ORGANIC CHEMISTRY –II

2. ALCOHOLS ETHERS AND PHENOLS

ALCOHOLS : Alcohols are the organic compounds with – OH group as the functional group. They are monoalkyl derivatives of water.

- Based on the number of OH groups alcohols are classified as

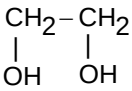
1) Monohydric 2) Dihydric 3) Trihydric 4) Polyhydric

Monohydric alcohols → one – OH group

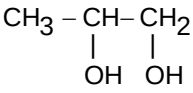
Eg: $CH_3 – OH$, $C_2H_5 – OH$

Dihydric alcohols → two – OH groups

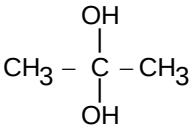
(glycols)


→ ethylene glycol

$CH_2 – CH(OH)_2$ → ethyledene glycol


→ propylene glycol

$CH_3– CH_2 – CH (OH)_2$ → n propyledene glycol

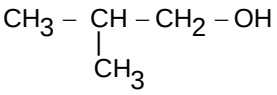

→ isopropyledene glycol

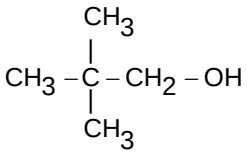
- Based on the carbon to which OH group is attached alcohols are of 3 types.

1) primary alcohols 2) Secondary alcohols of 3) Tertiary alcohols

Primary alcohols:

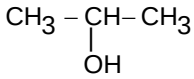
$CH_3 – CH_2 – OH$ $CH_3 – CH_2 – CH_2 – OH$

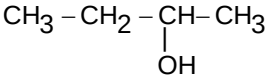




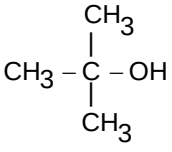
(Ethyl alcohol) (Propylalcohol) (Iso butyl alcohol) (neo-pentyl alcohol)

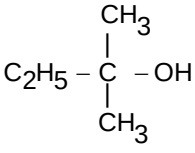
Secondary alcohols :





Tertiary alcohols :





(Isopropyl alcohol) (sec butylalcohol) (tertiary butyl alcohol) (tertiary amyl alcohol)

- **Isomerism in alcohols :**

They exhibit chain, position, functional isomerism.

For saturated monohydric alcohols → $C_nH_{2n+2}O$ (or) $C_n H_{2n+1}OH$

$C_2H_6O \rightarrow$ functional isomers are

$H_3C – CH_2 – OH$ (ethyl alcohol)

$H_3C – O – CH_3$ (dimethyl ether)

$C_2H_6O_2 \rightarrow$ positional isomers are

$CH_3 – CH(OH)_2$ (ethyledene glycol)

$CH_2(OH) – CH_2(OH)$ (ethyleneglycol)

$C_3H_8O \rightarrow$ $CH_3 – CH_2 – CH_2 – OH$ (n – propyl alcohol)

$CH_3 – CH(OH) – CH_3$ (isopropyl alcohol)

$CH_3 – O - C_2H_5$ (methyl ethyl ether)

$C_4H_{10}O \rightarrow$ a) $CH_3 – CH_2 – CH_2 – CH_2 – OH$ (n – butyl alcohol)

b) $CH_3 – CH_2 – CH(OH) – CH_3$ (sec butyl alcohol)

c) $CH_3 – CH(CH_3) – CH_2 – OH$ (isobutyl alcohol)

$CH_3 – CH_2 – O – CH_2 – CH_3$ (diethyl ether)

$CH_3 – O – CH_2 – CH_2 – CH_3$ (methyl propyl ether)

d) $CH_3 – C(CH_3)_2 – OH$ (tertiary butyl alcohol)

$CH_3 – O – CH(CH_3) – CH_3$ (isopropyl methyl ether)

a, b → position ; a, c → chain

a, d→position and chain b, c → position and chain

b, d → chain c, d → position

- If tetrahedral carbon is bonded to four different atoms or different groups of atoms it is called asymmetric carbon.
- Organic compound containing one or more asymmetric carbons will exhibit optical isomerism.
- Certain alcohols having asymmetric carbon will exhibit optical isomerism.

