyl halides to obtain phosphonium salt.



**B.** the phosphonium salt formed in step A is treated with strong base, which abstract hydrogen and produce dialkylidene triphenylphosphorane (ylid) commonly known as Wittig reagent. Because of negative charge on carbon atom the Wittig reagent possess

sufficient basicity and nucleophilicity and add rapidly with carbonyl group and form the basis of Wittig synthesis of alkenes



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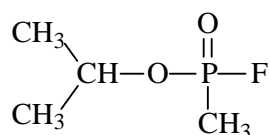
 10.15 BIOLOGICAL ROLE OF PHOSPHORUS
 

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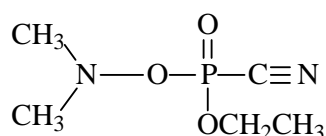
 COMPOUNDS
 

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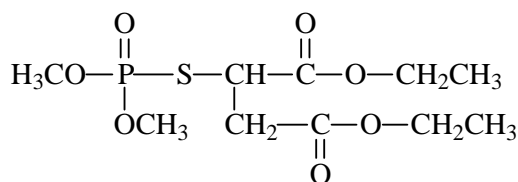
The organophosphorus compounds have several industrial, agricultural, medicinal properties; they are used in synthesis of alkenes by the Wittig reaction and as anthelmintics. They are potentially toxic and used as insecticides, fungicides, herbicides in agriculture worldwide. The organophosphate group is the largest group of insecticide among agrochemicals. The O.P. insecticides are also biodegradable like malathion and parathion. Organophosphorus compounds *e.g.* neguvon, ruelene, dioxathion, diazinon etc. are used in veterinary medicine for control the animal disease *e.g.* ticks. These organic phosphorous compounds such as sarin and tabun are developed as nerves agents that are most dangerous and may be used as chemical warfare agents. These compounds block activity of acetulcholinesterase. Phosphorus compounds play key role in living system. They are essential for energy transfer (ATP-ADP + E), DNA, the genetic material is made up of nucleotide which contains phosphorus as one of the element in its structural framework.



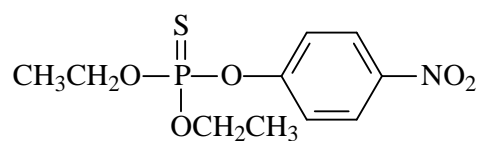
sarin



tabun



malathion



parathion



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**10.16 SUMMARY**

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At the end of this unit it can be summarized that the organophosphorus and organosulphur compounds find very important place in organic chemistry. Regarding these compounds the present unit educates us about organic compounds containing sulphur like thiols, the sulphur analogue of alcohols having –SH functional group. The –SH functional group is known as sulphhydryl or mercapto group. Examples are  $\text{CH}_3\text{SH}$  (methanethiol),  $\text{C}_2\text{H}_5\text{SH}$  (ethanethiol),  $\text{CH}_3\text{CH}_2\text{CH}_2\text{SH}$  (propane-1-thiol),  $\text{CH}_3\text{CHSHCH}_3$  (propane-2-thiol). Thioethers the sulphur analogue of ethers with the general formula  $\text{R-S-R}'$ . Some examples of thioethers are  $\text{CH}_3\text{SCH}_3$  (dimethyl sulphide),  $\text{C}_2\text{H}_5\text{SCH}_3$  (ethyl methylsulphide),  $\text{C}_2\text{H}_5\text{SC}_2\text{H}_5$  (diethyl sulphide) etc. We learned about method of preparation, physical and chemical reaction along with the biological role of organosulphur compounds. This unit also describes the preparation, nomenclature, physical and chemical properties of organophosphorus compounds with their biological role.

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**10.17 TERMINAL QUESTIONS**

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**Section -A****Q.1. Long answered questions**

10. What are thiols? Describe the general methods of preparation and chemical properties of thiols.
- 2 What are thioethers? Describe the general methods of preparation, physical and chemical properties of thioethers.
- 3 What are organophosphorus compounds? Discuss methods for the synthesis of organophosphorus compounds.
- 4 Discuss biological role of organophosphorus and organosulphur compounds with some examples
- 5 Discuss nomenclature of organosulphur and organophosphorus compounds.

**Section -B**

**Q.2. Sort answered questions**

20. Write a short note on organosulphur and organophosphorus compounds.
21. What are organophosphorous compounds? How can they synthesize?
22. How can you prepare thiols from (i) alcohols (ii) alkyl halides (iii) alkyl disulphides?
23. How can you prepare thioethers :
- (i) ethers
  - (ii) thiols
  - (iii) Grignard reagent?
- (a) Explain the followings:
- (e) Thiols have lower boiling points than corresponding alcohols.
  - (f) Thioethers have higher boiling point than corresponding ethers.
  - (g) Thiols and thioethers are insoluble in water.
24. How can you convert?
- (i) Thiols into thioethers
  - (j) Thiols into thioesters
  - (k) Thioethers into alcohols
25. How will you obtained:
- (i) Thiols from Grignard reagent
  - (j) Thioethers from thiols
  - (k) Thioethers from alkyl halides
  - (l) Sulphonic acid from thiols

**Section –C****Q.3. Multiple choice questions (MCQ)**

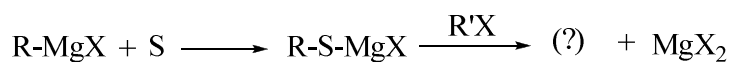
1. Which functional group is present in an organosulphur compounds?
- (a) -COOH
  - (b) -COOCOR
  - (c) C-O-C
  - (d) C-S-C
2. Which class of organic compounds can be represented as R-S-R'?

