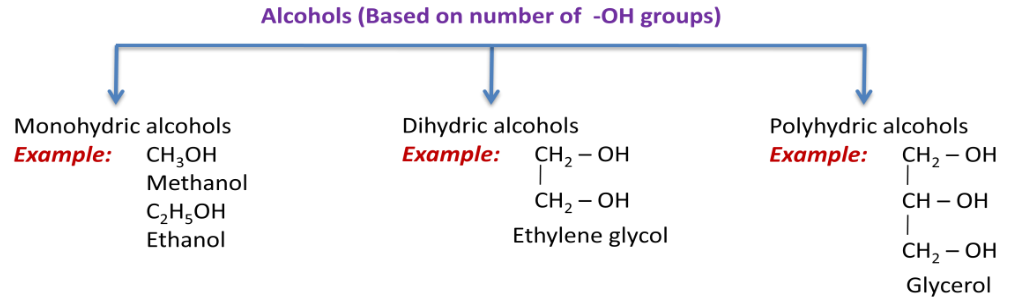
Alcohols, Phenols and Ethers

Module 33.1: Alcohols-Nomenclature, Preparation methods

An alcohol is an organic compound in which a hydroxyl group (-OH) is bound to a carbon atom of an alkyl or substituted alkyl group. An important group of alcohols is formed by the simple acyclic alcohols, the general formula is $C_nH_{2n+1}OH$, ethanol (C_2H_5OH) is the type of alcohol found in alcoholic beverages; In common speech the word alcohol means, specifically, ethanol.

Classification of Alcohols:

Alcohols are classified as mono, di and trihydric alcohols according to the number of -OH groups contained in their molecules.



Monohydric Alcohols:

Alcohols in which there is only one -OH group are known as monohydric alcohols.

Example: Methanol CH_3OH

Ethanol CH_3CH_2OH

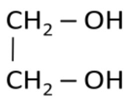
Propanol $CH_3CH_2CH_2OH$

Dihydric alcohols:

Alcohols in which there are two -OH groups are known as Dihydric alcohols.

Example:

Ethylene glycol



$$\begin{array}{l} CH_2-OH \\ | \\ CH_2-OH \end{array}$$

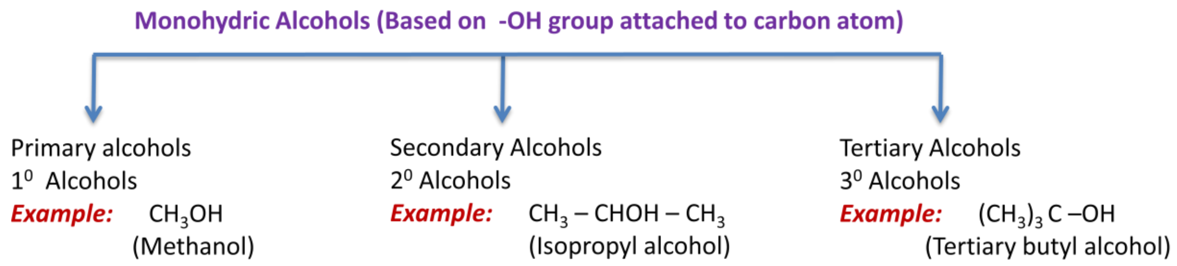
Polyhydric Alcohols:

Alcohols in which there are more than two -OH groups are known as polyhydric alcohols.

Example: Glycerol $CH_2OH-CHOH-CH_2OH$

Sorbitol $CH_2OH-(CHOH)_4-CH_2OH$

Monohydric alcohols are again classified as primary, secondary and tertiary alcohols depending upon whether the hydroxyl group is attached to a primary or a secondary or a tertiary carbon atom.



Primary Alcohols or 1^0 Alcohols:

Primary alcohols are those alcohols in which the carbon atom to which the hydroxyl group (OH) attached is at the end of the chain.

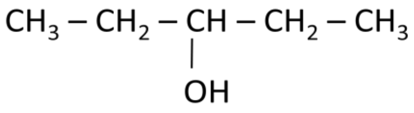
Example: Methanol CH_3OH

Ethanol C_2H_5OH

Secondary Alcohols (or) 2^0 Alcohols:

In secondary alcohols, the carbon atom to which OH group is attached is bonded to two other carbon atoms.

Example:



$$CH_3-CH_2-\underset{\underset{OH}{|}}{CH}-CH_2-CH_3$$

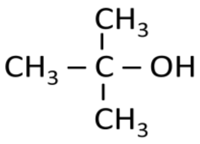
3-pentanol

Tertiary Alcohols or 3^0 Alcohols:

Tertiary alcohols are those alcohols in which the carbon atom to which OH group is attached is bonded to three other carbon atoms.

Example:

Tertiary butyl alcohol



$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH$$

Nomenclature:

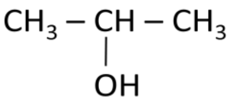
The common name of an alcohol is written from the name of the alkyl group and adding the word alcohol to it.

Example:

Methyl alcohol CH_3OH

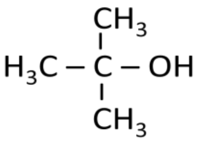
n-propyl alcohol $CH_3-CH_2-CH_2OH$

Iso propyl alcohol



$$CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$$

Tertiary butyl alcohol



$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH$$

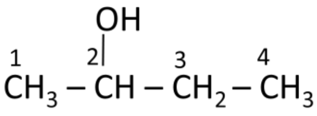
In the IUPAC system, the names of saturated alcohols are derived from the names of the corresponding alkane by replacing "e" in the name of the alkane with the suffix "ol"

Example:

CH_3-CH_2-OH	Ethanol;	The corresponding alkane ⇒ Ethane
$CH_3-CH_2-CH_2-OH$	Propanol;	The corresponding alkane ⇒ n- propane

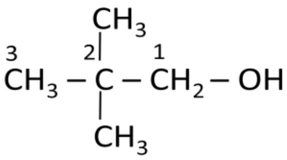
The numbering of carbon atoms is done such that the carbon attached to the -OH group gets the lowest number.

Example:



$$\overset{1}{CH_3}-\overset{\overset{OH}{|}}{\overset{2}{CH}}-\overset{3}{CH_2}-\overset{4}{CH_3}$$

Butan -2 -ol

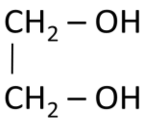


$$\overset{3}{CH_3}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{\overset{2}{C}}}-\overset{1}{CH_2}-OH$$

2, 2 -Dimethyl propan -1 -ol

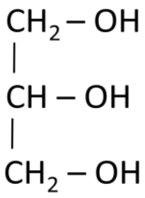
For naming polyhydric alcohols, the name of the alkane is retained and the ending "-e" is not dropped. The position of carbon atom carrying -OH groups are indicated by numerical written after the name of alkanes. The number of hydroxyl groups is indicated by adding the prefix di, tri, tetra etc; before the suffix -ol.

Example:



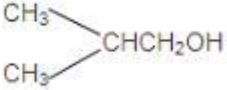
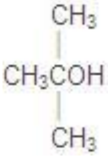
$$\begin{array}{l}CH_2-OH\\|\\CH_2-OH\end{array}$$

Ethane -1,2 -diol



$$\begin{array}{l}CH_2-OH\\|\\CH-OH\\|\\CH_2-OH\end{array}$$

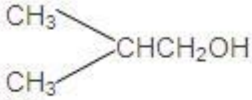
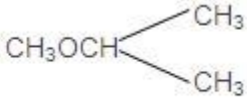
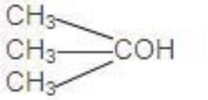
Propane 1, 2, 3 -triol.

Nomenclature :	**Common name**	**Carbinol name**	**IUPAC name**
CH_3OH	methyl alcohol	carbinol	methanol
CH_3CH_2OH	ethyl alcohol	methyl carbinol	ethanol
$CH_3CH_2CH_2OH$	n-propyl alcohol	ethyl carbinol	propanol-1
$CH_3CHOHCH_3$	isopropyl alcohol	dimethyl carbinol	propanol-2
$CH_3CH_2CH_2CH_2OH$	n-butyl alcohol	propyl carbinol	butanol-1
	isobutyl alcohol	isopropyl carbinol	2-methylpropanol-1
$CH_3CH_2CHOHCH_3$	sec.butyl alcohol	ethylmethylcarbinol	butan-2-ol
 $CH_3\overset{CH_3}{\underset{CH_3}{C}}OH$	t-butyl alcohol	trimethyl carbinol	2-methylpropan-2-ol

Isomerism:

Molecular formula $C_nH_{2n+1}OH$ of alcohols show following types of isomerism.

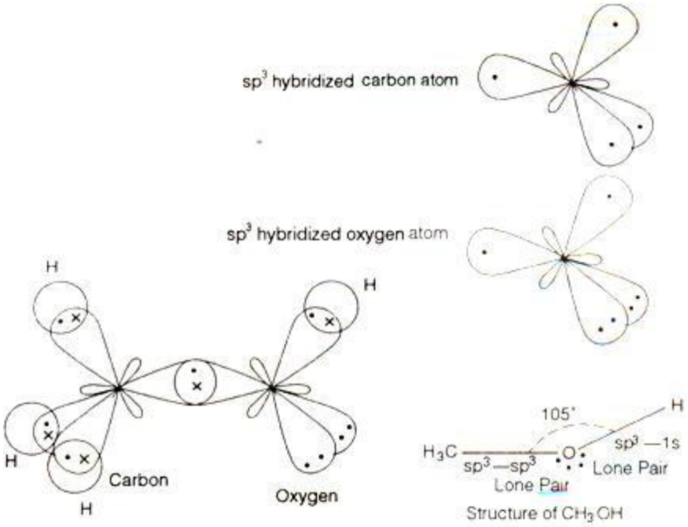
C_3H_8O : $CH_3CH_2CH_2OH$ and $CH_3CHOHCH_3$ are position isomers

	Alcohols	**Ethers**
$C_4H_{10}O$:	(a) $CH_3CH_2CH_2CH_2OH$	(e) $CH_3CH_2OCH_2CH_3$
	(b) $CH_3CH_2CHOHCH_3$	(f) $CH_3OCH_2CH_2CH_3$
	(c) 	(g) 
	(d) 	

In all 7 isomers of $C_4H_{10}O$ are noticed among which are **chain isomers (a & c), position isomers (a & b), functional isomers (an alcohol & an ether) as well as metamers (e, f, g).** Also formula (b) **shows optical isomers** for butan-2-ol as it has one asymmetric carbon atom C*.

Structure:

In alcohols carbon as well as oxygen both show sp^3 hybridization. In carbon all the four sp^3 hybridized orbitals have on electron in each orbital whereas in oxygen two of the four sp^3 hybridized orbitals have one electron & rest two orbitals have on electron pair in each. These two completely filled orbitals in oxygen atom do not take part in bonding and give rise to contraction in bond angles due to lone pair effect and therefore the bond angle C-O-H is 105° which is lesser than the normal tetrahedral structure.



Methods of preparation of Alcohols from alkyl halides:

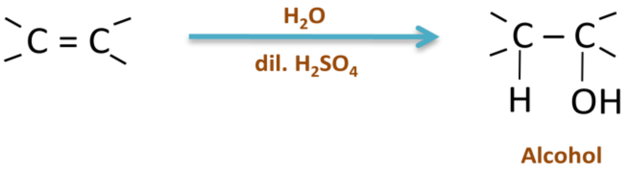
An alkyl halide, on hydrolysis, with aqueous sodium hydroxide or potassium hydroxide or moist silver oxide forms an alcohol.

$$R - X \xrightarrow[\text{Moist . } Ag_2O]{\text{aq. KOH (or)}} R - OH$$

a. Hydration of alkenes:

Alkenes undergo hydration (addition of water in the presence of dilute H_2SO_4 to produce alcohols. The alkyl hydrogen sulphate is formed first, after that, on reaction with hot water it undergoes hydrolysis and gives alcohol.

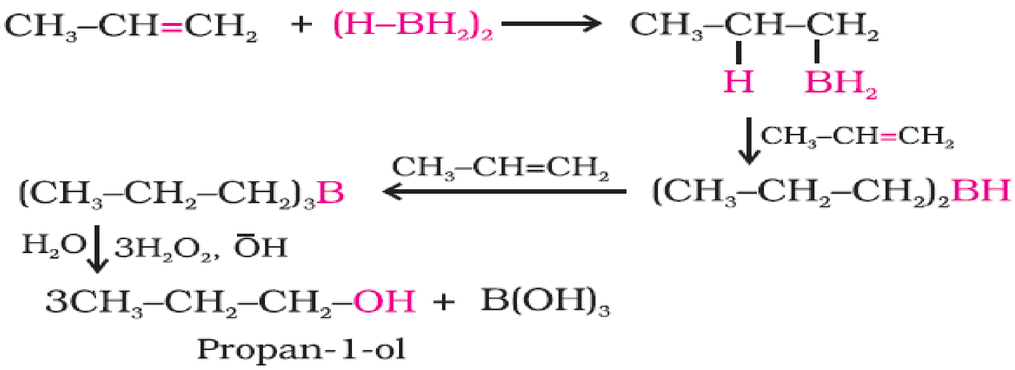
$$>C=C< + \text{dil.}H_2SO_4 \longrightarrow >\underset{H}{C}-\underset{SO_3H}{C}<$$



$$>C=C< \xrightarrow[\text{dil. } H_2SO_4]{H_2O} >\underset{H}{C}-\underset{OH}{C}<$$

The addition of water to the double bond takes place in accordance with Markownikov's rule.

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



b. From cracking process:

The alkene is obtained by cracking of hydrocarbons. The alkene is absorbed when it is passed into conc.H_2SO_4 at 353 K and 30 atm. The product is diluted and treated with steam to release the alcohol.

$$CH_2=CH_2 + \text{conc.}H_2SO_4 \longrightarrow \underset{\text{Ethyl hydrogen sulphate}}{CH_3\,CH_2\,HSO_4} \xrightarrow[-\,H_2SO_4]{H_2O} \underset{\text{Ethanol}}{CH_3\,CH_2\,OH}$$

c. From aldehydes and ketones:

Aldehydes and ketones are reduced to the corresponding alcohols by

i. **Hydrogenation:** Reaction of aldehyde with hydrogen in the presence of a catalyst (Finely divided Pt, Pd, Ni and Ru).

Example:

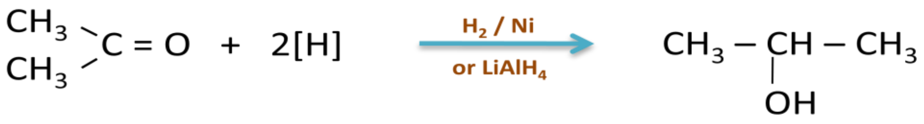
$$R - CHO + H_2 \xrightarrow{Pd\ /\ \Delta} R\,CH_2\,OH$$

ii. **Treatment with chemical** (reducing agent) such as sodium borohydride [$NaBH_4$] (or) Lithium aluminium hydride [$LiAlH_4$]

$$CH_3\,CHO + 2[H] \xrightarrow[\text{or } LiAlH_4]{H_2\ /\ Ni} CH_3\,CH_2\,OH$$

Ethanol

On reduction aldehydes yield primary alcohols while ketones give secondary alcohols.



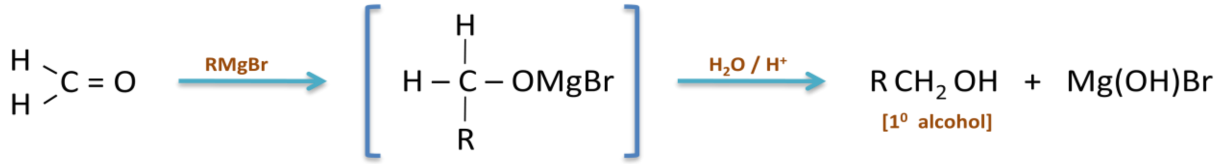
$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>C = O + 2[H] \xrightarrow[\text{or } LiAlH_4]{H_2\ /\ Ni} CH_3 - \underset{\displaystyle OH}{\underset{|}{CH}} - CH_3$$

Propan - 2 -ol

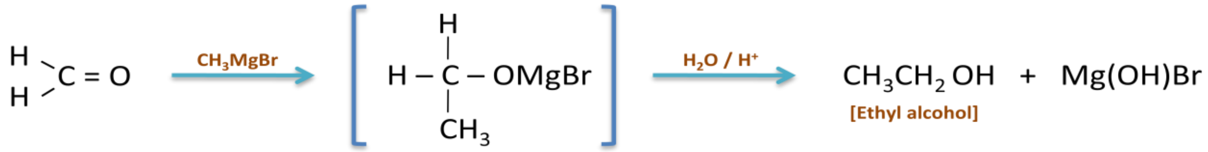
iii. **From Grignard reagent:**

Grignard reagents react with aldehydes and ketones to form products, These decompose with dil. HCl or dil. H_2SO_4 to give primary(1^0), secondary(2^0) and tertiary alcohols(3^0), depending upon the aldehdye or the ketone used in the reaction.

Formaldehyde always produces a 1^0 Alcohol.

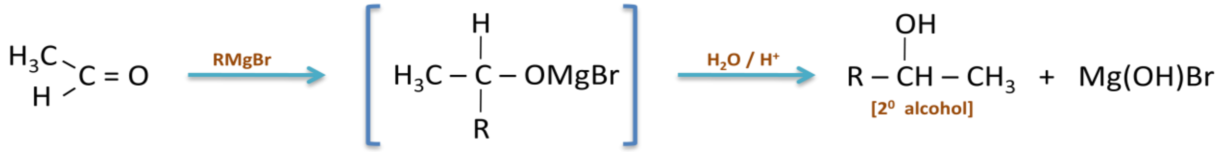


$$\begin{matrix}H\\H\end{matrix}\!\!>C=O \xrightarrow{RMgBr} \left[H-\overset{\displaystyle H}{\underset{\displaystyle R}{C}}-OMgBr\right] \xrightarrow{H_2O\,/\,H^+} RCH_2OH + Mg(OH)Br$$

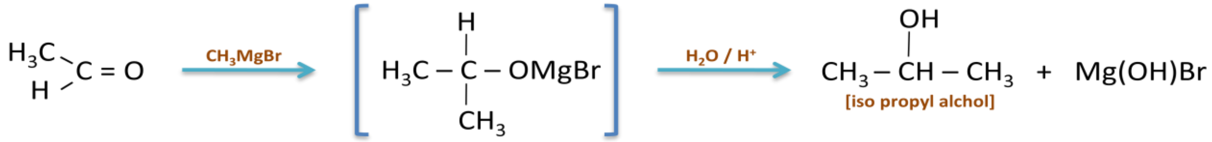


$$\begin{matrix}H\\H\end{matrix}\!\!>C=O \xrightarrow{CH_3MgBr} \left[H-\overset{\displaystyle H}{\underset{\displaystyle CH_3}{C}}-OMgBr\right] \xrightarrow{H_2O\,/\,H^+} CH_3CH_2OH + Mg(OH)Br$$

Aldehydes other than formaldehyde give a secondary alcohol with RMgX and on hydrolyzing the intermediate with an acid.