$CH_3 – OH$

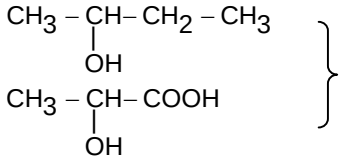
$CH_3 – CH_2 – OH$

$CH_3 – CH_2 – CH_2 –$

$CH_3 – CH(CH_3) – OH$

} Doesn't show optical isomerism

OH



Exhibits optical isomerism

- **Ethyl alcohol :**
  Grain alcohol or spirit of wines (C_2H_5OH)
- **Preparation :**
  By the hydrolysis of ethyl halide : (industrial method)
  Ethyl halide on hydrolysis with aqueous sodium hydroxide or potassium hydroxide gives ethyl alcohol.

$$C_2H_5X + NaOH \rightarrow CH_3CH_2OH + NaX \ ; \ X = Cl, Br, I$$

  In the place of NaOH or KOH, AgOH can be used.
- **By the hydrolysis of ester :** Hydrolysis of ethyl acetate with aqueous alkali gives ethyl alcohol.

$$CH_3COOC_2H_5 + KOH_{(aq)} \rightarrow CH_3COOK + C_2H_5OH$$

- **By the hydration of Ethylene :(**industrial method) Ethylene on reaction with conc. sulphuric acid at 75–80°C gives ethylalcohol.

$$CH_2 = CH_2 + H - HSO_4 \rightarrow CH_3 - CH_2 - HSO_4$$

$$CH_3 - CH_2 - HSO_4 + H - OH \rightarrow CH_3 - CH_2 - OH + H_2SO_4$$

- **By the reduction of Acetaldehdye (CH_3–CHO) :** Acetaldehyde on reduction with Hydrogen and Nickel or Lithium aluminum hydride gives ethyl alcohol.

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

- **From Grignard reagent and formaldehyde:** Methyl magnesium halide on reaction with formaldehyde followed by hydrolysis gives ethyl alcohol.

$$\overset{\delta+}{H_2}C = \overset{\delta-}{O} + \overset{\delta-}{CH_3} - \overset{\delta+}{MgBr} \rightarrow CH_3 - CH_2 - OMgBr \xrightarrow{H-OH} CH_3 - CH_2OH + Mg(OH)Br$$

  Formaldehyde+any grignard reagent→ primary alcohol
- **Fermentation of molasses :**
  The breaking of complex organic molecule into smaller ones in the presence of enzymes is called fermentation. In any fermentation process the by product is CO_2. Molasses is a dark, brown coloured liquor left after the crystallization of sugar. Molasses still contain about 40% sugar. It is diluted to 10% sugar and yeast cells are added. P^H is maintained at 4 by adding dilute H_2SO_4. Temperature is maintained between 30^0C and 40^0C. Ammonium Sulphate or Ammonium phosphate is added to yeast cells which acts as food for yeast.
- Yeast cells produce invertase and zymase enzyme
- In presence of invertase enzyme sucrose (sugar) is hydrolysed to glucose and fructose

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Invertase}} \underset{(\text{Glucose})}{C_6H_{12}O_6} + \underset{(\text{Fructose})}{C_6H_{12}O_6}$$

- Glucose or fructose is then converted into alcohol in presence of zymase enzyme.

$$C_6H_{12}O_6 \xrightarrow{\text{zymase}} 2C_2H_5OH + 2CO_2$$

  The alcohol obtained above is 6 – 10% pure which is called as wash or wort.
- Wash is further concentrated to the 95.6% by fractional distillation. 95.6% alcohol is called rectified spirit. 95.6 % alcohol and 4.4% water will form constant boiling mixture [azeotropic mixture] therefore it can't be further concentrated to 100% alcohol by normal distillation methods.
  Quicklime (CaO) or magnesium ethoxide [$Mg(OC_2H_5)_2$] can be used to convert 95.6% into 100%

alcohol which is called absolute alcohol or absolute spirit.