- (a) Esters (b) Thiols  
c) Thioether (d) Alcohols
3. Which one of the following is a thiol?  
(a)  $\text{CH}_3\text{SH}$  (b)  $\text{CH}_3\text{COOH}$   
(c)  $\text{CH}_3\text{OH}$  (d)  $\text{CH}_3\text{SCH}_3$
4. What is the IUPAC name of  $\text{CH}_3\text{CH}_2\text{SH}$  compound?  
(a) Ethyl sulphide (b) Ethanethiol  
(c) Ethyl thioether (d) Ethyl hydrogen sulphide
5. Thios can be obtained  
(a) By heating haloalkanes with potassium sulphide.  
(b) By the oxidation of alcohols with  $\text{KMnO}_4$ .  
(c) By heating alkyl halide with alcoholic  $\text{AgNO}_2$ .  
(d) By heating alcohols with phosphorus pentasulphide.
6. Which compound is a thioether?  
(a)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{SH}$  (b)  $\text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_3$   
(c)  $\text{CH}_3\text{CH}_2\text{Br}$  (d)  $\text{CH}_3\text{CH}_2\text{SCH}_2\text{CHO}$
7. Which functional group is present in thiols?  
(a)  $\text{R-O-R}'$  (b)  $-\text{SCN}$   
(c)  $-\text{SH}$  (d)  $-\text{NH}_2$
8. Thioethers are  
(a) Sulphur analogues of ethers (b) Nitrogen analogues of ethers  
(c) Sulphur analogues of alcohols (d) Sulphur analogues of alcohols
9. Which property is generally characteristic of thioethers?  
a. Their boiling points are lower than corresponding ethers.  
b. Their boiling points are higher than corresponding ethers.  
c. They are colourless.  
d. They have unpleasant order.
10. Which of the following statement regarding organosulphur is false?

- a. Thiols are more nucleophilic than alcohols.  
 b. Dialkyl sulphide can act as a nucleophile.  
 c. Thiols are more acidic than alcohols.  
 (d) Thiols are good oxidizing agents.
11. Thiols are produced by heating sulphur with..  
 (a) Grignard's reagent (b) Millon reagent  
 (c) Tollen's reagent (d) Fehling solution
12. On reaction with aldehydes and ketons in the presence of HCl, thiols produce  
 (a) Sulphone (b) Sulphinic acid  
 (c) Thioacetal (d) Diethyl sulphoxide
13. Which compound will yield alcohol when hydrolyzed?  
 (a) Ethanamide (b) Ethane sulphonic acid  
 (c) Ethylamine (d) Diethyl sulphide
14. Which is the main product of the following reaction?



- (a) Thioethers (b) Acyl halides  
 (c) Thiols (d) Ethanamine
15. Which is the main product of the following reaction?



- (a) Thioethers (b) Amine  
 (c) Halo acids (d) Thiols
16. What is the main product obtained by the oxidation of thioethers with  $\text{KMnO}_4$   
 (a) Sulphide (b) Sulphone  
 (c) Sulphoxide (d) Thioacetals
17. Thioesters are formed by the reaction of thiols with  
 (a) Acid chlorides (b) Carboxylic acids

- (c) Acid anhydrides (d) All of these
18. On reaction with hydrogen peroxide thioethers gives  
(a) Sulphones (b) Sulphoxides  
(c) Disulphides (d) Sulphinic acid
19. Thiols undergo desulphurization with Raney nickel gives  
(a) Ethane (b) Hydrogen peroxide  
(c) Methane (d) Thioethers
20. Thioethers are hydrolyzed with boiling sodium hydroxide into  
(a) Mercatols (b) Carboxylic acids  
(c) Thioethers (d) Alcohols
21. The organophosphorus compounds are prepared by:  
(a) Arbusov reaction (b) Perkin reaction  
(c) Wittig reaction (d) All of them
22. Pentahydride of phosphorus is known as  
(a) Phosphine (b) Phosphorane  
(c) Phosphine oxide (d) phosphinic acid
23. Which is phosphorus containing compound?  
(a) Diethyl thioether (b) ATP  
(c) Malathion (d) both b and c
24. Penicillin is a;  
(a) Organic compound containing phosphorus  
(b) Organic compound containing aluminium  
(c) Organic compound containing Sn  
(d) None of them
25. Wittig reagent is:  
(a) Phosphorus containing organic compound  
(b) Nitrogen containing organic compound  
(c) Sulphur containing organic compound  
(d) Both sulphur and nitrogen containing compound

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**10.18 ANSWERS (MCQs)**

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1. (d)	2. (c)	3. (a)	4. (b)	5. (d)
6. (a)	7. (c)	8. (a)	9. (b)	10. (d)
11. (a)	12. (c)	13. (d)	14. (c)	15. (a)
16. (b)	17. (d)	18. (b)	19. (a)	20. (d)
21. (a)	22. (b)	23. (d)	24. (a)	25. (a)

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**10.19 REFERENCES**

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