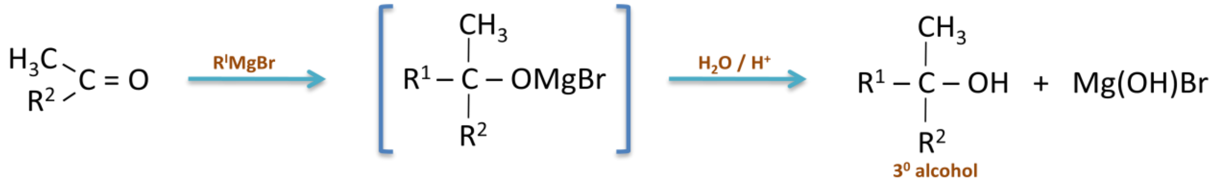


$$\begin{matrix}H_3C\\H\end{matrix}\!\!>C=O \xrightarrow{RMgBr} \left[H_3C-\overset{\displaystyle H}{\underset{\displaystyle R}{C}}-OMgBr\right] \xrightarrow{H_2O\,/\,H^+} R-\overset{\displaystyle OH}{CH}-CH_3 + Mg(OH)Br$$

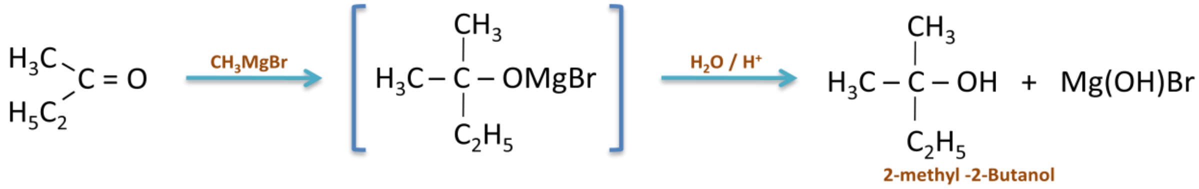


$$\begin{matrix}H_3C\\H\end{matrix}\!\!>C=O \xrightarrow{CH_3MgBr} \left[H_3C-\overset{\displaystyle H}{\underset{\displaystyle CH_3}{C}}-OMgBr\right] \xrightarrow{H_2O\,/\,H^+} CH_3-\overset{\displaystyle OH}{CH}-CH_3 + Mg(OH)Br$$

A ketone gives a 3^0 alcohol as a final product.



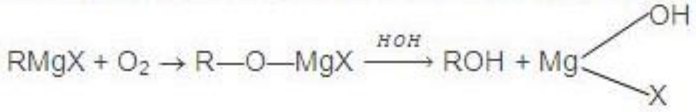
$$\begin{matrix}H_3C\\R^2\end{matrix}\!\!>C=O \xrightarrow{R^IMgBr} \left[R^1-\overset{\displaystyle CH_3}{\underset{\displaystyle R^2}{C}}-OMgBr\right] \xrightarrow{H_2O\,/\,H^+} R^1-\overset{\displaystyle CH_3}{\underset{\displaystyle R^2}{C}}-OH + Mg(OH)Br$$

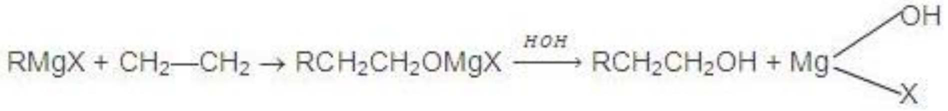


$$\begin{matrix}H_3C\\H_5C_2\end{matrix}\!\!>C=O \xrightarrow{CH_3MgBr} \left[H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle C_2H_5}{C}}-OMgBr\right] \xrightarrow{H_2O\,/\,H^+} H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle C_2H_5}{C}}-OH + Mg(OH)Br$$

Note:

Grignard reagents also reacts with O_2 and epoxides to give alcohols.

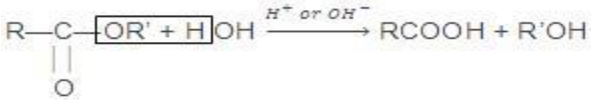




iv. **By the hydrolysis of ethers:**

$$\text{R-O-R'} + \text{HOH} \xrightarrow[\text{high P, T}]{\text{dil } H_2SO_4} \text{R-OH} + \text{R'OH}$$

v. **By the hydrolysis of esters :**



$$\underset{\underset{O}{\|}}{R-C}-\boxed{OR' + H}OH \xrightarrow{H^+ \text{ or } OH^-} RCOOH + R'OH$$

vi. **By the reduction of acids and their derivatives :**

$$RCOOH \xrightarrow[\text{NaBH}_4 \text{ or } C_2H_5OH/Na]{LiAlH_4 \text{ or}} RCH_2OH$$

$$(RCO_2)O \xrightarrow{\text{As above}} RCH_2OH$$

$$RCOCl \xrightarrow{\text{As above}} RCH_2OH$$

$$RCOOR' \xrightarrow{\text{As above}} RCH_2OH + R'OH$$

Note: If C_2H_5OH + Na are used as reducing agent, the reduction is known as Bouveault-Blane reaction.

vii. **By fermentation (only for ethyl alcohol):**

Fermentation is the slow decomposition of complex organic compounds into simpler organic compounds by the activity of enzymes. Enzymes are complex, nitrogenous (proteins), non living macro molecules of high molecular weight derived from living organisms. These are also known as biological catalysts.

Fermentation processes is generally accompanied with evolution of gases like CO_2 & CH_4 and are exothermic in nature. The alcoholic fermentation involves conversion of sugar into ethyl alcohol by yeast. The starting material for alcoholic fermentation is starch (potato, rice, barley, maize). The source of starch depends upon its availability in that country. In India, alcoholic fermentation is made by molasses. It is the dark coloured syrupy liquid left after crystallization of sugar from sugar cane juice.

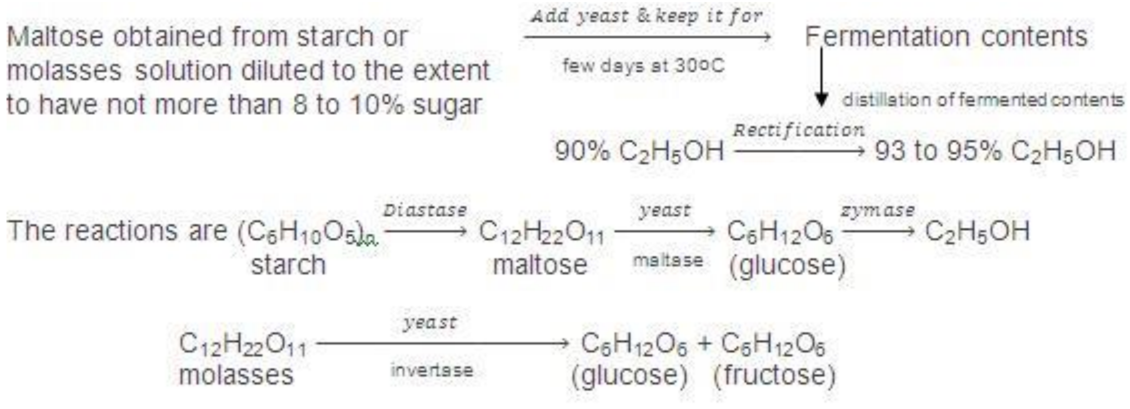
An outline of alcoholic fermentation is given below:

Step I: **from starch:**

Common source of starch are wheat, barley, potato etc. The grain is washed with hot water. It is then heated with freshly germinated barley (malt) at $50^{o}C$ for one hour. Malt contains the enzyme diastase. Diastase converts starch into the sugar, maltose, by hydrolysis.

From molasses: Molasses contains about 30-40% sucrose which is a disaccharide like maltose.

Step II:



Maltose obtained from starch or molasses solution diluted to the extent to have not more than 8 to 10% sugar $\xrightarrow[\text{few days at } 30^{o}C]{\text{Add yeast \& keep it for}}$ Fermentation contents

$\downarrow$ distillation of fermented contents

$$90\%\ C_2H_5OH \xrightarrow{\text{Rectification}} 93 \text{ to } 95\%\ C_2H_5OH$$

The reactions are $\underset{\text{starch}}{(C_6H_{10}O_5)_n} \xrightarrow{\text{Diastase}} \underset{\text{maltose}}{C_{12}H_{22}O_{11}} \xrightarrow[\text{maltase}]{\text{yeast}} \underset{\text{(glucose)}}{C_6H_{12}O_6} \xrightarrow{\text{zymase}} C_2H_5OH$

$$\underset{\text{molasses}}{C_{12}H_{22}O_{11}} \xrightarrow[\text{invertase}]{\text{yeast}} \underset{\text{(glucose)}}{C_6H_{12}O_6} + \underset{\text{(fructose)}}{C_6H_{12}O_6}$$

Physical properties:

The properties of alcohols are mainly due to the -OH group.

a. Physical state:

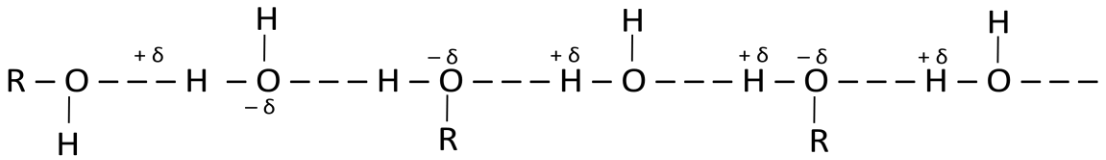
The lower members of alcohols are colorless, volatile liquids with a characteristic alcoholic smell and burning taste where as higher alcohols are odorless and tasteless (Liquids or solids). Above C_{12}, alcohols are solids.

b. Solubility in H_2O:

The first three members are completely miscible with water. The solubility rapidly decreases with increase in molecular mass. The higher molecules are almost insoluble in water but are soluble in organic solvent like benzene and others *etc*.

The solubility of lower alcohols is due to the formation of hydrogen bonds between water and the -OH group of alcohol molecules.

The -OH group in alcohols contain electronegative oxygen atom. The O–H bond is polarized as $O^{-\delta}$– $H^{+\delta}$. They form hydrogen bonds with water molecules which are also polar molecules. Thus inter molecular H–bond formation results in the solubility of alcohols.



$$R-\underset{\substack{|\\H}}{O}---\overset{+\delta}{H}\ -\underset{-\delta}{\overset{\substack{H\\|}}{O}}---H-\underset{\substack{|\\R}}{\overset{-\delta}{O}}---\overset{+\delta}{H}-\overset{\substack{H\\|}}{O}---\overset{+\delta}{H}-\underset{\substack{|\\R}}{\overset{-\delta}{O}}---\overset{+\delta}{H}-\overset{\substack{H\\|}}{O}---$$

As the size of the alkyl group increases its influence on the solubility increases. So higher alcohols dissolve in H_2O to a lesser extent or become immiscible with H_2O.

In addition, among the isomeric alcohols, the solubility increases with branching of chain. As surface area of the non-polar part in the molecules decreases, the solubility increases.

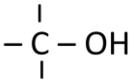
SAQs:

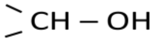
1. Hydrogen bonding is maximum in

   a. Ethanol
   b. Diethyl ether
   c. Methanol
   d. Tri ethyl amine

Solution: a)

2. The functional group in an aliphatic, saturated alcohol is

a. 
$-\overset{|}{\underset{|}{C}}-OH$

b. 
$>CH-OH$

c. $-CH_2OH$

d. All

Solution: d)

3. Ethyl alcohol is ________ in water

a. Soluble in all proportions
b. Soluble only on heating
c. Insoluble
d. Soluble in all proportions at any temperature.

Solution: d)

4. In the reduction

$CH_3-CHO + H_2 \xrightarrow[\Delta]{\text{Catalyst}} CH_3CH_2OH$; the catalyst is

a. Ni
b. Pd
c. Pt
d. All the above.

Solution: d)

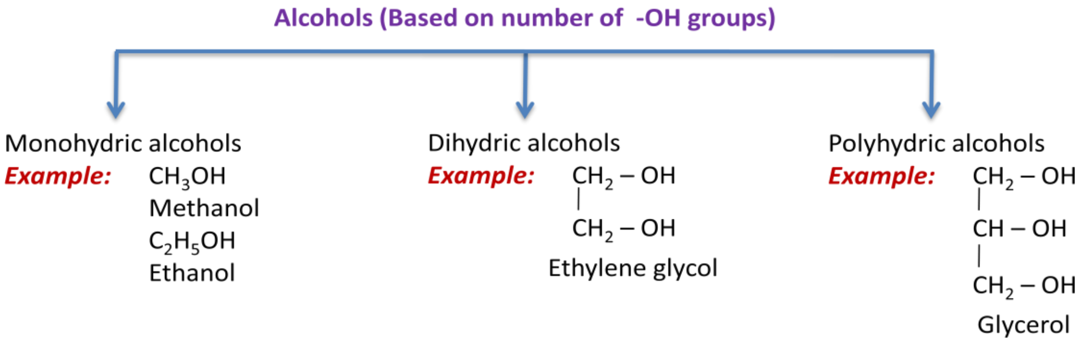
LAQs:

1. Explain the classification of alcohols based on the number of hydroxyl groups. Give one example for each.

Solution:

Classification of Alcohols:

Alcohols are classified as mono, di and trihydric alcohols according to the number of -OH groups contained in their molecules.



2. What happens when ethyl bromide is treated with
   i. Moist Ag_2O
   ii. Aqueous KOH

Solution:

An alkyl halide, on hydrolysis, with aq. NaOH or aq.KOH or moist silver oxide forms an alcohol.

$$R-X \xrightarrow[\text{Moist . }Ag_2O]{\text{aq. KOH (or)}} R-OH$$

3. Write two important methods of preparation of an alcohol taking ethyl alcohol as an example.

Solution:

Hydrogenation: Hydrogen in the presence of a catalyst.

Finely divided Pt, Pd, Ni and Ru.

Example:

$$R-CHO + H_2 \xrightarrow{Pd / \Delta} R\,CH_2\,OH$$

Treatment with chemical (reducing agent) such as sodium borohydride [$NaBH_4$] or Lithium aluminium hydride [$LiAlH_4$]

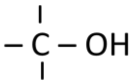
$$CH_3\,CHO + 2[H] \xrightarrow[\text{Or } LiAlH_4]{H_2 / Ni} \underset{\text{Ethanol}}{CH_3\,CH_2\,OH}$$

Problem set:

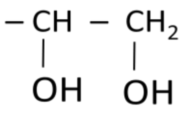
1. The characteristic group of a tertiary alcohol is

a. $-CH_2OH$

b. $-CH\,(OH)_2$

c. 

$$-\overset{|}{\underset{|}{C}}-OH$$

d. 

$$-\underset{OH}{\underset{|}{CH}} - \underset{OH}{\underset{|}{CH_2}}$$

Solution: c)

2. Excessive solubility of ethyl alcohol in water is due to

a. Ionic bond in the alcohol
b. Covalent bond in -OH group
c. Hydrogen bonding with water molecules
d. H- bonding between the alcohol molecules

Solution: c)

3. Butan-2-ol is a

a. 1^0 alcohol
b. 2^0 alcohol
c. 3^0 alcohol
d. Phenol.

Solution: b)

4. How is ethylene converted to ethyl alcohol?

Solution:

From cracking process:

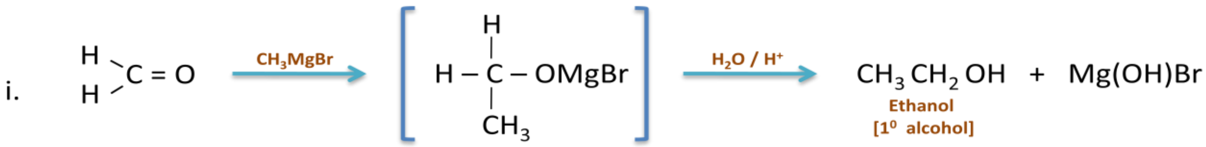
The alkene is obtained by cracking of hydrocarbons. The alkene is then absorbed by passing into conc .H_2SO_4 at 353 K and 30 atm. The product is diluted and treated with steam to release the alcohol.

$$CH_2 = CH_2 + \text{conc. } H_2SO_4 \longrightarrow \underset{\text{Ethyl hydrogen sulphate}}{CH_3\,CH_2\,HSO_4} \xrightarrow[-\,H_2SO_4]{H_2O} \underset{\text{Ethanol}}{CH_3\,CH_2\,OH}$$

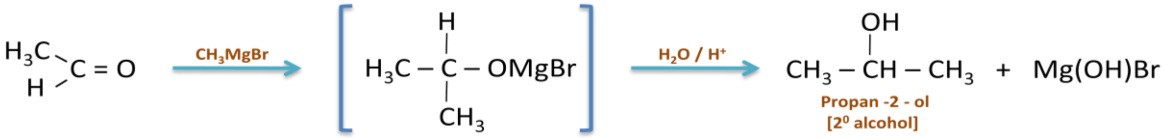
5. How are the following converted into alcohols using Grignard reagent (CH_3MgBr)?

i. HCHO
ii. CH_3CHO

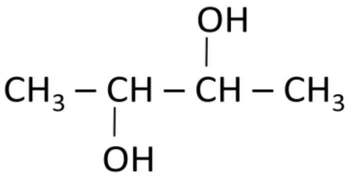
Solution:



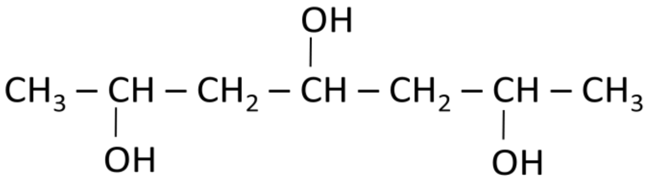
$$\text{i.}\quad \begin{matrix}H\\H\end{matrix}\!\!>C=O \xrightarrow{CH_3MgBr} \left[H-\overset{\overset{H}{|}}{\underset{\underset{CH_3}{|}}{C}}-OMgBr \right] \xrightarrow{H_2O\,/\,H^+} \underset{\substack{\text{Ethanol}\\ \text{[}1^0\text{ alcohol]}}}{CH_3\,CH_2\,OH} + Mg(OH)Br$$

ii. 

6. Name the following compounds

a. 

$$CH_3-\underset{\underset{OH}{|}}{CH}-\overset{\overset{OH}{|}}{CH}-CH_3$$

b. 

$$CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-\overset{\overset{OH}{|}}{CH}-CH_2-\underset{\underset{OH}{|}}{CH}-CH_3$$

Solution: a) Butane 2, 3-diol

b) Heptane 2, 4, 6-triol

Exercise questions:

1. Give the mechanism for the dehydration of ethanol in the presence of H_2SO_4 at 413 K.
2. The solubility's of 3^0-butanol and diethyl ether are 9 g and 7.5 g per 100 ml respectively. Assign proper reasons for the similar solubilities.
3. What happens when ter-butyl chloride is warmed with sodium ethoxide? Give proper reasons for the product along with suitable equations. Will it follows S_N1 or S_N2 mechanism?
4. Arrange the following in the order of increasing boiling points.
   a. 1- proponol
   b. Butan- 2- ol
   c. Ethanol
   d. 1- pentanol
   e. 1- butanol
   f. methanol
5. Select the correct order of increasing boiling points

a. n- butane < pentanal < ethoxy ethane < 1- pentanol
b. 1- pentanol < ethoxy ethane < pentanal < n- butane
c. n- butane < ethoxy ethane < pentanal < 1-pentanol
d. Ethoxy ethane < pentanal < 1- pentanol < n- butane.