- Anhydrous $CaCl_2$ is laboratory desiccant but $CaCl_2$ should not used for drying alcohol as if forms an addition compound with it. That addition compound is $CaCl_2.3C_2H_5OH$.
- **Fermentation of starch :**

  Starch is present in wheat, maize, potato etc. The source of starch is crushed and treated with steam and the product is called Mash.

  The product is added to germinated Barley seeds which is called malt.
- Malt contains diastase enzyme. In presence of diastase enzyme starch is hydrolyzed to give maltose

$$\underset{(\text{starch})}{2(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{\text{diastase}} \underset{(\text{maltose})}{nC_{12}H_{22}O_{11}}$$

Yeast cells are added to produce maltase and zymase enzymes.

In presence of maltase, maltose, converts into glucose which then converts into ethyl alcohol in the presence of zymase enzyme.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{maltose}} \underset{(\text{glucose})}{2C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow{\text{zymase}} 2C_2H_5 - OH + 2CO_2 \uparrow$$

The ethyl alcohol obtained is 6 – 10%. It is further concentrated to 100% alcohol as listed above.

Physical properties :

1) It is a colourless liquid with characteristic smell.
2) It has burning taste
3) It forms hydrogen bonds with water and also with it itself therefore it exists as associated liquid, soluble in water and boiling point is very high (78.1 ^{0}C).
4) It's dissolution in H_2O is exothermic and there is slight contraction in volume.
5) Non ideal solution.

- **Chemical reactions:**
- The reactions of alcohols involve either cleavage of O – H bond or C – OH bond.
- Reactivity of alcohols involved in cleavage of O – H

$$R - O - \overset{\vdots}{H}$$

Primary alcohol>secondary alcohol>tertiary alcohol

- Reactivity of alcohols which involve cleavage of C–OH

$$R - \overset{\vdots}{O} - H$$

Primary alcohol<secondary alcohol < tertiary alcohol

1) with Na or K : Ethyl alcohol on reaction with Na or K liberates hydrogen gas.

$$2C_2H_5OH + 2Na \rightarrow 2C_2H_5ONa + H_2$$

based on the above reaction we can say alcohols are slightly acidic. But alcohol is less acidic than even water but more acidic than acetylene.

$$H_2O > C_2H_5 - OH > CH \equiv CH > CH_2 = CH_2 > CH_3 - CH_3$$

primary alcohol>secondary alcohol>tertiary alcohol

2) with grignard reagent : Ethyl alcohol on reaction with Grignard reagent forms alkane.

$$C_2H_5OH + CH_3 - MgBr \rightarrow CH_4 + C_2H_5OMgBr$$

3) with acetic acid (esterification) : Ethyl alcohol on reaction with carboxylic acid gives ester. This reaction is catalysed by mineral acid.

$$C_2H_5OH + CH_3COOH \underset{}{\overset{H_3O^+}{\rightleftharpoons}} CH_3COOC_2H_5 + H - OH$$

This reaction is called Fischer esterification

4) **With acetyl chloride and acetic anhydride :** With acetyl chloride and acetic anhydride also ethyl alcohol gives ester.

$$C_2H_5OH + CH_3COCl \rightarrow CH_3COOC_2H_5 + HCl$$

$$C_2H_5OH + (CH_3CO)_2O \rightarrow CH_3COOH + CH_3COOC_2H_5$$

5) **With hydrogen halides :** Ethyl alcohol on reaction with hydrogen halides in the presence of anhydrous $ZnCl_2$ gives ethyl halide.

$$C_2H_5OH + HCl \xrightarrow[ZnCl_2]{\text{anhydrous}} C_2H_5 - Cl + H_2O$$

$$C_2H_5OH + HBr \rightarrow C_2H_5Br + H_2O$$

6) **With phosphorous halides :** Ethyl alcohol on reaction with phosphorus halides gives ethyl halides.

$$3\,C_2H_5OH + PCl_3 \rightarrow 3C_2H_5Cl + H_3PO_3$$

$$3\,C_2H_5OH + PBr_3 \longrightarrow 3C_2H_5Br + H_3PO_3$$

$$3\,C_2H_5OH + PI_3 \longrightarrow 3C_2H_5I + H_3PO_3$$

$$C_2H_5 - OH + PCl_5 \rightarrow C_2H_5Cl + POCl_3 + HCl$$

8) **With $SOCl_2$:** Thionyl chloride reacts with ethyl alcohol to give ethyl chloride.

$$C_2H_5OH + SOCl_2 \rightarrow C_2H_5Cl + SO_2 + HCl$$

9) **Dehydration :** Ethyl alcohol on dehydration gives different products at different temperatures.

$$C_2H_5OH \xrightarrow[110^0C]{\text{con.}H_2SO_4} C_2H_5 - HSO_4 + H_2O$$

(ethylhydrogen sulphate)

$$2C_2H_5OH \xrightarrow[140^0C]{\text{conc.}H_2SO_4} C_2H_5 - O - C_2H_5 + H_2O$$

(diethyl ether)

$$C_2H_5OH \xrightarrow[170^0C]{\text{conc.}H_2SO_4} C_2H_4 + H_2O$$

(ethylene)

- In presence of excess of H_2SO_4 product is C_2H_4 with excess of alcohol the product is diethyl ether. Instead of conc. H_2SO_4, Alumina can be used.

$$2C_2H_5OH \xrightarrow[250^0C]{\text{conc.}Al_2O_3} C_2H_5 - O - C_2H_5 + H_2O$$

$$C_2H_5OH \xrightarrow[350^0C]{\text{conc.}Al_2O_3} C_2H_4 + H_2O$$

10) **Reduction :** Ethyl alcohl is reduced to ethane by HI / red P.

$$C_2H_5OH + 2HI \xrightarrow{\text{red P}} C_2H_6 + I_2 + H_2O$$

11) **Dehydrogenation (oxidation):**

a) Ethyl alcohol in the presence of copper at 300°C gives acetaldehyde.

$$CH_3 - CH_2 - OH \xrightarrow{Cu,300^0C} CH_3 - CHO + H_2$$

(acetaldehyde)

b) On oxidation with acidified potassium permanganate ($KMnO_4$) or potassium dichromate ($K_2Cr_2O_7$)
ethyl alcohol forms acetic acid.

$$CH_3 - CH_2 - OH + [O] \xrightarrow[K_2Cr_2O_7]{KMnO_4 \text{ or}} \underset{\text{pri aldehyde}}{CH_3 - CHO} \xrightarrow{[O]} CH_3 - COOH$$

12) with Chlorine : Chlorine oxidises ethyl alcohol to chloral.

$$CH_3 - CH_2 - OH + 3Cl_2 \rightarrow \underset{\text{chloral}}{CCl_3 - CHO} + 3HCl$$

13) **with bleaching powder** : Ethyl alcohol and bleaching powder mixture on distillation gives chloroform.

$$C_2H_5OH + CaOCl_2 + H_2O \rightarrow CHCl_3 + (HCOO)_2Ca + HCl$$

14) **Iodoform reaction** : Yellows crystals of CHI_3 will be formed when ethylalcohol is treated with I_2 solution and potassium hydroxide.

$$C_2H_5OH + 4I_2 + 6KOH \rightarrow CHI_3 \downarrow + 5KI + HCOOK + 5H_2O$$

- Alcohols containing $CH_3 - \underset{OH}{\underset{|}{CH}} -$ or Aldehydes or ketones containing $CH_3 - \underset{O}{\overset{\|}{C}} -$ will react with iodine and alkali to give iodoform which is yellow crystalline solid.