Solutions:

1. **Step – 1:**

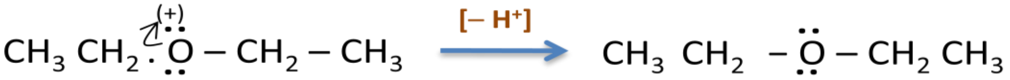
$$CH_3CH_2\ddot{\underset{..}{O}}H + H^+ \longrightarrow CH_3\,CH_2\cdot\overset{(+)}{\underset{H}{\ddot{O}}}H$$

Protonation of alcohol with an acid

Step – 2:

$$CH_3\,CH_2\cdot\ddot{\underset{..}{O}}H + CH_3CH_2\overset{(+)}{\underset{H}{\ddot{O}}}H \longrightarrow CH_3\,CH_2-\overset{(+)}{\underset{H}{\ddot{O}}}-CH_2\,CH_3 + H_2O$$

Step – 3:

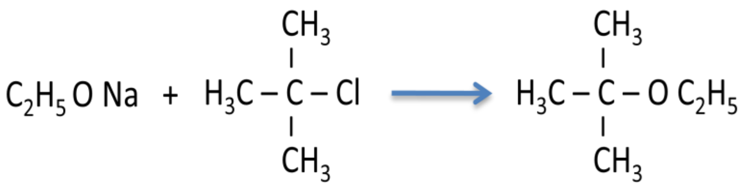


$$CH_3\,CH_2\cdot\overset{(+)}{\underset{..}{\ddot{O}}}-CH_2-CH_3 \xrightarrow{[-H^+]} CH_3\,CH_2-\ddot{\underset{..}{O}}-CH_2\,CH_3$$

This method is suitable only for compound with primary alkyl groups.
2^0 and 3^0 alcohols give alkenes preferably.

2. Both diethyl ether and 1- Butanol form hydrogen bonds with water. Both has same mole weights. (74 g mol^{-1}). Therefore their solubilities are similar. They differ slightly due to the difference in the H- bonding.

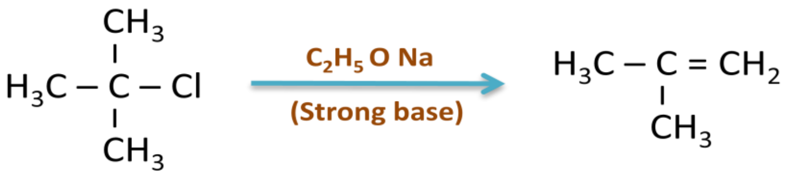
3. The expected reaction is



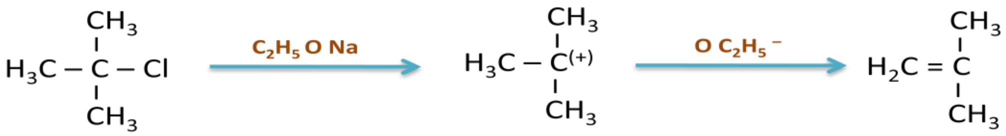
$$C_2H_5ONa + H_3C-\overset{CH_3}{\underset{CH_3}{C}}-Cl \longrightarrow H_3C-\overset{CH_3}{\underset{CH_3}{C}}-OC_2H_5$$

t -Butyl alcohol

But an alkene is formed by dehydro halogenation.



$$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-Cl \xrightarrow[\text{(Strong base)}]{C_2H_5ONa} H_3C-\underset{CH_3}{C}=CH_2$$



$$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-Cl \xrightarrow{C_2H_5ONa} H_3C-\overset{CH_3}{\underset{CH_3}{C^{(+)}}} \xrightarrow{OC_2H_5^{-}} H_2C=\overset{CH_3}{\underset{CH_3}{C}}$$

The reaction steps indicate the S_N1mechanism. The reaction rate depends on the rate of formation of the 3^0- carbocation.

4. $f < c < a < b < e < d$

5. c)

Reason: i. Increase in molecular weight

ii. Hydrogen bonding.

IIT Questions:

1. The compound which reacts fastest with Lucas reagent at room temperature is
   a. 1 - butanol
   b. 2 - butanol
   c. 2 - methylpropanol
   d. 2- methylpropan-2-ol
2. An industrial method of preparation of methanol is
   a. Catalytic reduction of carbon monoxide in presence of ZnO - Cr_2O_3.
   b. By reacting methane with steam at 900^0 C with a nickel catalyst.
   c. By reducing formaldehyde with lithium aluminium hydride
   d. By reacting formaldehyde with aqueous sodium hydroxide solution
3. Hydrogen bonding is maximum in
   a. Ethanol
   b. Diethyl ether
   c. Ethyl chloride
   d. Triethyl amine
4. Which of the following alcohols is expected to have minimum boiling point?
   a. 1 - Butanol
   b. 2 - Butanol
   c. 2 - Methyl - 2 - propanol
   d. 1 - pentanol
5. Among the following compounds , the strongest acid is
   a. $HC \equiv CH$
   b. C_6H_6
   c. C_2H_6
   d. CH_3OH
6. A ________ diol has two hydroxyl groups on _______ carbon atoms.

7. Glycerine contains one _____ hydroxyl group.

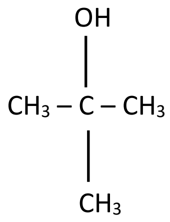
8. Hydrogen bonding is maximum in:
   a. ethanol
   b. diethyl ether
   c. ethyl chloride
   d. triethyl amine

9. In CH_3CH_2OH, the bond that undergoes heterolytic cleavage most readily is:
   a. C – C
   b. C – O
   c. C – H
   d. O – H

Solutions:

1. d

Tertiary alcohol reacts fastest with Lucas reagent. The compound is



$$CH_3-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_3$$

2. a

Catalytic reduction of carbon monoxide in presence of ZnO - Cr_2O_3 constitutes industrial method of preparation of methanol.

3. a

Ehanol involves maximum hydrogen bonding amongst the given compounds.

4. c

More branched alcohol (2 - methyl - 2 - propanol) has minimum boiling point.

5. d

CH_3OH is the strongest acid amongst the given compounds.

6. Vicinal, adjacent
7. Secondary
8. (a)

Hydrogen bonding is maximum in ethanol because hydrogen is bonded to highly electronegative oxygen.

9. (d) $C_2H_5OH + Na \longrightarrow C_2H_5ONa + \frac{1}{2} H_2$

Alcohols, Phenols and Ethers

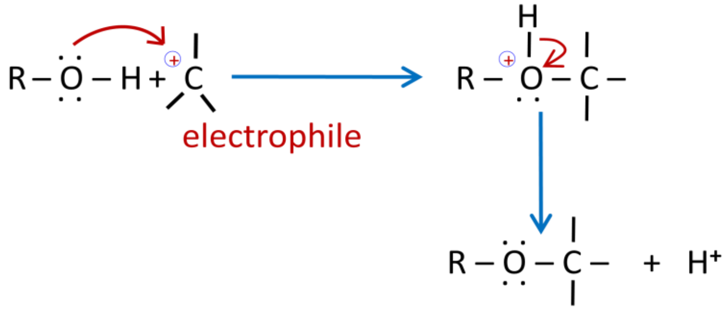
Module 33.2: Chemical properties of alcohols

In alcohols, –OH is the functional group. Thus the chemical properties of alcohols generally undergo substitution as well as elimination reactions.
Reactions of alcohols are classified into three types

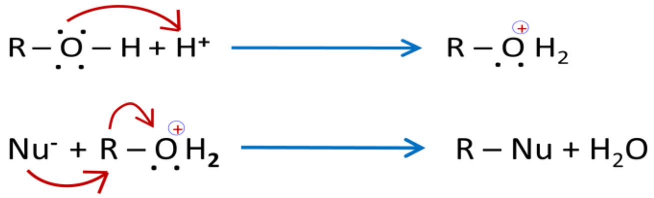
a. Reactions involving cleavage of O–H bond
b. Reactions involving cleavage of C–O bond
c. Reactions involving the cleavage of C–H and O–H bond

Alcohols are versatile compounds. They react both as nucleophiles and also as electrophiles.

i. The bond between O – H is broken when alcohols react as nucleophiles.



ii. The bond between C – O is broken when they react as electrophiles. Protonated alcohols react in these reactions.



1. Reactions involving cleavage of O – H bond:

i. Reaction with metals:

Alcohols react with metals such as sodium, potassium and aluminium to yield corresponding alkoxides and hydrogen.

$$2\ R-O-H\ +2Na \longrightarrow \underset{\text{Sodium Alkoxide}}{2\ RONa}\ +\ H_2$$

$$6\ \ R_3C-O-H\ +2Al \longrightarrow 2\ [R_3CO]_3\ Al\ \ +3H_2$$

ii. Acidic nature of alcohols:

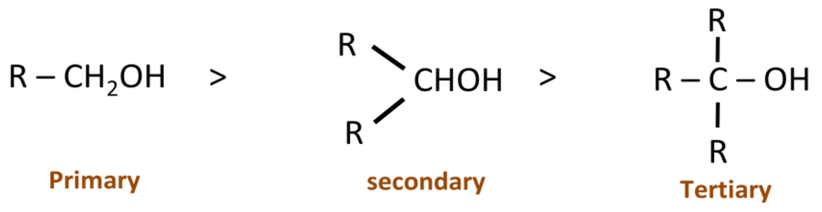
On treating an alkoxide with water, the corresponding alcohol is obtained.

$$\underset{\text{Base}}{R-\ddot{\underset{\cdot\cdot}{O}}^{-}}\ +\ \underset{\text{Acid}}{H_2O} \longrightarrow \underset{\text{Conjugate acid}}{R-OH}\ +\ \underset{\text{Conjugate base}}{{}^{-}OH}$$

The reaction shows that water is better proton donor than alcohol *i.e.,* alcohols are very weak acids even weaker than water. They do not turn blue litmus to red.

The acidic character of alcohols is due to the presence of the polar O–H group. Due to greater electronegativity of oxygen atom, the shared pair of electrons between O and H is drawn towards the oxygen atom. It helps in the release of H^+ ion.

The acid strength of alcohols decreases in the following order



$$\underset{\text{Primary}}{R-CH_2OH} > \underset{\text{secondary}}{R_2CHOH} > \underset{\text{Tertiary}}{R_3C-OH}$$

An electron releasing alkyl group [$-CH_3$, $-C_2H_5$] increases electron density over the oxygen atom. This decreases the polarity of O–H bond. It decreases the acid strength.

iii. Esterification of alcohols:

Alcohols react with carboxylic acids, acid chlorides and acid anhydrides to form esters. The reaction between alcohols and acids are carried out in the presence of a small amount of concentrated H_2SO_4 or a Lewis acid. H_2SO_4 acts as a protonating agent as well as a dehydrating agent. This reaction is known as **Fischer esterification reaction.**

$$ROH\ \ +R^1COOH \overset{H^+}{\rightleftharpoons} R^1COOR\ +\ H_2O$$

The reaction is reversible and therefore water is removed as soon as it is formed.

$$ROH + (R^1CO)_2O \xrightarrow{H^+} R^1COOR\ +\ R^1COOH$$

The reaction with acid chloride is carried out in the presence of a base (pyridine). The base removes HCl. It also shifts the equilibrium to the right hand side.

$$ROH + R^1COCl \xrightleftharpoons{\text{Pyridine}} R^1COOR + HCl$$

iv. Action of Grignard reagent:

Alcohol reacts with alkyl magnesium halide to form an alkane.

$$R - OH + R^1MgX \longrightarrow R^1 - H + Mg(OR)X$$

2. Reactions involving cleavage of C –O bond:

i. Reaction with hydrogen halide:

$$ROH + HX \longrightarrow R - X + H_2O$$

Alcohols react with hydrogen halide (HX) to form an alkyl halide.

The order of reactivity of alcohols towards HX, is **tertiary > secondary > primary**.

The order of reactivity of hydrogen halide is

HI > HBr > HCl

Distinction between primary, secondary and tertiary alcohols:

In this test, the alcohol is treated with Lucas reagent, which is equimolar mixture of concentrated HCl and anhydrous $ZnCl_2$. Alcohols are soluble in Lucas reagent. They form a clear solution. Insoluble alkyl chlorides are formed. The solution becomes cloudy.

If cloudiness appears immediately, tertiary alcohol is indicated. If cloudiness appears within five minutes secondary alcohol is indicated.

If cloudiness appears only upon heating, or after a very long time a primary alcohol is indicated.

ii. Reaction with PCl_3 or PCl_5 or $SOCl_2$:

Alcohols react with phosphorous halides or thionyl chloride to form alkyl halides.

$$3ROH + PCl_3 \longrightarrow 3RCl + H_3PO_3$$

$$ROH + PCl_5 \longrightarrow RCl + POCl_3 + HCl$$

Alkyl chlorides are prepared by reacting an alcohol with thionylchloride.

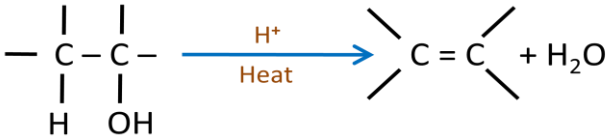
$$ROH + SOCl_2 \longrightarrow RCl + SO_2 + Cl_2$$

The reaction with thionyl chloride is preferred as the byproducts are all gases.

iii. Dehydration:

Alcohols undergo dehydration to form alkenes [removal of a molecule of water on treating with a protonic acid].

Concentrated H_2SO_4, H_3PO_4 or catalyst such as anhydrous $ZnCl_2$ (or) alumina must be present to dehydrate an alcohol.



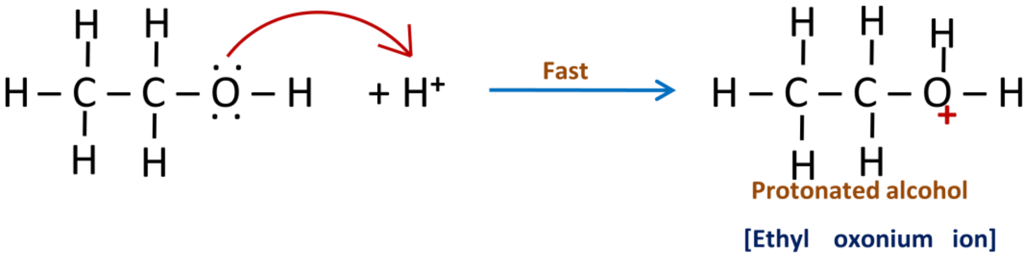
The relative ease of dehydration of alcohols follows the order

Tertiary alcohol > secondary alcohol > primary alcohol

Mechanism: dehydration of ethanol is taken as an example

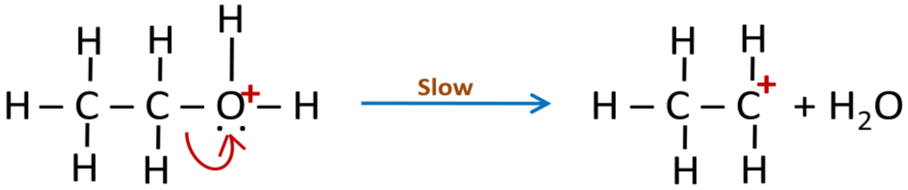
The mechanism of dehydration of ethanol involves the following steps:

Step 1: Formation of protonated alcohol or an oxonium ion.



Step 2: Formation of carbocation

It is the slow step and hence the rate determining step of the reaction.



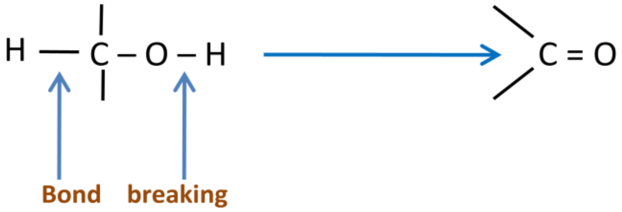
Step 3: Formation of ethene

The acid used in step (1) is finally released after the reaction.

3. Reactions involving the cleavage of C – H and O – H bonds:

Oxidation of alcohols:

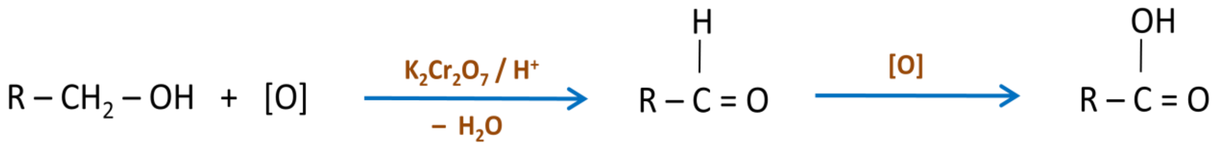
Oxidation of alcohols involves the formation of carbon–oxygen double bond with cleavage of an OH as well as C – H bonds.



Such a cleavage and formation of bonds occurs in oxidation reaction. These are also known as dehydrogenation reactions as these involve loss of dihydrogen from alcohol molecules.

The oxidising agent and the nature of alcohols used, are determine the products of oxidation reactions.

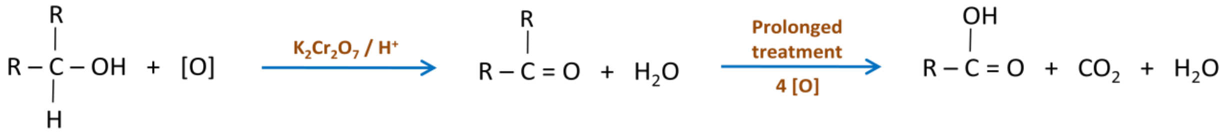
For example a primary alcohol on oxidation with acidified potassium dichromate first gives an aldehyde, which on further oxidation gives an acid with the same number of carbon atoms as the original alcohol.



$$R-CH_2-OH + [O] \xrightarrow[-\,H_2O]{K_2Cr_2O_7\,/\,H^+} R-\overset{\overset{H}{|}}{C}=O \xrightarrow{[O]} R-\overset{\overset{OH}{|}}{C}=O$$

Strong oxidising agents such as acidified KMnO4 are used for getting carboxylic acids directly. Cr (VI) in anhydrous medium is used as the oxidising agent for the isolation of aldehydes.

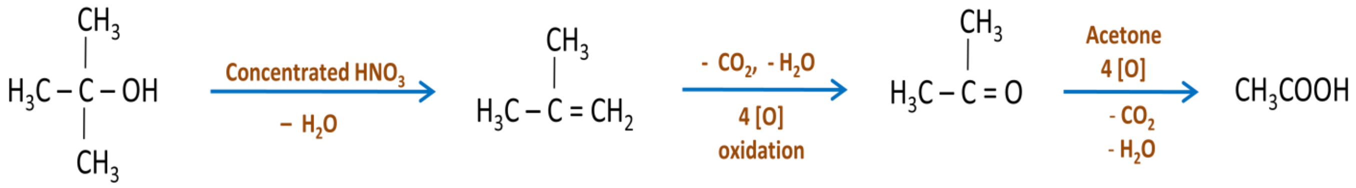
Secondary alcohols are oxidised to ketones by acidified potassium dichromate. The ketone has the same number of carbon atoms as the original alcohol.



$$R-\underset{\underset{H}{|}}{\overset{\overset{R}{|}}{C}}-OH + [O] \xrightarrow{K_2Cr_2O_7\,/\,H^+} R-\overset{\overset{R}{|}}{C}=O + H_2O \xrightarrow[4\,[O]]{\text{Prolonged treatment}} R-\overset{\overset{OH}{|}}{C}=O + CO_2 + H_2O$$

The above reaction is known as oxidative degradation of alcohols.

Tertiary alcohols having no hydrogen on carbon bearing –OH group do not undergo oxidation easily. Reaction with strong oxidising agent and at elevated temperatures Tertiary alcohols are finally oxidised to carboxylic acids, containing lesser number of carbon atoms than the starting alcohol.



$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH \xrightarrow[-\,H_2O]{\text{Concentrated } HNO_3} H_3C-\overset{\overset{CH_3}{|}}{C}=CH_2 \xrightarrow[\text{4 [O] oxidation}]{-\,CO_2,\ -H_2O} H_3C-\overset{\overset{CH_3}{|}}{C}=O \xrightarrow[-\,CO_2,\ -\,H_2O]{\text{Acetone } 4\,[O]} CH_3COOH$$

The reactions which distinguish the three types of alcohols (*i.e.,* 1^0, 2^0 and 3^0 alcohols) are given below

Serial. No	**Test**	**Primary alcohol**	**Secondary alcohol**	**Tertiary alcohol**
1.	Oxidation with acidified KMnO4 solution	Aldehydes are formed first. Then carboxylic acids are formed finally	Ketones are formed first, which give degradation products on further oxidation	Degradation products are formed
2.	Lucas reagent	Turbidity is	Turbidity is given	Turbidity is

		given very slowly i.e., after a very long time	within 5 minutes	given within 30 seconds
3.	Alcohol vapours are passed over Cu metal at 573K	Aldehydes are formed	Ketones are formed	Alkenes are formed

SAQs:

1. **1.** Alcohols undergo _____ reactions
   - a. Electrophilic
   - b. Nucleophilic
   - c. Elimination
   - d. All the above

Solution: d)

2. The acidic strength of alcohols increases in the following order
- a. $R_3COH < R_2CHOH < RCH_2OH$
- b. $RCH_2OH < R_2CHOH < R_3COH$
- c. $RCH_2OH < R_3COH < R_2CHOH$
- d. $R_3COH < RCH_2OH < R_2CHOH$

Solution: a)

LAQs:

1. How do you distinguish between primary, secondary and tertiary alcohols

Solution:

The reactions which distinguish the three types of alcohols (*i.e.*, 1^0, 2^0 and 3^0 alcohols) are given below

Serial. No	**Test**	**Primary alcohol**	**Secondary alcohol**	**Tertiary alcohol**
1.	Oxidation with acidified $KMnO_4$ solution	Aldehydes are formed first. Then carboxylic acids are formed finally	Ketones are formed first, which give degradation products on	Degradation products are formed

			further oxidation	
2.	Lucas reagent	Turbidity is given very slowly i.e., after a very long time	Turbidity is given within 5 minutes	Turbidity is given with in 30 seconds
3.	Alcohol vapours are passed over Cu metal at 573K	Aldehydes are formed.	Ketones are formed.	Alkenes are formed.

2. Write the chemical equations for the reactions of alcohol with
   a. Na   b. R^1MgX

Solution:

a. Reaction with metals:

Alcohols react with metals such as sodium, potassium and aluminium to yield corresponding alkoxides and hydrogen.

$$2\ R-O-H\ +2Na \longrightarrow \underset{\text{Sodium Alkoxide}}{2\ RONa} + H_2$$

b. Action of Grignard reagent:

Alcohol reacts with alkyl magnesium halide to form an alkane.

$$R-OH\ + R^1MgX \longrightarrow R^1-H + Mg(OR)X$$

3. What happens when alcohols are treated with
   a. PCl_3 b. PCl_5

Solution:

Reaction with PCl_3 or PCl_5 or $SOCl_2$:

Alcohols react with phosphorous halides or thionyl chloride to form alkyl halides.

$$3ROH\ + PCl_3 \longrightarrow 3RCl + H_3PO_3$$

$$ROH\ + PCl_5 \longrightarrow RCl + POCl_3 + HCl$$

Problem set:

1. Sodium ethoxide is obtained by the reaction of ethyl alcohol with_____
   a. NaOH
   b. Na

c. NaCl
d. $NaHCO_3$

Solution: b)

2. Grignard reagent CH_3MgI reacts with ethyl alcohol to produce______

a. C_2H_6
b. CH_4
c. $CH_3.C_2H_5$
d. $CH_3OC_2H_5$

Solution: b)

3. $CH_3CH_2OH \xrightarrow[\text{Cu metal}]{300\ ^{o}c}$

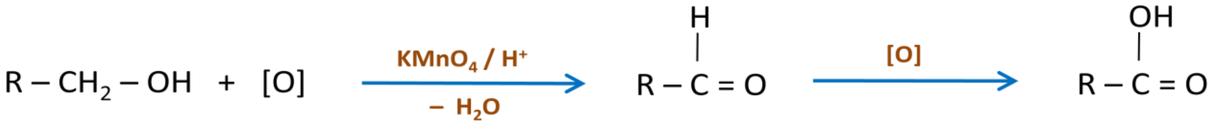
a. C_2H_6
b. CH_3COCH_3
c. CH_3CHO
d. CH_3COOH

Solution: c)

4. What happens when alcohols are treated with $KMnO_4$ + dilute H_2SO_4?

Solution:

Strong oxidising agents such as acidified $KMnO_4$ are used for getting carboxylic acids directly.



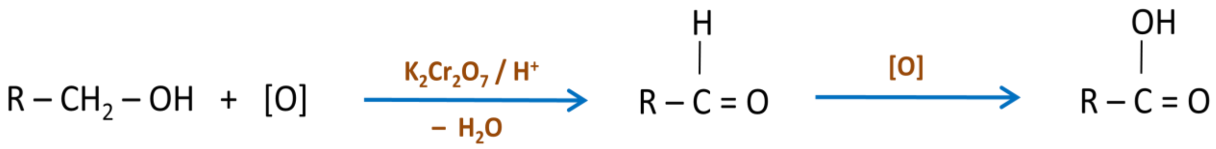
$$R-CH_2-OH + [O] \xrightarrow[-\ H_2O]{KMnO_4\ /\ H^+} R-\overset{H}{\overset{|}{C}}=O \xrightarrow{[O]} R-\overset{OH}{\overset{|}{C}}=O$$

5. How is an acetaldehyde prepared from alcohol?

Solution:

The oxidising agent and the nature of alcohols used, determine the products of oxidation reactions.

For example a primary alcohol on oxidation with acidified potassium dichromate first gives an aldehyde, which on further oxidation gives an acid with the same number of carbon atoms as the original alcohol.



Strong oxidising agents such as acidified $KMnO_4$ are used for getting carboxylic acids directly. Cr (VI) in anhydrous medium is used as the oxidizing agent for the isolation of aldehydes.

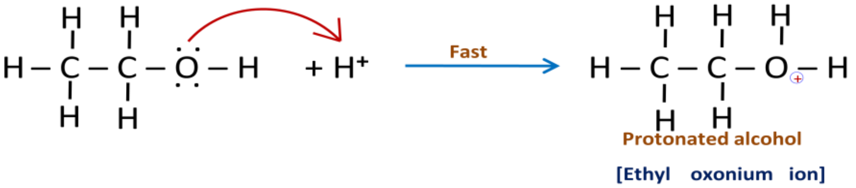
6. Give the mechanism of dehydration of a 1^0 alcohol

Solution:

Mechanism: dehydration of ethanol is taken as an example

The mechanism of dehydration of ethanol involves the following steps:

Step 1: Formation of protonated alcohol or an oxonium ion



Step 2: Formation of carbocation

It is the slow step and hence the rate determining step of the reaction.

Step 3: Formation of ethene

The acid used in step (1) is finally released after the reaction.

Exercise question:

1. In Fischer esterification of a primary alcohol which of the following bonds undergoes cleavage?
   a. "C – O" bond of an alcohol
   b. "O – H" bond of an acid
   c. "C – O" bond of an acid
   d. "C – C" bond of an alcohol

2. In the following sequence of reactions, B is

$$CH_3CH_2OH \xrightarrow{PCl_5} A \xrightarrow{\text{alcoholic NaOH}} B$$

   a. Ethyne
   b. Ethene
   c. Ethanal
   d. Ethane

3. Identify Z in the following series:

$$\text{Ethanol} \xrightarrow{PBr_3} X \xrightarrow{\text{alcoholic KOH}} Y \xrightarrow[\text{(ii) } H_2O\text{; Heat}]{\text{(i) dil.}H_2SO_4\text{; room temperature}} Z$$

   a. $CH_2 = CH_2$
   b. CH_3CH_2OH
   c. $CH_3CH_2 – O – CH_2CH_3$
   d. $CH_3CH_2 – SO_3H$
4. Explain how water is a stronger acid than an alcohol.
5. How do convert
   i. Propene into 2- propanol. (in 1 step)
   ii. Methyl magnesium Bromide into
       2- methyl propan-2-ol. (in 2 steps)
6. 3- methyl butane- 2- ol $\xrightarrow{HBr}$ 2-Bromo 2- methyl butane.
   Explain the formation of the product in the reaction.
7. How do you prepare ethyl alcohol from the following? Write the reagents and the equations.
   i. C_2H_5Br
   ii. $CH_3COOC_2H_5$
   iii. CH_3CHO
   iv. C_2H_2

Solutions:

1. c
2. b
3. b
4. Water is a stronger acid than alcohols. This can be shown by the reaction of water with an alkoxide.

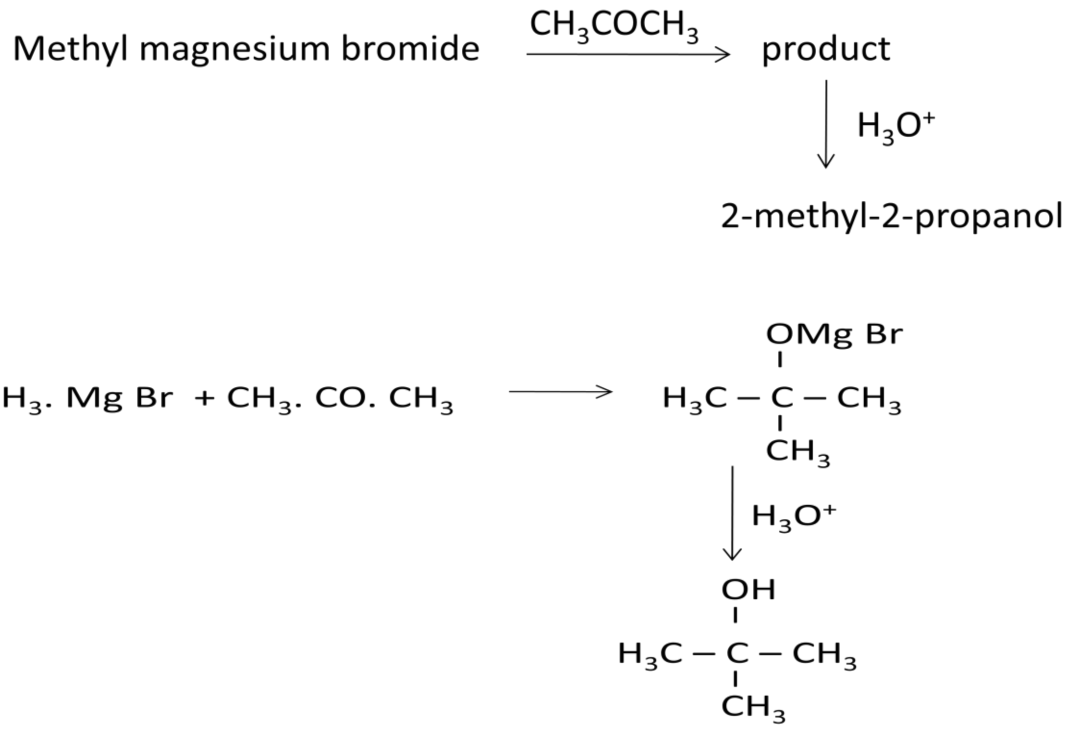
   $R - ONa + H_2O \longrightarrow R - OH \quad + Na$

   A stronger acid displaces a weaker acid from its salts. Alcohol is weaker than water and hence is displaced from sodium alkoxide.

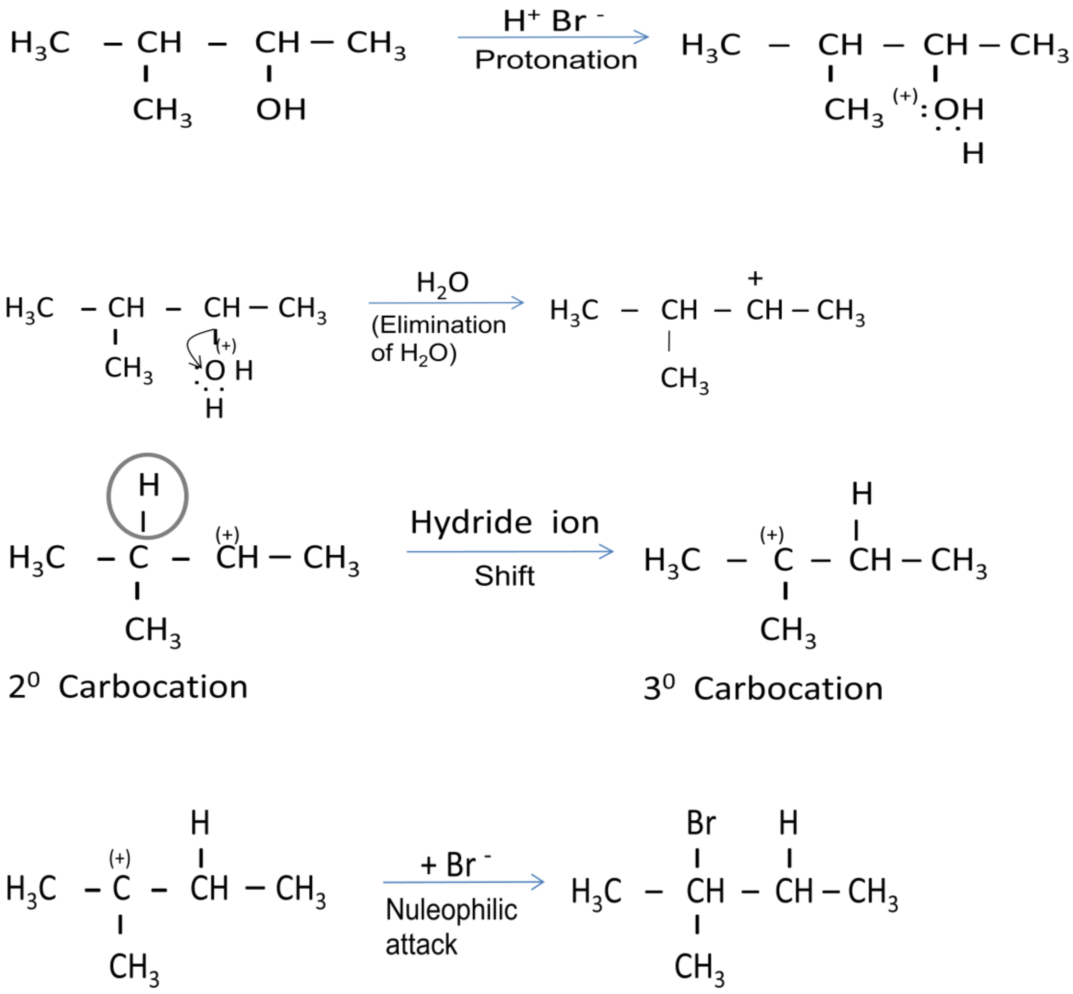
5.

   i. $\text{Propene} \xrightarrow{\text{Hydration}} \text{2-propanol}$

   ii.



6. In the presence of an acid, HBr, alcohol gets protonated. Eliminating H_2O it is converted into a secondary carbocation. As it is relatively unstable it rearranges into a more stable tertiary carbocation by a hydride ion shift from third carbon atom. Then nucleophilic attack by Br^- gives the product.



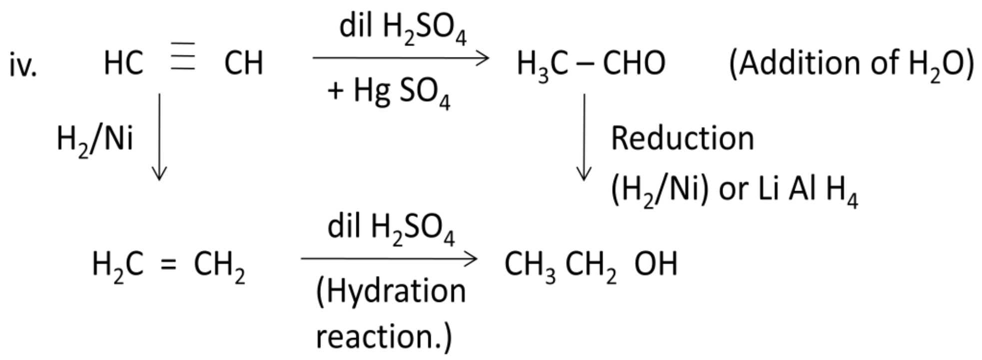
7.

i. $C_2H_5Br \xrightarrow[\text{or moist } Ag_2O]{KOH_{aq}} C_2H_5OH$

ii. $CH_3COOC_2H_5 \xrightarrow{\text{acid}} CH_3COOH + C_2H_5OH$

iii. $CH_3CHO \xrightarrow{\text{Li } AlH_4 \text{ in ether}} CH_3CH_2OH$

$CH_3CHO \xrightarrow[\text{Reduction}]{H_2 / Ni} CH_3CH_2OH$



CAT:

1. Lucas reagent is a mixture of
   a. Concentrated HCl + anhydrous $ZnCl_2$
   b. Concentrated HCl + hydrated $ZnCl_2$
   c. Concentrated HNO_3 + hydrated $ZnCl_2$
   d. Dilute HNO_3 + anhydrous $ZnCl_2$

Solution: a)

2. Lucas reagent produces cloudiness immediately with
   a. n- propanol
   b. Isopropanol
   c. n- butanol
   d. Tertiary butanol

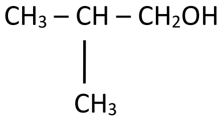
Solution: d)

3. An alcohol on oxidation with Alc.$KMnO_4$ gives a ketone with same number of carbons as in alcohol. The ketone on further oxidation gives acetic acid. Then the alcohol is a _______
   a. Primary alcohol
   b. Secondary alcohol
   c. Tertiary alcohol
   d. Both (b) and (c)

Solution: b)

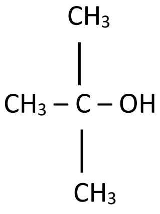
IIT Questions:

1. HBr reacts fastest with
   a. 2-methylpropan-2-ol
   b. Propan-1-ol
   c. Propan-2-ol
   d. 2-methylpropan -1 -ol
2. Which of the following compounds is oxidized to prepare methyl ethyl ketone?
   a. 2 - propanol
   b. 1 - butanol
   c. 2 - butanol
   d. tert-butyl alcohol
3. The compound which gives the most stable carbonium ion on dehydration is
   a.



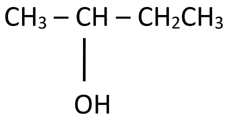
$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2OH$

   b.



$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH$

   c. $CH_3CH_2CH_2CH_2OH$



$CH_3-\underset{OH}{\underset{|}{CH}}-CH_2CH_3$

d.

4. The order of reactivity of HX towards ROH is
   a. HI > HBr > HCl
   b. HI < HBr <HCl
   c. HI > HBr < HCl
   d. HI < HBr > HCl
5. The relative order of basicity of conjugate bases is
   a. $OH^- < OR^- < HC \equiv C^-$
   b. $OH^- < HC \equiv C^- < OR^-$
   c. $HC \equiv C^- < OH^- < OR^-$
   d. $HC \equiv C^- < OR^- < OH^-$
6. The relative order of esterification of acids is
   a. $1^0 < 2^0 < 3^0$
   b. $1^0 > 2^0 > 3^0$
   c. $1^0 > 3^0 > 2^0$
   d. $1^0 < 3^0 < 2^0$

7. Ethanol vapour is passed over heated copper and the product is treated with aqueous NaOH. The final product is_______
8. 1-propanol and 2-propanol can be best distinguished by:
   a. oxidation with alkaline $KMnO_4$ followed by reaction with Fehling solution
   b. oxidation with acidic dichromate followed by reaction with Fehling solution
   c. oxidation by heating with copper followed by reaction with Fehling solution
   d. oxidation with concentrated H_2SO_4 followed by reaction with Fehling solution

9. Match the following choosing one item from column '*X*' and the appropriate item from column *Y*. Write down the matched pair on the answer script.