ETHERS : [$R - O - R^1 \rightarrow$alkoxy alkanes]

- ether is the dialkyl derivative of water $\begin{bmatrix} H-O-H \\ R-O-R \end{bmatrix}$
- ether is the anhydride of alcohol.

Naming of ethers	***IUPAC***	**Common name**
$CH_3 - O - CH_3$	Methoxy methane	Dimethyl ether
$CH_3 - O - C_2H_5$	methoxy ethane	ethyl methyl ether
$C_2H_5 - O - C_2H_5$	Ethoxy ethane	Diethyl ether
$CH_3 - O - CH_2 - CH_2 - CH_3$	1 – methoxy propane	Methyl – n – propy ether
$CH_3 - O - \underset{CH_3}{\overset{CH_3}{\diagup\diagdown CH}}$	2 – methoxy propane	Methyl isopropyl ether
$C_2H_5 - O - \underset{CH_3}{\underset{\|}{CH}} - CH_2 - CH_3$	2 – ethoxy butane	Ethyl secondary butyl ether

- Ethers are classified into two types based on the nature of alkyl groups.
  1) Symmetrical ethers (or) simple ethers are
     $R = R'$ $R - O - R$
     $CH_3 - O - CH_3$
     $C_2H_5 - O - C_2H_5$
  2) unsymmetrical ethers (or) mixed ethers :
     $R \neq R'$ $R - O - R'$
     $CH_3 - O - C_2H_5$
     $C_2H_5 - O - CH_2 - CH_2 - CH_3$
- **Isomerism shown by ethers:**
  Ethers will exhibit metamerism, functional isomerism and chain isomerism.

$CH_3 - O - CH_3$
$C_2H_5 - OH$ } Functional isomers

$C_2H_5 - O - C_2H_5$
$CH_3 - O - CH_2 - CH_2 - CH_3$
$CH_3 - O - \underset{\underset{CH_3}{|}}{CH} - CH_3$ } Metamers

- General molecular formula of ether $\rightarrow C_nH_{2n+2}O$

Diethyl ether (sulphuric ether) : Preparation :

1) Dehydration :

a) By the dehydration of ethyl alcohol in the presence of conc. H_2SO_4 at 140^0C.

$$2C_2H_5OH \xrightarrow[140^0C]{conc.H_2SO_4} C_2H_5 - O - C_2H_5 + H_2O$$

b) By the dehydration of ethyl alcohol in presence of anhydrous alumina at 250^0C.

$$2C_2H_5OH \xrightarrow[250^0C]{Al_2O_3} C_2H_5 - O - C_2H_5 + H_2O$$

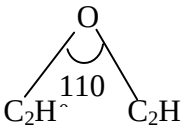
2) From ethyl chloride : By the reaction of ethyl chloride with dry silver oxide.

$$2C_2H_5Cl + Ag_2O \rightarrow C_2H_5 - O - C_2H_5 + 2AgCl$$

3) Williamson's synthesis : Alkyl halides react with sodium alkoxides to produce ethers. This method is suitable for the preparation of both simple and mixed ethers.

$$C_2H_5Cl + NaOC_2H_5 \rightarrow C_2H_5 - O - C_2H_5 + NaCl$$

- **Physical properties :**
  1) It is a colourless liquid with pleasant smell.
  2) It does not form hydrogen bonds and will not exist as associated liquid. Therefore it is highly volatile, low boiling point 307.5^0C and it is slightly miscible with water.
  3) It is inflammable.
  4) It's vapours cause unconsciousness.
  5) It forms explosive mixture with air [ether $+O_2 \rightarrow$ etherperoxide]



- In ether 'O' is sp^3 hybridised, shape is angular.
- Bond angle is 110^0 due to the repulsions between bond pair and because of bulky nature of alkyl groups.
- It is slightly polar and its $\mu \neq 0$.