X	**Y**
Williamson's synthesis	*Tert*-alcohol
Neutral $FeCl_3$ test	*Ether*
Lucas test	*Phenol*

10. State the conditions under which the following preparations are carried out. Give necessary equations which need not be balanced.
   (i) Ethanol from acetaldehyde
   (ii) Lead tetraethyl from ethyl bromide
   (iii) Methyl chloride from aluminum carbide

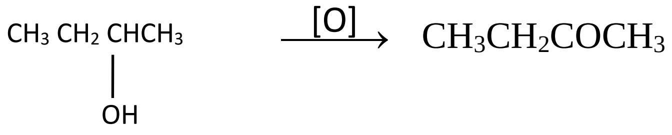
11. Give a chemical test to distinguish between methanol and ethanol
12. Write down the main product of the following reaction:

$$\text{Ethanol} \xrightarrow{I_2/\text{NaOH}}$$

13. Give reasons for the following in one or two sentences.
"Acid catalysed dehydration of *t*-butanol is faster than that of *n*-butanol."

Solutions:

1. a
   Tertiary alcohol (2 - methylpropan - 2 - ol) reacts fastest with HBr.
2. c



$$CH_3CH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_3 \xrightarrow{[O]} CH_3CH_2COCH_3$$

2-Butanol

3. b
   3^0 carbocation given by compound D is most stable.
4. a
   The order of reactivity of HX towards ROH is HI > HBr > HCI.
5. a
   The relative order of basicity follows reverts order as given in Q.14. The correct order is

   $OH^- < OR^- < HC \equiv C^-$

6. b

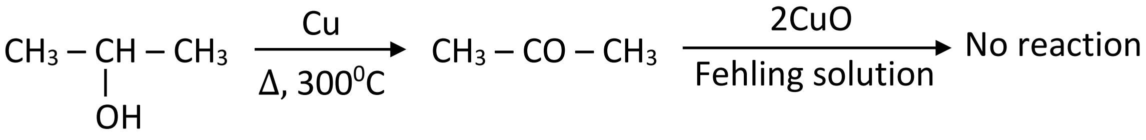
Increasing crowdiness near the site of esterification decreases the rate of esterification. Hence, the correct order is $1^0 > 2^0 > 3^0$

7. Aldol

8. (c)

$$CH_3 - CH_2 - CH_2OH \xrightarrow[\Delta,\ 300^0C]{Cu} CH_3 - CH_2 - CHO$$

$$\xrightarrow[\text{Fehling solution}]{2CuO} \underset{\text{red ppt.}}{Cu_2O \downarrow} + CH_3CH_2 - COOH$$



$$\underset{\displaystyle OH}{CH_3 - \overset{}{\underset{|}{CH}} - CH_3} \xrightarrow[\Delta,\ 300^0C]{Cu} CH_3 - CO - CH_3 \xrightarrow[\text{Fehling solution}]{2CuO} \text{No reaction}$$

2-propanol

9.

X	**Y**
Williamson’s synthesis	*Ether*
Neutral $FeCl_3$ test	*Phenol*
Lucas test	*Tert-alcohol*

10. (i) **Ethanol from acetylene:**

$$\underset{\text{acetylene}}{HC \equiv CH} \xrightarrow[HgSO_4]{H_2SO_4} CH_3CHO \xrightarrow[H_2]{\text{catalyst}} CH_3 - CH_2OH$$

(ii) **Lead tetraethyl form sodium-lead alloy:**

$$4C_2H_5Br + 4\underset{\text{sodium lead alloy}}{\left(Na/Pb\right)} \rightarrow \underset{\text{tetra ethyl lead}}{Pb\left(C_2H_5\right)_4} + 4NaBr + 3Pb$$

(iii) **Methyl chloride from aluminium carbide:**

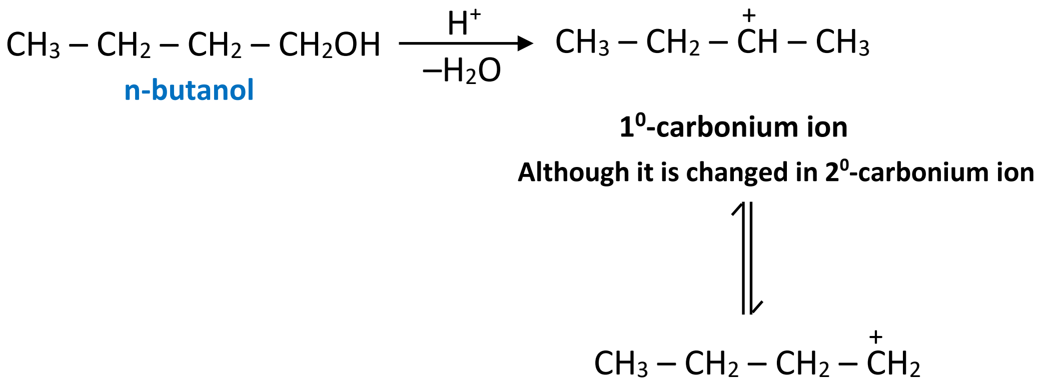
$$Al_4C_3 \xrightarrow{H_2O} CH_4 \xrightarrow[hv]{Cl_2} CH_3Cl$$

11. Ethanol give iodoform test, while methanol does not,

$$C_2H_5OH + 4I_2 + 6NaOH \longrightarrow \underset{\textbf{Iodoform}}{CHI_3\downarrow} + 5NaI + HCOONa + 5H_2O$$

12. $C_2H_5OH + 4I_2 + 6NaOH \longrightarrow \underset{\textbf{Iodoform}}{CHI_3\downarrow} + HCOONa + 5NaI + H_2O$

13. Due to formation of more stable 3^0-carbonium ion with *t*-butanol than 1^0-carbonium ion in *n*-butanol



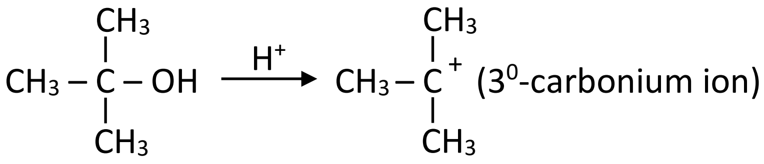
$$\underset{\textbf{n-butanol}}{CH_3-CH_2-CH_2-CH_2OH} \xrightarrow[-H_2O]{H^+} CH_3-CH_2-\overset{+}{C}H-CH_3$$

1^0-carbonium ion

Although it is changed in 2^0-carbonium ion

$$\rightleftharpoons$$

$$CH_3-CH_2-CH_2-\overset{+}{C}H_2$$



$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OH \xrightarrow{H^+} CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}{}^{+} \; (3^0\text{-carbonium ion})$$

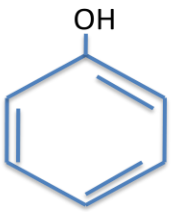
Alcohols, Phenols and Ethers

Module 33.3: Phenols

Classification of phenols:

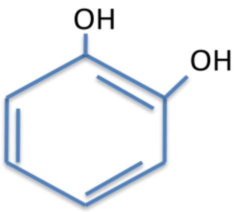
Classification of phenols is similar to that of alcohols. Phenols are classified as mono- , di-, trihydric compounds depending on whether they contain one, two or three hydroxy groups respectively in their structures as given below.

Example:



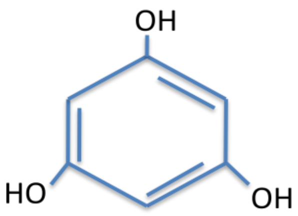
Phenol

Monohydric



Catechol

Dihydric phenol



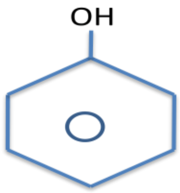
Phloroglucinol

Trihydric phenol

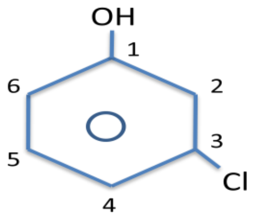
Nomenclature of phenols:

Phenols are named as derivatives of the parent compound of this class *i.e,* phenol.

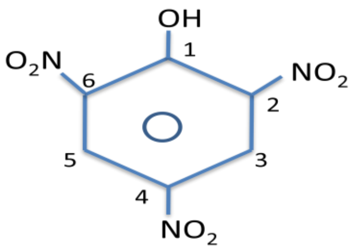
Example:



Phenol

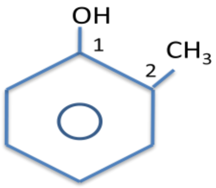


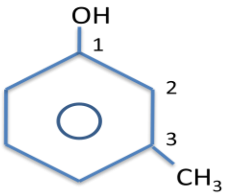
3-chlorophenol

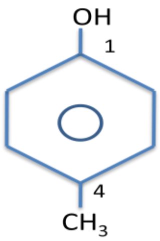


2, 4, 6 - Trinitrophenol

Methyl substituted of phenols is commonly called as cresols.

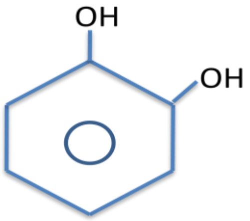


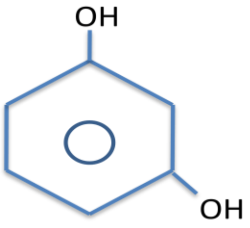




Common name:	*o*-Cresol	*m*-Cresol	*p*-Cresol
IUPAC name:	2-methyl phenol	3-methyl phenol	4-methyl phenol

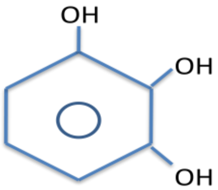
Dihydroxy phenols:

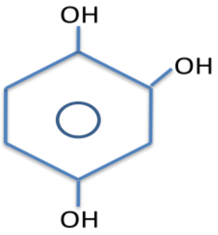


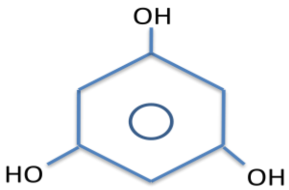


Common name:	Catechol	Resorcinol	Quinol
IUPAC name:	Benzene-1, 2-diol;	Benzene-1, 3-di-ol;	Benzene-1, 4-diol

Trihydroxy phenols:







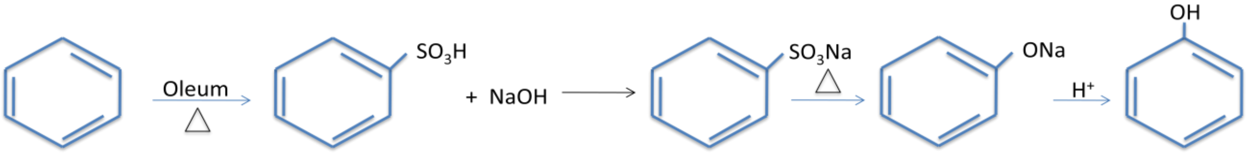
Common name:	Pyrogallol	Hydroxy quinol	Phloroglucinol
IUPAC name:	Benzene-1, 2, 3-triol;	Benzene-1, 2, 4-triol;	Benzene-1, 2, 5-triol

Preparation of phenol:

In the early nineteenth century, phenol was prepared from coal tar by destructive distillation. Now phenol is commercially produced synthetically. The laboratory methods of preparation of phenols are:

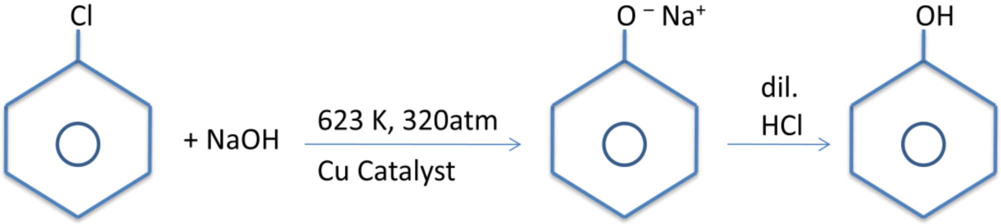
i. From aryl sulphonic acids

An aryl sulphonic acid yields the corresponding phenol on heating it with molten sodium hydroxide at 570-620 K. The sodium salt is obtained. The salt is hydrolysed with an acid to obtain free phenol.



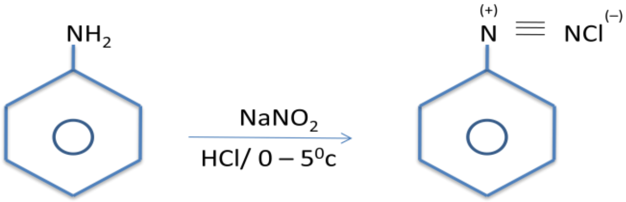
ii. From haloarenes

Chlorobenzene (an Haloarene) is hydrolysed by treating it with 10% NaOH at 623 K and 320 atm in the presence of Cu catalyst. Phenol is obtained by acidification of sodium phenoxide.

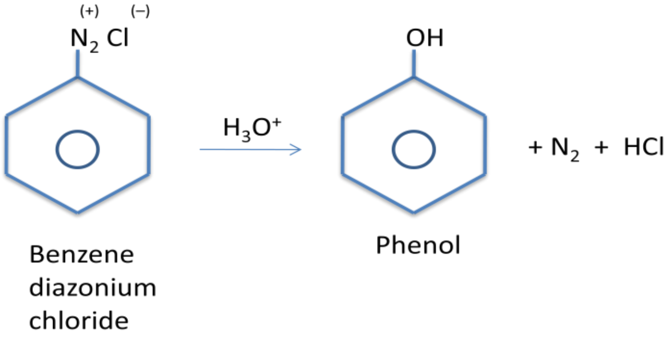


iii. Hydrolysis of diazonium salts

A diazonium salt is formed by treating an aromatic primary amine with nitrous acid. The HNO_2 is obtained from a mixture of $NaNO_2$ and HCl. The reaction is known as **diazotization**. It is carried out at low temperature of 273 K to 278 K.

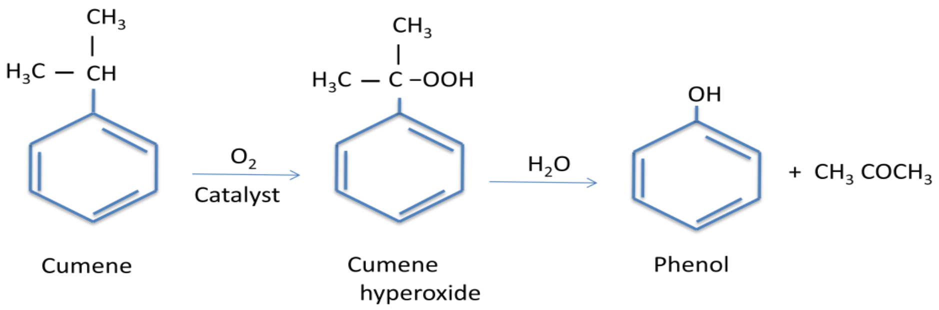


Diazonium salts are hydrolysed to phenols on treating with dilute acids.



iv) From Cumene

Phenol is manufactured from the hydrocarbon, cumene. Cumene [*i.e.* isopropyl benzene] is oxidised in the presence of air to cumene hyperoxide. It is converted to phenol and acetone by treating it with a dilute acid. Acetone is also obtained in large quantities by this method as an important by product.



Physical properties of phenols:

Pure phenol is a white crystalline solid, having a characteristic smell. It has to be handled with great care because it causes white blisters on the skin.

The –OH groups in monohydric phenols form intermolecular hydrogen bonding due to which phenols have higher. Boiling points than the corresponding arenes(hydrocarbons) (or) haloarenes (or) ethers of (nearly) same molecular weight. As the hydracarbon part increases in size and mass, the solubility in water decreases.

Chemical properties

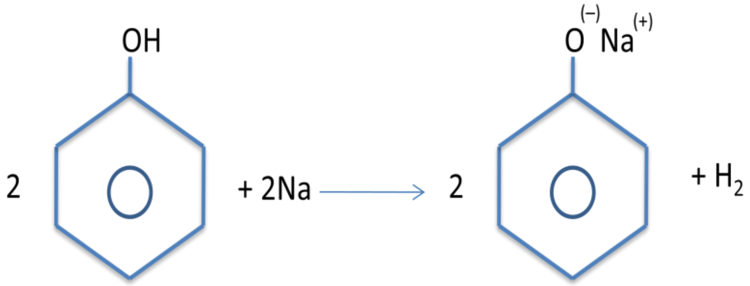
The chemical properties of phenol are of three types

a. Reactions involving cleavage of O–H bond.
b. Electrophilic substitution reactions.
c. Other reactions.

a) Reaction involving cleavage of O–H bond

i)Reaction with metals

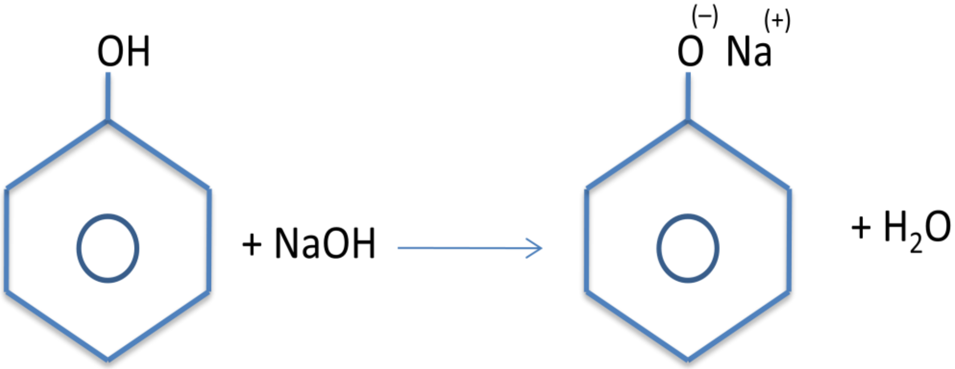
Phenols react with active metals like Na, K, or Al to yield phenoxides. Hydrogen is also formed.



Sodium phenoxide

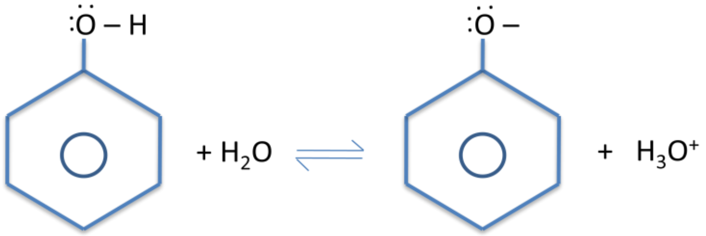
ii)Acidity of phenols:

Phenols react with sodium hydroxide solution and form phenoxides.

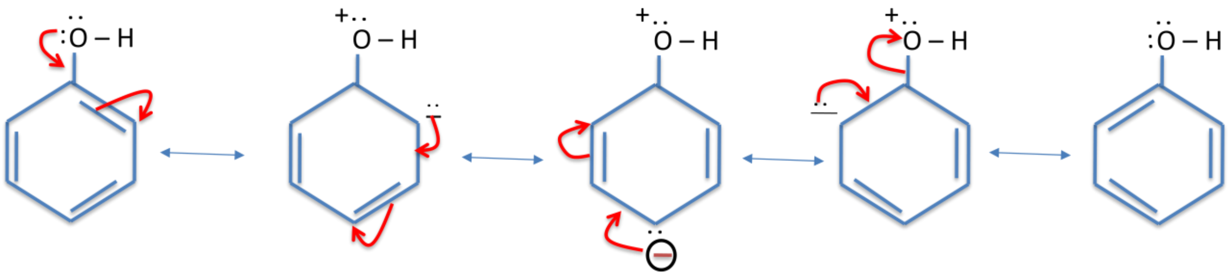


Phenols turn blue litmus to red. They react with metals and liberate hydrogen. However they do not react with metal carbonates or bicarbonates.

Phenols behave as acids because of the presence of polar OH group in them. They ionise in aqueous solutions to give H^+ ions.



Phenols as well as phenoxide ions, both are resonance stabilized. The various contributing structures of phenol are given below.