Chemical reactions:

Ethers are chemically inert because 'O' is flanked in between two bulky alkyl groups.

- Therefore ethers are not easily oxidisable and they will not decolourise permanganate or dichromate.

1) α - halogenation : The α - hydrogens present in ether are substituted by halogen atoms.

$$CH_3 - CH_2 - O - CH_2 - CH_3 + 2Cl_2 \xrightarrow{dark} CH_3 - \underset{\underset{Cl}{|}}{\overset{\alpha}{C}}H - O - \underset{\underset{Cl}{|}}{\overset{\alpha^1}{C}}H - CH_3 + 2HCl$$ (α, α^1 –dichloro diethyl ether)

$$CH_3-CH_2-O-CH_2-CH_3 + 2Cl_2 \xrightarrow{\text{sunlight}} CH_3-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}-O-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}-CH_3$$ ($\alpha\alpha$, $\alpha^1\alpha^1$ –tetrachloro diethyl ether)

In dark the two α - hydrogens are substituted by two chlorines on reaction with chlorine.

2) with air : Diethyl ether when exposed to air forms a mixture due to the formation of diethyl peroxide.

$$C_2H_5-O-C_2H_5 + \frac{1}{2}O_2 \rightarrow C_2H_5-\underset{\text{(explosive)}}{O-O}-C_2H_5 \text{ (or) } C_2H_5-\underset{\underset{O}{\downarrow}}{O}-C_2H_5$$ It is

freed from peroxide by treating with ferrous sulphate.

3) with dil.H_2SO_4 : Diethyl ether is hydrolysed to ethyl alcohol in presence of sulphuric acid

$$C_2H_5-O-C_2H_5 + H-OH \xrightarrow{\text{dil.}H_2SO_4} 2C_2H_5OH$$

4) with cold and conc. mineral acids.

Ether reacts with cold and conc. mineral acids like HCl, H_2SO_4, HNO_3 etc. to form oxonium salts. Formation of these oxonium salts with the mineral acids is the indication of its basic nature.

$$(C_2H_5)_2\ddot{O} + HCl \rightarrow (C_2H_5)_2OH^+Cl^-$$ (diethyl oxonium chloride)

$$(C_2H_5)_2\ddot{O} + H_2SO_4 \rightarrow \left[(C_2H_5)_2OH\right]_2^+SO_4^{-2}$$

(diethyl oxonium sulphate)

5) with HI: With cold HI, one C – O bond is cleaved and the products are ethyl alcohol and ethyl iodide. $C_2H_5-O-C_2H_5 + HI \rightarrow C_2H_5-OH + C_2H_5-I$

- With hot and excess of HI , both C – O bonds are cleaved and two moles of C_2H_5 – I are formed
  $C_2H_5-O-C_2H_5 + 2HI \rightarrow 2C_2H_5-I + H_2O$
- In case of mixed ethers I^- of HI is added to smaller alkyl group.
  $CH_3-O-C_2H_5 + HI \rightarrow CH_3-I + C_2H_5-OH$
- Ziesel's method is useful to detect and estimate the number of methoxy groups present in the given ether.
- The reaction of ether with HI forms the basis for Ziesel's method.