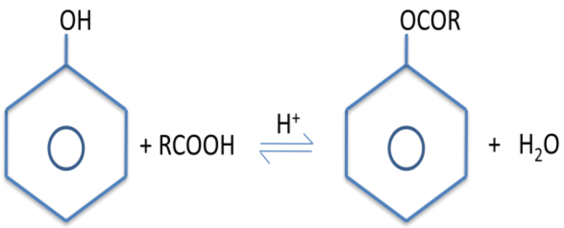


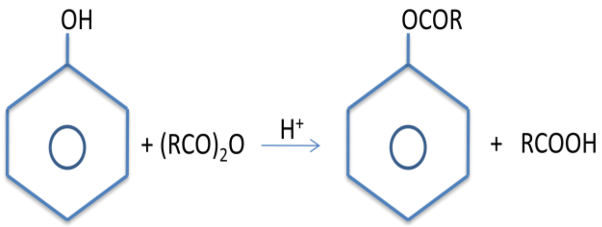
Since phenoxide ion is more stabilized than phenol, phenoxide and phenol furnishes a high concentration of phenoxide and H^+ ion. So phenol behaves as a fairly strong acid. In case of alcohols neither alcohol nor alkoxide ion is stabilized by resonance. Therefore they are weaker acids than phenols.

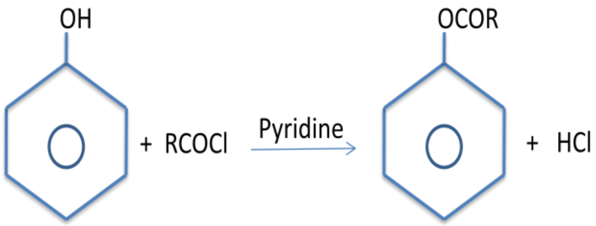
iii) Esterification of phenols

This reaction is an esterification reaction.

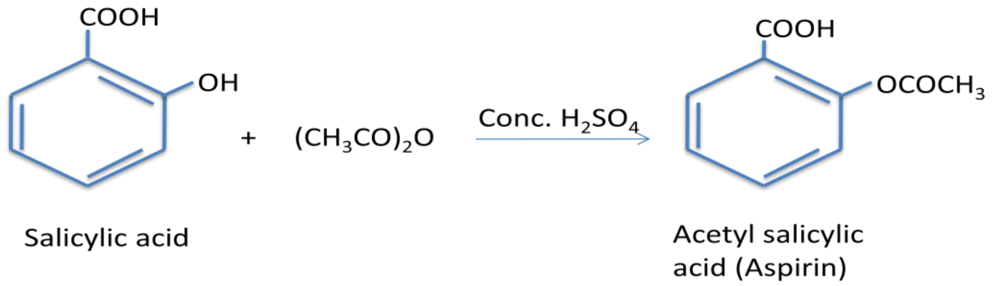
Phenols react with carboxylic acids, acid chlorides and acid anhydrides to form esters. The reaction between phenols and acids are carried out in the presence of a small amounts of conc. H_2SO_4, H_2SO_4 acts as a protonating agent as well as dehydrating agent.







One important reaction of a phenolic compound is acetylation of salicylic acid. It produces aspirin. It possesses analgesic, anti-inflammatory and antipyretic properties.

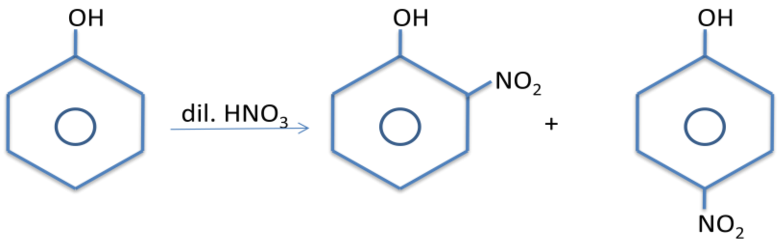


b) Electrophilic aromatic substitution reaction

In electrophilic substitution reactions of phenols, reactions that are similar to those of benzene is take place -OH group ring activating and ortho and para directing group. ortho- and para-positions get more electron density through resonance structures. So ortho, para substitutions occur.

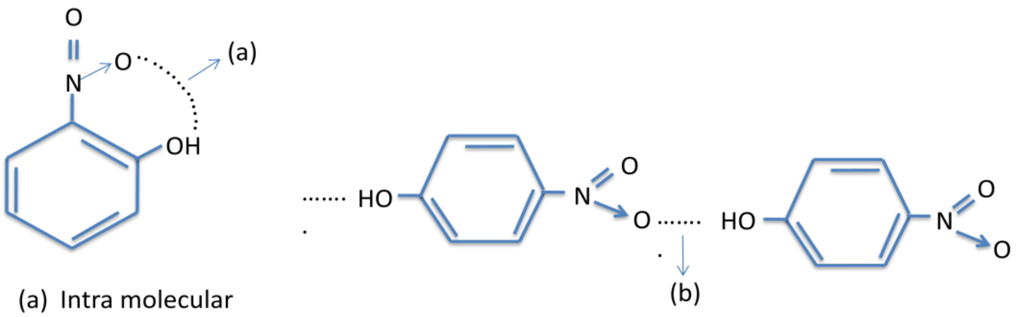
Common electrophilic aromatic substitution reactions taking place in phenol are as follows.

Nitration: With dilute nitric acid at low temperature (298 K) mono nitration takes place. Phenol yields a mixture of ortho and para nitro phenols.



o-nitrophenol p-nitrophenol

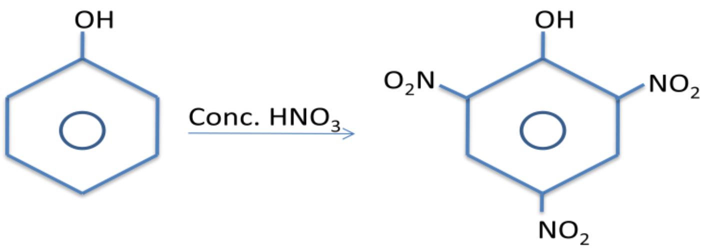
The ortho and para nitrophenols can be separated by steam distillation. o-nitro phenol is steam volatile due to presence of intra molecular hydrogen bonding. And p-nitro phenol is less volatile due to inter molecular hydrogen bonding. It causes association of molecules.



(a) Intra molecular hydrogen bonding in o-nitro phenol. Steam volatile compound.

(b) p-nitro phenol with inter molecular hydrogen bonding Not steam distilled

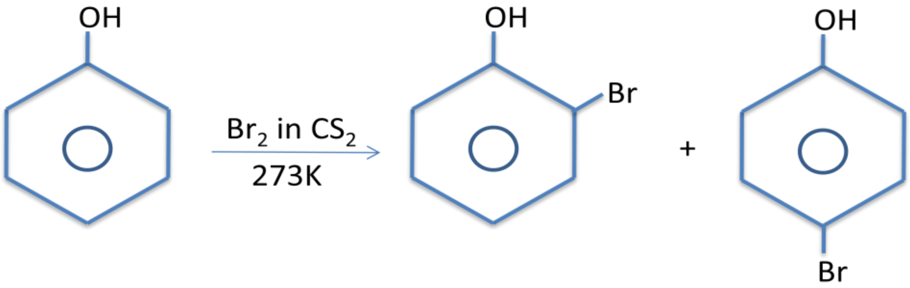
Withconc.HNO_3, phenol is converted to 2, 4, 6-trinitro phenol. This reaction may involve nitration as well as oxidation of phenol.



2, 4, 6 -tri nitro phenol
(picric acid)

Halogenations

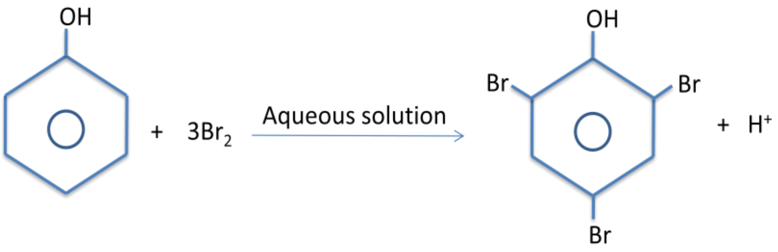
On treating phenol with bromine, different reaction products are formed. When the reaction is carried out in a solvent of low polarity such as $CHCl_3$ or CS_2 and at low temperature, monobromo phenol is formed.



Minor product (20%) Major product (80%)

When the reaction is carried out in aqueous medium (polar solvent) *i.e.,* bromine water

2, 4, 6-tribromophenol is formed.

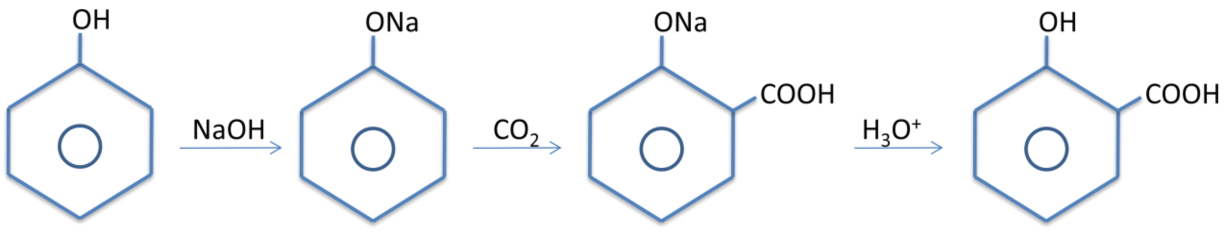


2, 4, 6-tribromophenol

C) Other reactions

i. Kolbe's reaction

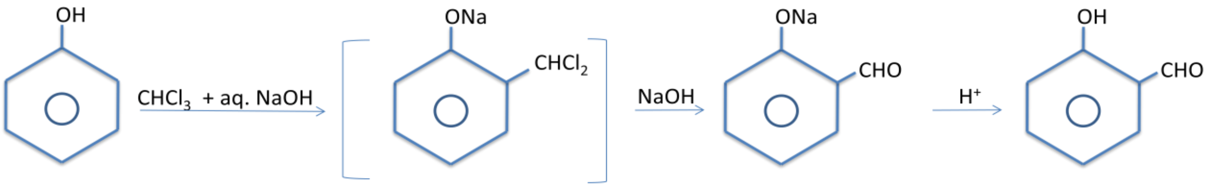
Sodium salt of phenol reacts with CO_2 gas. At 400 K and 4 -7 atm, ortho hydroxy benzoic acid(Salicylic acid) can be produced as the main product.



Salicylic acid

ii. Reimer-Tiemann reaction

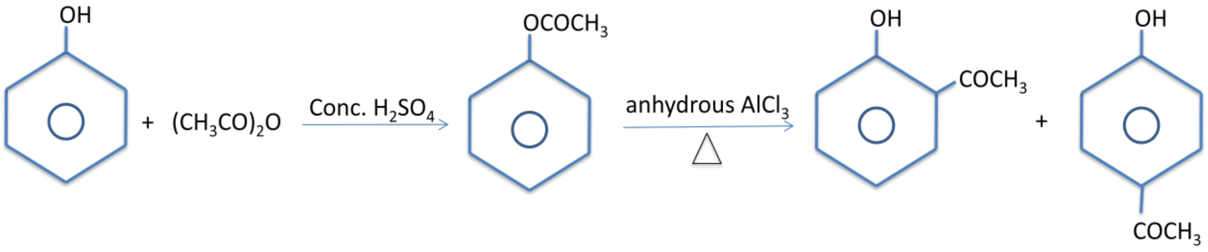
On treating phenol with chloroform in the presence of sodium hydroxide at 340 K, a –CHO group is introduced at ortho position in benzene ring. This reaction is known as Reimer-Tiemann reaction. This results in the formation of o-hydroxy benzaldehyde [salicylaldehyde]



Salicylaldehyde

iii. Frie's rearrangement

Esters of phenols yield phenolic ketones on heating with anhydrous aluminium chloride.

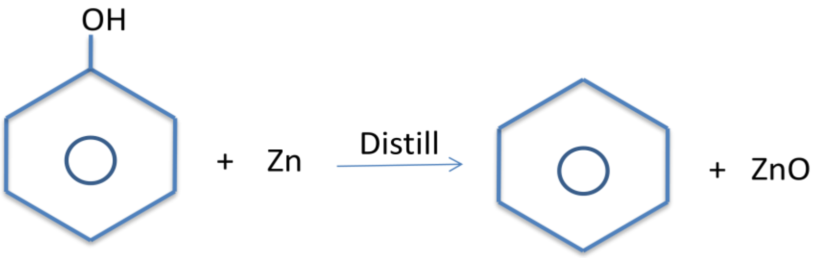


Phenolic ketone

This rearrangement is known as **Frie's rearrangement.**

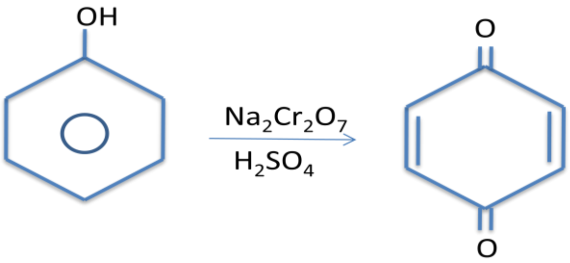
iv) Reaction of phenol with zinc dust:

An example, in which C – O bond cleavage in phenol takes place. The conversion of the phenol in to benzene on distilling with zinc dust is taking place in this reaction.



v) Oxidation:

Oxidation of phenol with chromic acid produces a coniugated diketone known as benzoquinone. In presence of air, phenols are slowly oxidized to dark coloured mixtures containing quinones.



benzoquinone

Example set

1. 2-Methyl phenol is called as ----------
   a. o-cresol
   b. p-cresol
   c. m-cresol
   d. 3-cresol

   Solution: a)

2. Cumene is -------
   a. o-methyl phenol

b. p-cresol
c. isopropyl benzene
d. phenyl n-propane

Solution: c)

3. Solubility of phenol in water is due to
a. Ionic bond formation
b. The cleavage of a covalent bond
c. Coordinate covalent bond formation
d. Hydrogen bonding formation with water.

Solution: d)

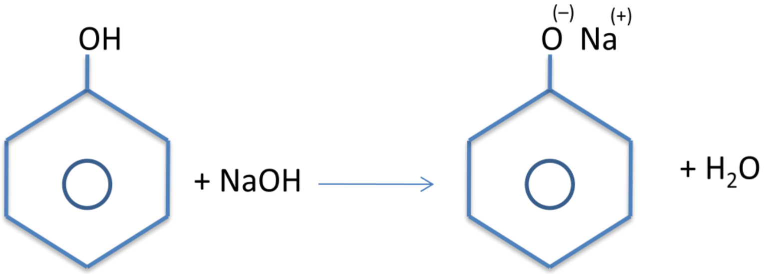
4. Acidity of phenol is due to
a. Resonance of phenoxide ion
b. Resonance in benzene ring.
c. Resonance in the phenol
d. All the above

Solution: d)

5. Explain the acidity of phenol

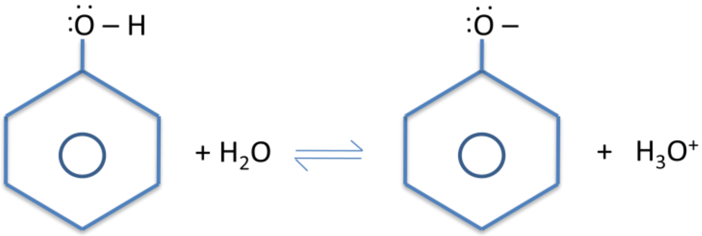
Solution: **Acidity of phenols:**

Phenols react with sodium hydroxide solution and form phenoxides.

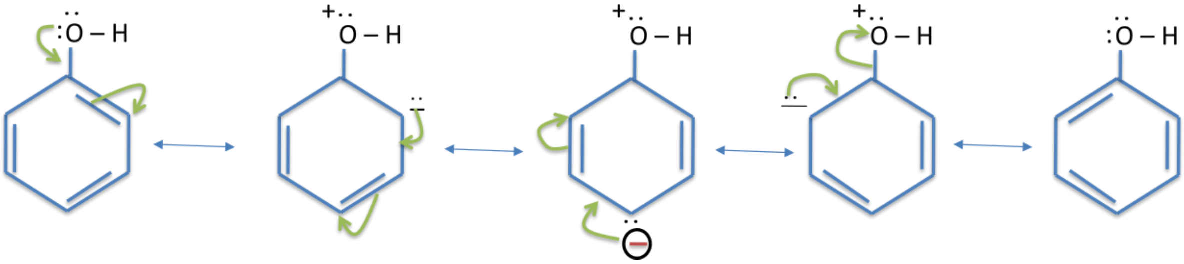


Phenols turn blue litmus to red. They react with metals and liberate hydrogen. However they do not react with metal carbonates or bicarbonates.

Phenols behave as acids because of the presence of polar OH group in them. They ionise in aqueous solutions to give H^+ ions.



Phenols as well as phenoxide ions, both are resonance stabilized. The various contributing structures of phenol are given below.



Since phenoxide ion is more stabilized than phenol, phenoxide and phenol furnishes a high concentration of phenoxide and H^+ ion. So phenol behaves as a fairly strong acid. In case of alcohols neither alcohol nor alkoxide is stabilized by resonance. Therefore they are weaker acids than phenols.

6. How is phenol prepared from

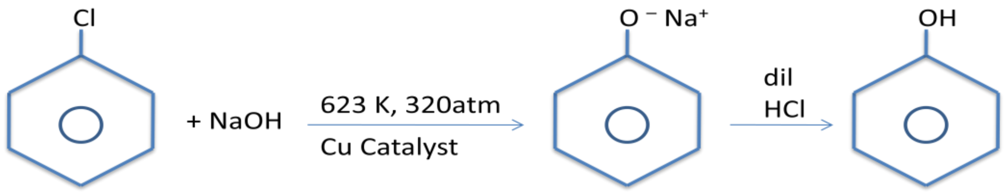
  a. Haloarenes
  b. Diazonium salts
  c. Cumeme

Give the equations.

Solution:

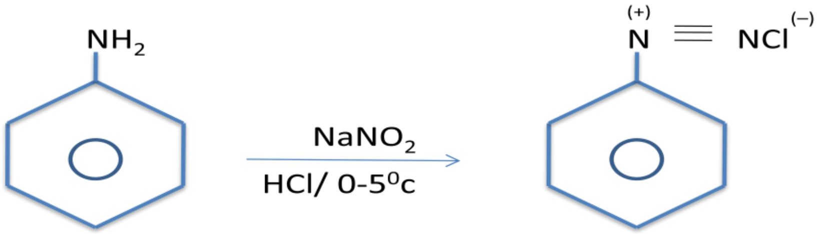
a. From haloarenes

Chlorobenezene (an Haloarene) is hydrolysed by treating it with 10% NaOH at 623 K and 320 atm in the presence of Cu catalyst. Phenol is obtained by acidification of sodium phenoxide.

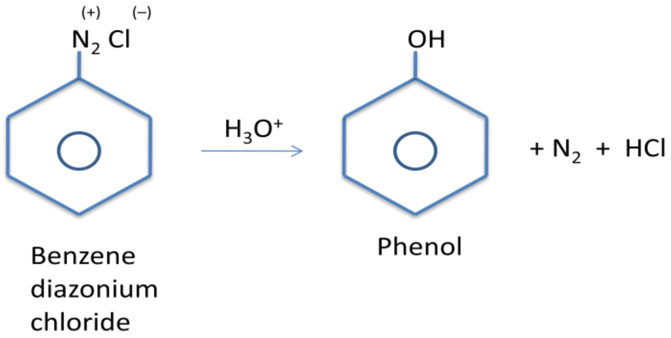


b. Hydrolysis of diazonium salts

A diazonium salt is formed by treating an aromatic primary amine with nitrous acid. The HNO_2 is obtained from a mixture of $NaNO_2$ and HCl. The reaction is known as diazotization. It is carried out at low temperature of 273 K to 278 K.

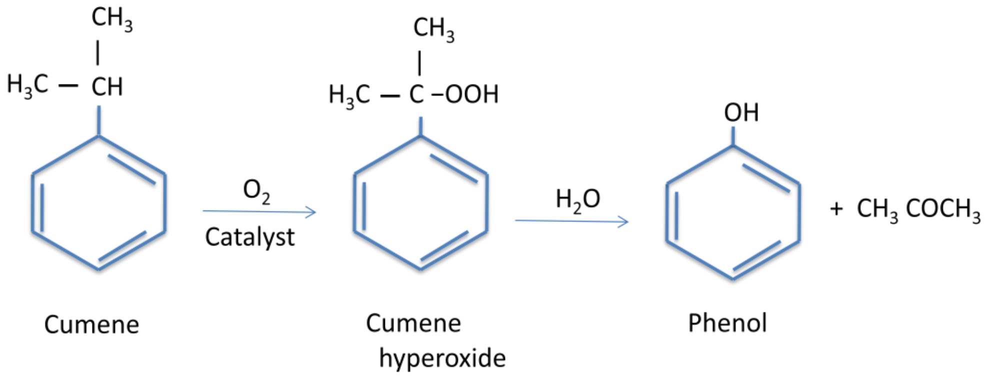


Diazonium salts are hydrolysed to phenols on treating with dilute acids.



C. From Cumene

Phenol is manufactured from the hydrocarbon, cumene. Cumene [*i.e.* isopropyl benzene] is oxidised in the presence of air to cumene hyperoxide. It is converted to phenol and acetone by treating it with a dilute acid. Acetone is also obtained in large quantities by this method as an important by product.

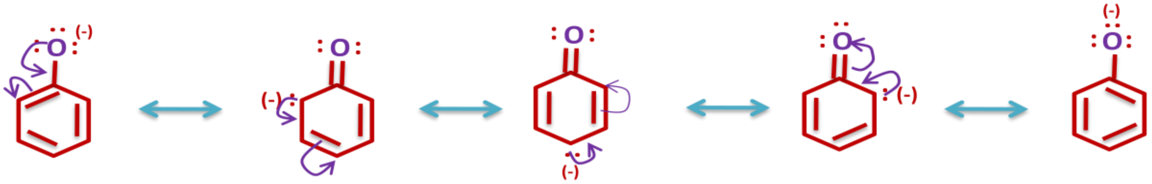


7. Write any two physical properties of phenol.

Solution: Pure phenol is a white crystalline solid, having a characteristic smell. It has to be handled with great care because it causes white blisters on the skin.

8. Write the various contributing structures of phenoxide ion.

Solution:



Problem set:

1. Phenol is an acidic substance but does not react with
   a. Na
   b. NaOH
   c. $NaHCO_3$
   d. All the above

Solution: c)

2. Phenol with cold, dilute HNO_3 gives
   a. ortho nitrophenel
   b. meta nitrophenol

c. ortho and para nitrophenols
d. picric acid

Solution: c)

3. At 600 ^{0}c, phenol was treated with chloroform and an exess of NaOH. The product was subsequently acidified. Then the product obtained is

a. 2-hydroxy benzoic acid
b. 2-hydroxy benzaldehyde
c. 4-hydroxy benzoic acid
d. 3-hydroxy benzaldehyde

Solution: b)

4. Phenol can be converted into o-hydroxy acetophenone by involving _________ reaction.

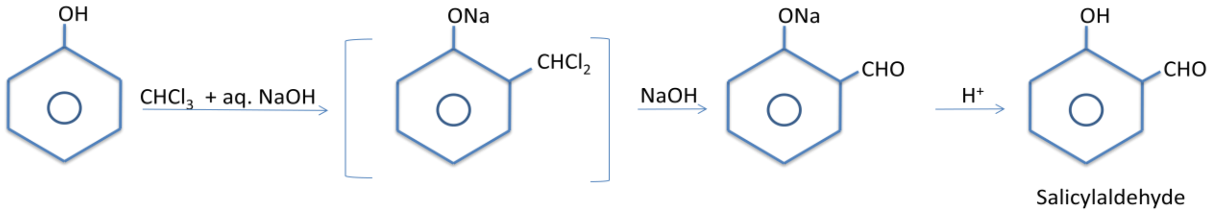
a. Rosenmund
b. Reimer-Tiemann
c. Kolbe
d. Frie's rearrangement

Solution: d)

5. What happens in Reimer-Tiemann reaction? Give the structure of the product formed in the reaction of a simple phenol. With alcoholic KOH + CHCl$_3$.

Solution: Reimer-Tiemann reaction

On treating phenol with chloroform in the presence of sodium hydroxide at 340 K, a –CHO group is introduced at ortho position in benzene ring. This reaction is known as Reimer-Tiemann reaction. This results in the formation of o-hydroxy benzaldehyde [salicylaldehyde].



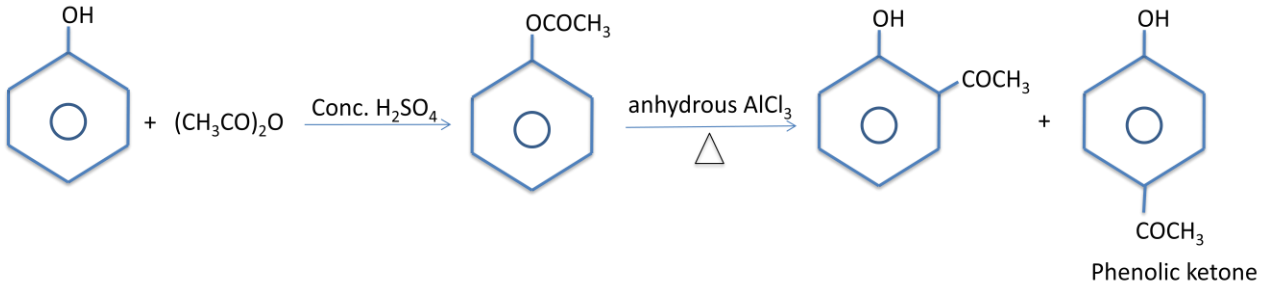
6. Write the various steps involved in the following reactions:

a. Frie’s rearrangement
b. Kolbe reaction

Solution:

a. Frie’s rearrangement

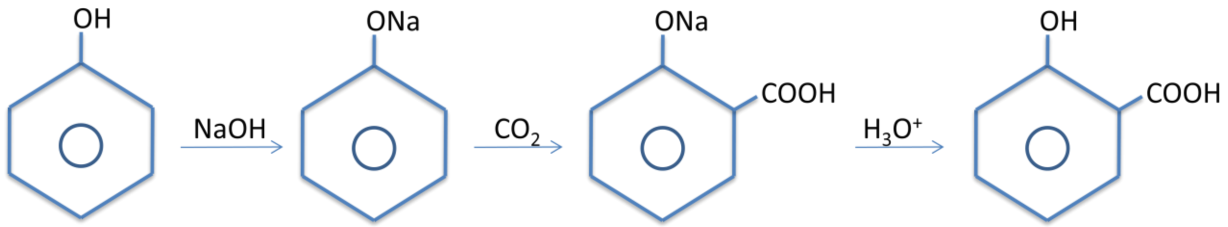
Esters of phenols yield phenolic ketones on heating with anhydrous aluminium chloride.



This rearrangement is known as **Frie’s rearrangement.**

b. Kolbe’s reaction

Sodium salt of phenol reacts with CO_2 gas. At 400 K and 4 -7 atm, ortho hydroxy benzoic acid can be produced as the main product.



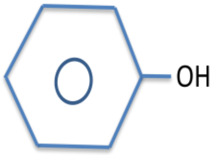
Salicylic acid

Exercise questions

1. Which of the following compounds are the most acidic compounds?

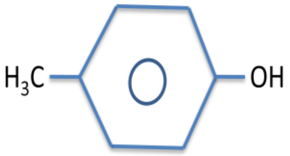
a) $CF_3\,CH_2OH$

b)



c) $H-C\equiv C-H$

d)

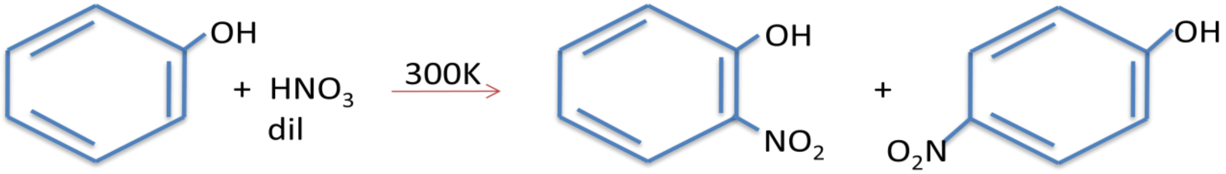


2. Under suitable conditions $C_6H_5CH_2OH$ (A), C_6H_5OH (B) and C_6H_5COOH (C) can act as acids. The increasing order of their acidic strength is
   a. A < B < C
   b. A < C < B
   c. B < A < C
   d. C < B < A
3. Explain the fact that the phenoxide ion is more stable than the phenol.
4. Salicylic acid can be esterified to aspirin with $(CH_3CO)_2O$ in the presence of conc. H_2SO_4. While with pyridine is added in reaction the reaction with $CH_3\,COCl$. Why?
5. Suggest a method for the separation of the compounds formed in the reaction between C_6H_5OH and dil HNO_3 at 300 K.

6. **How do you convert Toluene into Benzo trichloride?**

Solutions to Exercise questions

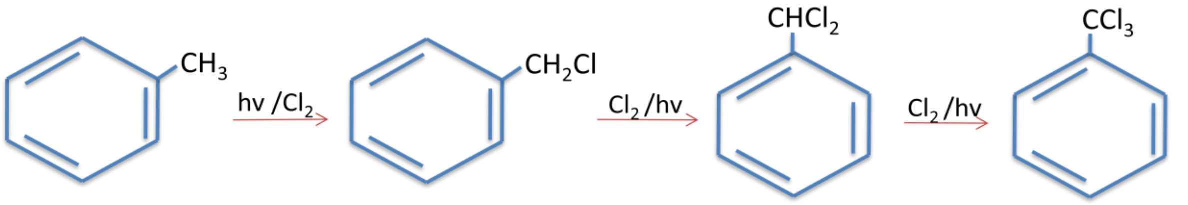
1. b)
2. a)
3. The delocalization of negative charge in the resonance structures of phenoxide ion makes phenoxide more stable and favours the ionization of phenol.
   In phenol molecule the resonance structures have charge separation. Due to this it is less stable than the phenoxide ion.
4. With $(CH_3CO)_2O$, water is formed. The reaction is reversible. Therefore water is removed as soon as it is formed with conc. H_2SO_4.
   The reaction with CH_3COCl produces HCl. Pyridine base neutralizes the HCl formed during the reaction. Pyridine, therefore, shifts the reaction to the right. *i.e.* ester formation.
5. The reaction is



o-nitrophenol and p-nitrophenol form H–bonding. o- $C_6H_5NO_2(OH)$ forms intramolecular H–bonds while p- C_6H_5 (OH) NO_2 forms intermolecular H–bonds.

They can be separated by steam distillation o- compound is steam volatile while p- compound is not. Hence they can be separated.

6.

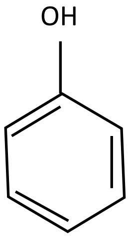


Benzo trichloride

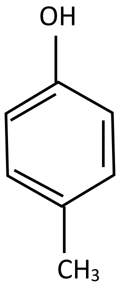
Under free radical Condition, substitution in the alkyl group takes place. But if the reaction is carried out in the presence of a halogen carrier, substitution in the ring takes place. *i.e.,* electrophilic substitution takes place.

IIT Questions:

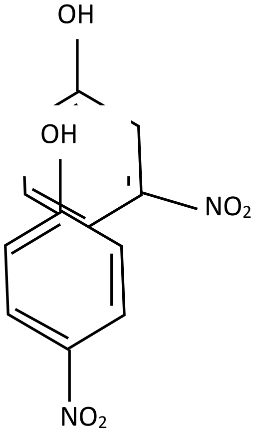
1. Phenol is less acidic than
    a. Acetic acid
    b. *p* - methoxyphenol
    c. *p* - nitrophenol
    d. ethanol
2. Which of the following statements regarding phenols is not correct?
    a. *o* - Nitrophenol has a much lower boiling point as compared to *p* - nitrophenol
    b. *o* - Nitrophenol has much lower solubility in water as compared to *p* - nitrophenol
    c. *o* - Nitrophenol is stronger acid than *p* - nitrophenol
    d. *o* - Nitrophenol can be steam distilled while *p* - nitrophenol cannot be.
3. Which of the following statements regarding phenols is not correct?
    a. Phenols are stronger acids than water and alcohols
    b. Phenols are weaker acids than carboxylic acids
    c. Phenols are soluble in both aqueous NaOH and aqueous $NaHCO_3$
    d. Phenoxide ions are more stable than the corresponding phenols.
4. Which of the following orders regarding acid strengths is correct?
    a. Benzyl alcohol > phenol > *p* - hydroxybenzoic acid
    b. Benzyl alcohol < phenol < *p* - hydroxybenzoic acid
    c. Benzyl alcohol < *p* - hydroxybenzoic acid < phenol
    d. phenol > Benzyl alcohol > *p* - hydroxybenzoic acid
5. In the following compound



I



II



IV

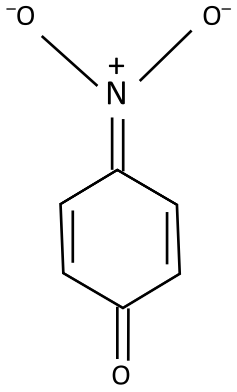
the order of acidity is

a. III > IV > I > II b. I > IV > III > II

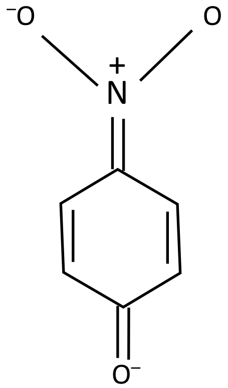
c. II > I > III > IV d. IV > III > I > II

6. The most unlikely representation of resonance structures of *p* - nitrophenoxide ion is

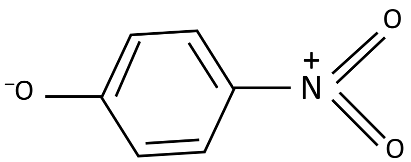
a.



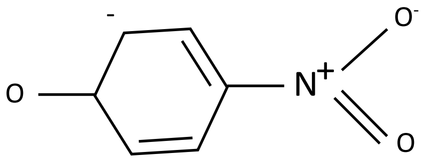
b.



c.



d.



7. Which of the following orders regarding the acid strength of aromatic acids is correct?
   a. *p* - nitrobenzoic acid < *p* - cyanobenzoic acid < *p* - chlorobenzoic acid
   b. *p* - nitrobenzoic acid > *p* – cyanobenzoic acid > *p* – chlorobenzoic acid
   c. *p* - nitrobenzoic acid < *p* - cyanobenzoic acid > *p* - chlorobenzoic acid
   d. *p* - nitrobenzoic acid > *p* - cyanobenzoic acid < *p* - chlorobenzoic acid
8. Which of the following orders regarding the basic strength of aromatic bases is correct?
   a. *p* - nitroaniline > *p* - cyanoaniline > *p* - chloroaniline
   b. *p* - nitroaniline < *p* - cyanoaniline < *p* - methylaniline
   c. *p* - nitroaniline > *p* - cyanoaniline < *p* - methylaniline
   d. *p* - nitroaniline < *p* - cyanoaniline > *p* - methylaniline
9. Which of the following orders regarding the acid strength of phenol is correct?
   a. *p* - aminophenol < *p* - chlorophenol < *p* - nitrophenol
   b. p - aminophenol > p - chlorophenol > p - nitrophenol
   c. p - aminophenol < p - chlorophenol > p - nitrophenol
   d. p - aminophenol > p - chlorophenol < p - nitrophenol

10. Formation of phenol form chlorobenzene is an example of _____ aromatic substitution.
11. Phenol is acidic because of resonance stabilization of its conjugate base, namely ____

12. When phenol is treated with excess bromine water, it gives:
    a. *m*-bromophenol
    b. *o*-and *p*-bromophenol
    c. 2, 4 dibromophenol
    d. 2, 4, 6 tribromophenol

13. Phenol reacts with bromine in carbon disulphide at low temperature to give:
    a. *m*-bromophenol
    b. *o*- and *p*-bromophenol
    c. *p*-bromophenol
    d. 2, 4, 6 tribromophenol

14. **Assertion:** Phenol is more reactive than benzene towards electrophilic substitution reaction.

    Reason: In the case of phenol, the intermediate carbocation is more resonance stabilised.
    a. both assertion and reason are correct and reason is the correct explanation of the assertion
    b. both assertion and reason are correct, but reason is not the correct explanation of the assertion
    c. assertion is correct, but reason is incorrect
    d. Assertion is incorrect, but reason is correct

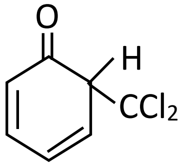
15. When phenyl magnesium bromide reacts with *t*-butanol, the product would be:
    a. benzene
    b. phenol
    c. *t*-butyl benzene
    d. *t*-butyl phenyl ether

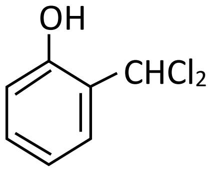
16. The best method to prepare cyclohexene from cyclohexanol is by using:
    a. Conc. HCl + $ZnCl_2$
    b. Conc. H_3PO_4
    c. HBr

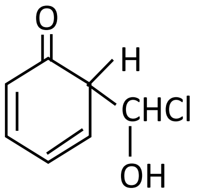
   d. Conc. HCl

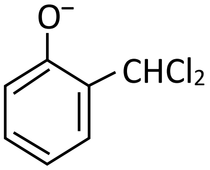
17. Phenol is less acidic than:
    a. Acetic acid
    b. *p*-methoxy phenol
    c. *p*-nitrophenol
    d. ethanol

18. When phenol is reacted with $CHCl_3$ and NaOH followed by acidification, salicylaldehyde is obtained. Which of the following species are involved in the above mentioned reaction as intermediates?

(a)


(b)


(c)


(d)


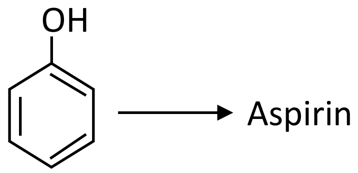
19. Give reason in one or two sentences for the following:
    "*o*-nitrophenol is steam volatile whereas *p*-nitrophenol is not."

20. A compound of molecular formula C_7H_8O is insoluble in water and dilute sodium bicarbonate but dissolves in dilute aqueous sodium hydroxide. On treatment with bromine water, it readily gives a precipitate of $C_7H_5OBr_3$. Write down the structure of the compound.

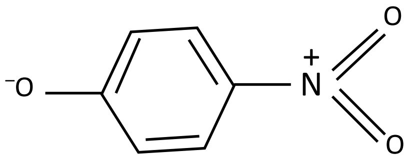
21. Explain the following in one or two sentences only:
    "Phenol is an acid, but it does not react with sodium bicarbonate."

22. Indicate steps which would convert:
    i) Phenol to acetophenone
    ii) Acetic acid to tert-butyl alcohol

23. Convert



Solutions:

1. a, c
   Carboxylic acid is more acidic than phenol. Electron - attracting group also increases the acidity of phenol. Thus, phenol is less acidic than acetic acid and *p* - nitrophenol.
2. c
   o - Nitrophenol is less strong acid than *p* - nitrophenol due to intramolecular hydrogen bonding. The choice C is incorrect.
3. c
   Phenols are insoluble in aqueous $NaHCO_3$ solution. The choice C is not correct.
4. b
   Alcohol is less acidic than phenol, and phenol is less acidic than carboxylic acid. The correct order is Benzyl alcohol < phenol < *p* - hydroxybenzoic acid.
5. d
   The correct order of acidity *p* - nitrophenol > m - nitrophenol > phenol > *p* - methylphenol
6. c
   

   The structure is most unlikely as N Containing 5 valence electrons should not carry positive charge.

7. b
   The expected trend is *p* - nitrobenzoic acid > *p* - cyanobenzoic acid > *p* - chlorobenzoic acid

8. b

The expected trend is *p* - nitroaniline < *p* - cyanoaniline < *p* – methylaniline

9. a

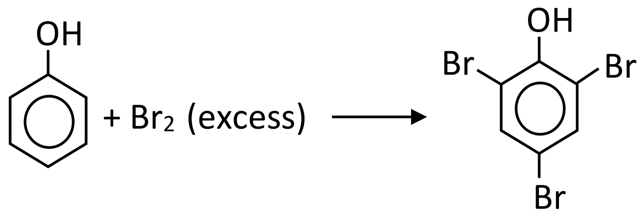
Electron attracting group makes phenol more acidic while electron releasing makes it less basic.

p - aminophenol < *p* - chlorophenol < *p* – nitrophenol

10. nucleophilic

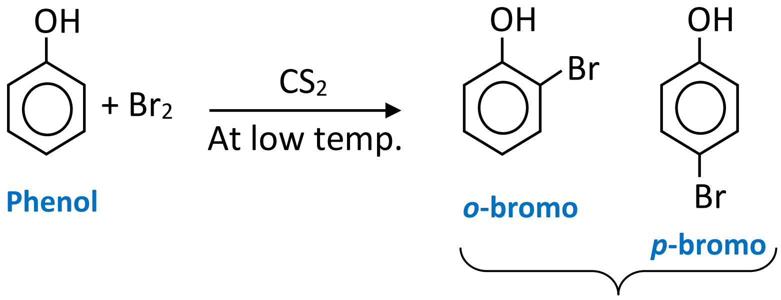
11.Phenoxide ion

12. (d)



2, 4, 6-tribromophenol

13. (b)



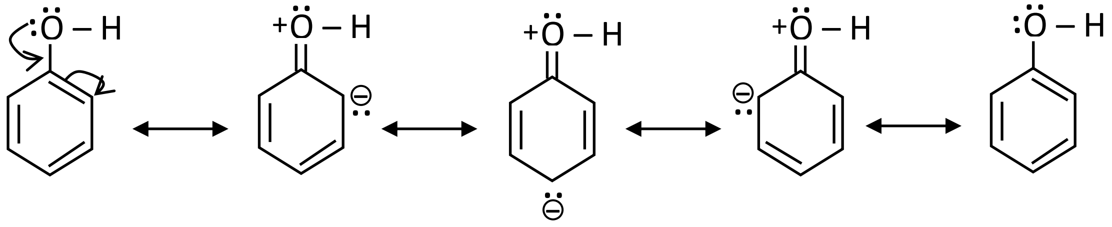
Phenol

***o*-bromo**

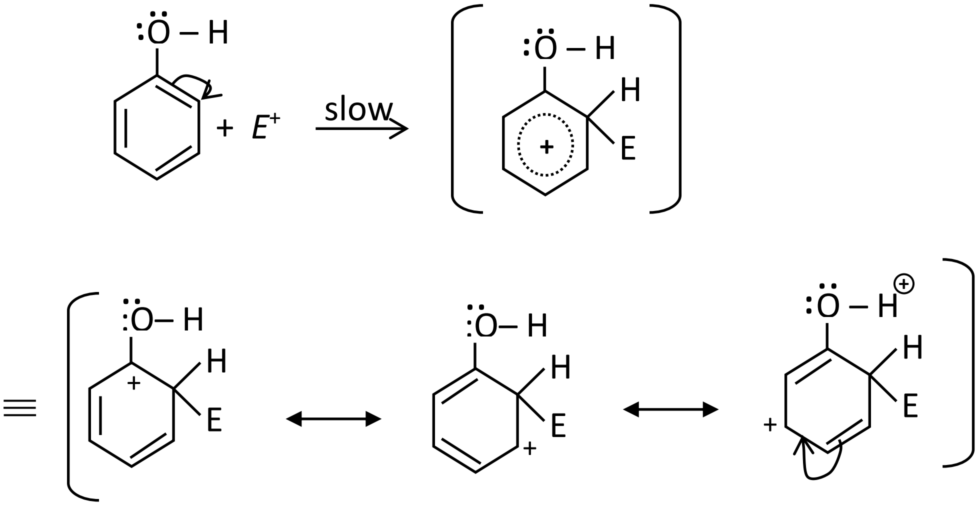
***p*-bromo**

Phenol

14. (c) in phenol, - OH group is attached with C-atom of benzene ring . OH-group shows + M effect so, it is able to activate the benzene ring as follows:

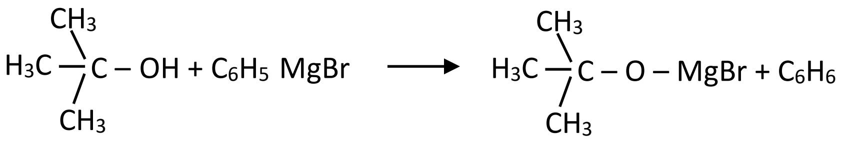


Thus, the electron density of *ortho* and *para*-position is higher in comparison to benzene. Hence, electrophile must be attacked on *olp*-positon.



15. (b) Phenyl magnesium bromide reacts with t-butanol to produce benzene because phenyl group (electronegative group) is associated with active hydrogen of alcohol *i.e.,* -H of –OH group of alcohol.

$$C_6H_5\boxed{MgBr + (CH_3)_3C - O -}H \longrightarrow \underset{\textbf{benzene}}{C_6H_6} + (CH_3)_3C - O - MgBr$$



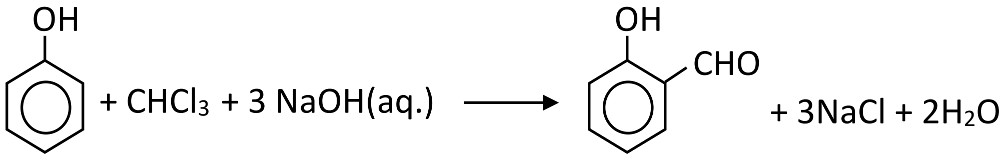
$$(CH_3)_3C - OH + C_6H_5\,MgBr \longrightarrow (CH_3)_3C - O - MgBr + C_6H_6$$

16. (b) The best method to prepare cyclohexene from cyclohexanol is by conc. H_3PO_4 because in given options dehydrating agent is conc. H_3PO_4

17. Both (a) and (c)

Phenol is less acidic than acetic than acetic acid and *p*-nitrophenol.

18. Both (a) and (d)

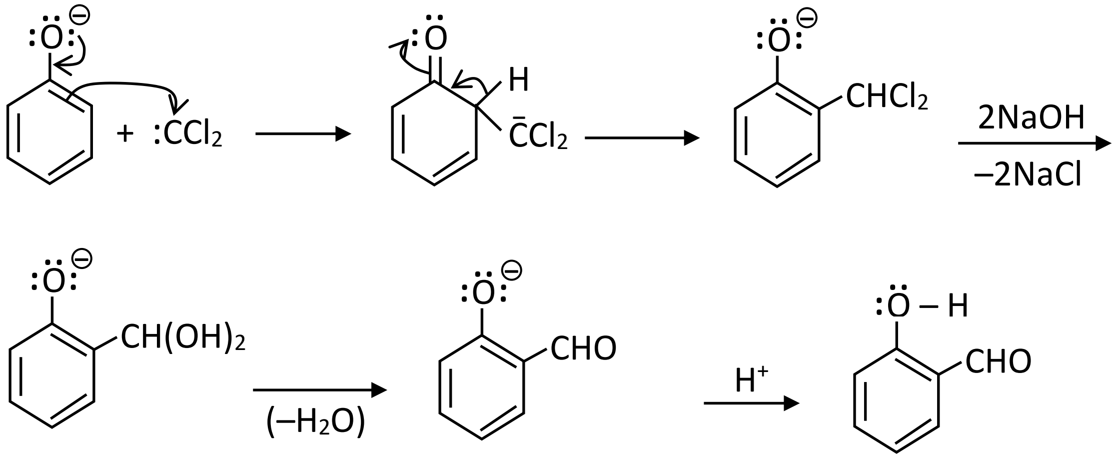


This reaction is Reimer-Tiemann reaction and the mechanism is represented as follows:

Mechansim step 1:

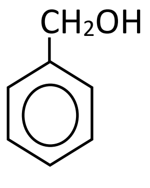
$$CHCl_3 + NaOH \longrightarrow \underset{\text{dichloro carbene}}{:CCl_2} + NaCl + H_2O$$

Step 2:

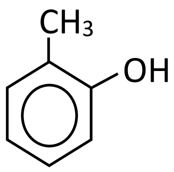


19. *o*-nitrophenol has lower boiling point so it is more volatile and is less miscible with steam than *p*-nitrophenol due to intramolecular hydrogen bonding, and hence can be separated by steam distillation.

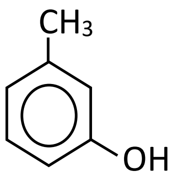
20. **C_7H_8O** has following isomeric compounds:



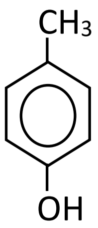
Benzyl alcohol



***o*-cresol**

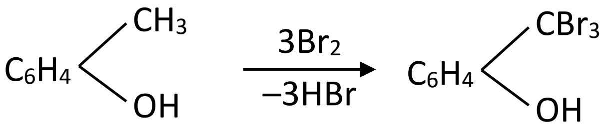


***m*-cresol**



***p*-cresol**

Since the compound is insoluble in water and $NaHCO_3$ but dissolve in NaOH, hence, it must be phenol i.e., *o-* , *p-* or *m*-cresol.



o, p-, m-cresol

($C_7H_5OBr_3$)

Thus, the compound may be a **cresol**.

21. Phenol is a very weak acid, hence, it does not react with sodium bicarbonate.

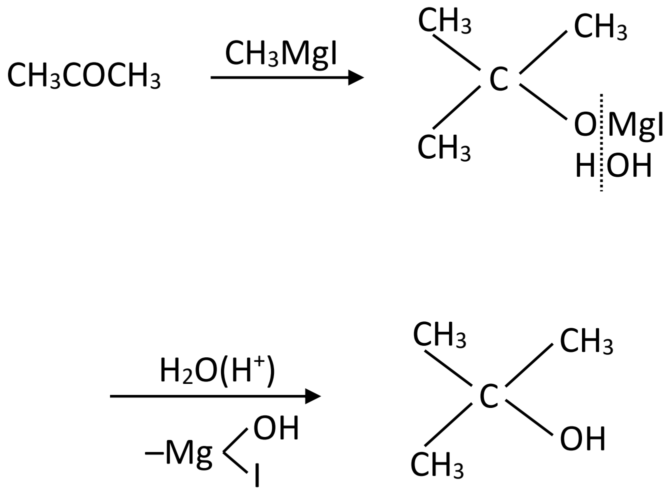
22.

(i) **Phenol to acetophenone:**

$$\underset{\text{phenol}}{C_6H_5OH} \xrightarrow[-ZnO]{\text{Zn dust}} \underset{\text{benzene}}{C_6H_6} \xrightarrow[\substack{\text{anhydrous } AlCl_3 \\ -HCl}]{CH_3COCl} \underset{\text{acetophenone}}{C_6H_5COCH_3}$$

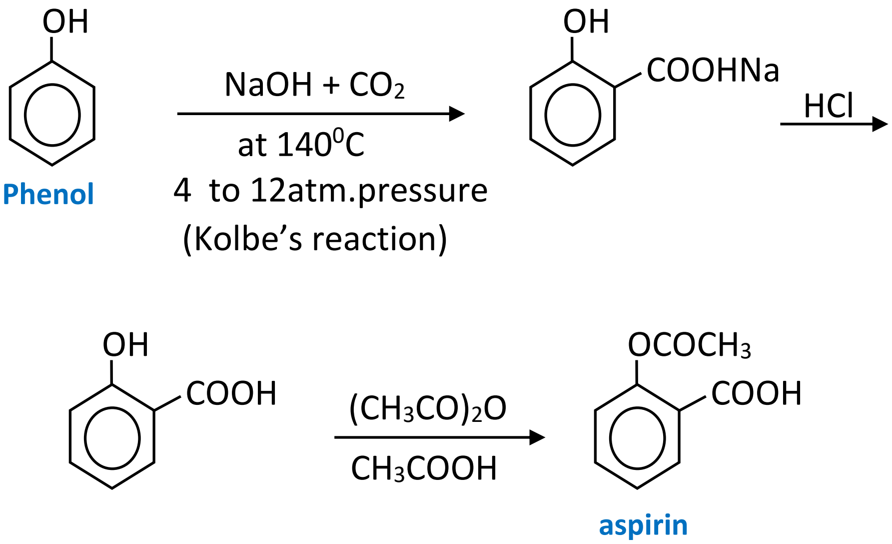
(ii) **Acetic acid to ter. butyl alcohol:**

$$\underset{\text{acetic acid}}{CH_3COOH} \xrightarrow{PCl_5} \underset{\text{acetyl chloride}}{CH_3COCl} \xrightarrow{CH_3Cl}$$



tert. Butyl alcohol

23.


OH
NaOH + CO$_2$
at 140^{0}C
4 to 12atm.pressure
(Kolbe's reaction)
OH
COOHNa
HCl
Phenol
OH
COOH
(CH$_3$CO)$_2$O
CH$_3$COOH
OCOCH$_3$
COOH
aspirin

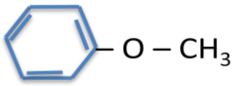
Alcohols, Phenols and Ethers

Module 33.4: Ethers

Genera formula of ethers is $C_nH_{2n+2}O$. Ethers consist of two alkyl groups attached on oxygen atom as R-O-R’.

Ethers are compounds having the general formula $R - O - R'$ where R and R' may be alkyl or aryl groups. They may be identical or may be different.

Ex: $C_2H_5 - O - C_2H_5$;



Diethyl ether   Methyl phenyl ether

Classification of ethers:

Ethers are mainly classified into two types.

Ethers

Simple or symmetrical

Ex: - $R - O - R$

$Ar - O - Ar$

$C_2H_5 - O - C_2H_5 \Longrightarrow$ Diethyl ether

Mixed or unsymmetrical

Ex: - $R - O - R^1$

$Ar - O - Ar^1$

$C_6H_5 - O - CH_3$

Methyl phenyl ether

a) Ethers are known as simple or symmetrical, if the two alkyl or aryl groups attached to the oxygen atom are same.
   Example: $C_2H_5–O–C_2H_5$ is called as diethyl ether and is simple ether.

b) Ethers are known as mixed or unsymmetrical if the two groups attached to the oxygen atom are different.
   Example: $C_2H_5–O–CH_3$ is called ethyl methyl ether and is mixed ether.

Nomenclature:

Common names of ethers:

The names of alkyl/aryl groups are written as separate words in alphabetical order. Then the word ether is added at the end.

In case of simple ethers, the prefix “di” is attached before the name of the alkyl group.

Example:

$C_2H_5–O–C_2H_5$ ——— Diethyl ether

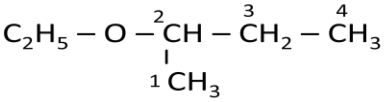
$C_6H_5–O–C_6H_5$ ——— Diphenyl ether

IUPAC Nomenclature:

According to IUPAC nomenclature ether are regarded as hydrocarbon derivative. In these compounds a hydrogen atom of an alkane is replaced by an alkoxy group, –OR; the large group (R) is chosen as the parent hydrocarbon. Ethers are named as alkoxy alkenes.

Examples:

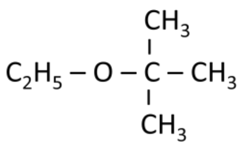
$CH_3 - O - C_2H_5$ Methoxy ethane



$$C_2H_5 - O - \underset{{}^{1}CH_3}{\underset{|}{\overset{2}{C}H}} - \overset{3}{C}H_2 - \overset{4}{C}H_3$$

2- Ethoxy butane

The numbering of parent hydrocarbon chain in ether is done so that the carbon atom linked to the O– atom gets the lowest number.

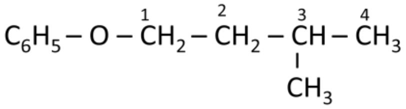


$$C_2H_5-O-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}-CH_3$$

2-ethoxy, -2-methyl propane

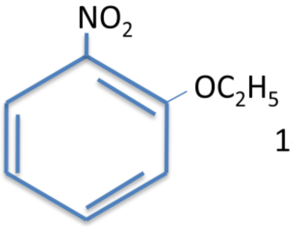
$$CH_3-O-\overset{1}{C}H_2-\overset{2}{C}H_2-O-CH_3$$

1, 2-dimethoxy ethane



$$C_6H_5-O-\overset{1}{C}H_2-\overset{2}{C}H_2-\underset{\displaystyle CH_3}{\underset{|}{\overset{3}{C}H}}-\overset{4}{C}H_3$$

3-methyl butoxy benzene



1-nitro-2-ethoxy benzene

Ethers show functional isomerism with alcohols.

CH_3OCH_3 & CH_3CH_2OH

(b) Ethers with at least four carbon atoms show metamerism due to different alkyl gps attached on bivalent O atom.

CH_3-O-CH_2-CH_2-CH_3 : CH_3-O-$CH(CH_3)_2$ and CH_3-CH_2-O -CH_2-CH_3

Structure:

In CH_3OCH_3, the central oxygen atom is sp^3 hybridized with two completely filled sp^3 orbitals having lone pair of electrons and two half filled sp^3 hybridized orbitals. Also carbon atoms are sp^3 hybridized and both the half filled sp^3 orbitals of O atom from strong s (C-O) bonds with half filled sp^3 orbitals of two adjacent carbon atoms of alkyl groups.

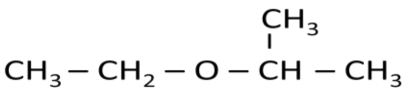
The C-O-C bond angle is about 110°C which is quite closer to 109° 28' of sp^3 hybridized nature, in spite of the fact that lone pair of electrons must result in contraction in bond angles. This is because of the fact that presence of alkyl groups on O atom counterbalances the repulsion between the lone pair - bond pair electrons and leads to the bond angle nearer to 109° 28'.

SAQs:

1. Which of the following is simple ether?
   - a. Methoxy n-propane
   - b. Methoxy ethane
   - c. Ethoxy ethane
   - d. Ethyl methyl ether

Solution: c)

2. The IUPAC name of the compound



$$CH_3-CH_2-O-\overset{\overset{\large CH_3}{|}}{C}H-CH_3$$

is

   - a. Ethoxy propane
   - b. Propoxy ethane
   - c. 2-Ethoxy propane
   - d. 2 -Propoxy ethane

Solution: c)

3. At room temperature diethyl ether is a _____
   - a. Sweet smelling substance
   - b. Volatile liquid
   - c. Water soluble liquid
   - d. All the above.

Solution: d)

1. Which of the following is an anaesthetic?
   - a. Ether
   - b. Ethyl chloride
   - c. Trichloro methane
   - d. All are correct

Solution: d)