6) with PCl_5 : with PCl_5 diethyl ether gives ethylchloride

$$C_2H_5-O-C_2H_5 + PCl_5 \xrightarrow{\Delta} 2C_2H_5Cl + POCl_3$$

7) Dehydation : on dehydration in the presence of alumina diethyl ether gives ethylene.

$$C_2H_5-O-C_2H_5 \xrightarrow[360^0C]{\text{an.}Al_2CO_3} 2C_2H_4 + H_2O$$

8) with CO: In the presence of BF_3 at 150°C and 500 atm pressure diethyl ether reacts with CO and forms ethyl propionate (Ester)

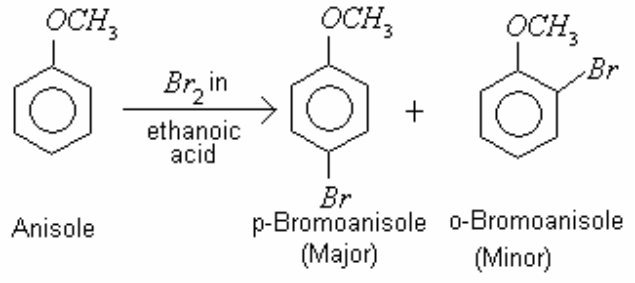
$$C_2H_5-O-C_2H_5 + CO \xrightarrow[500\text{ atm}]{BF_3,150^0C} C_2H_5-COOC_2H_5$$ (ethyl propionate)

9) Reduction : Diethyl ether reduces to ethane on reduction with Na/liq.NH_3.

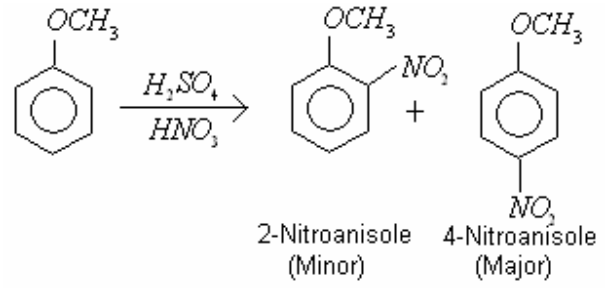
$$C_2H_5-O-C_2H_5 + 2H \xrightarrow{Na/liq.NH_3} C_2H_6 + C_2H_5OH$$

ELECTROPHILIC SUBSTITUTION.

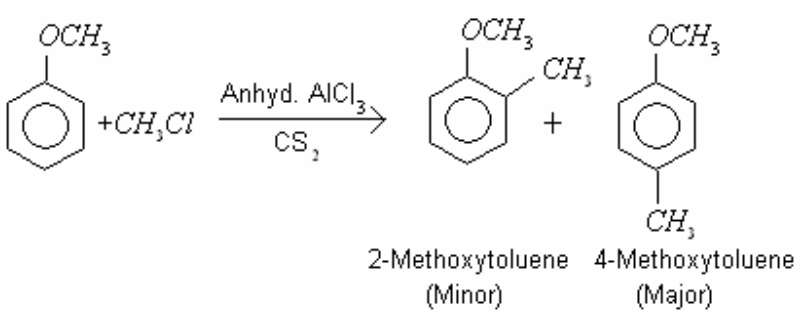
1) **HALOGENATION**:

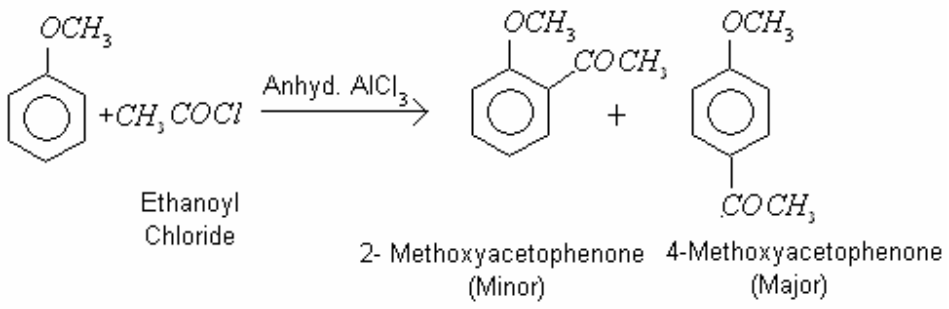


2) **NITRATION**:



3) **FRIEDEL-CRAFTS REACTION:**





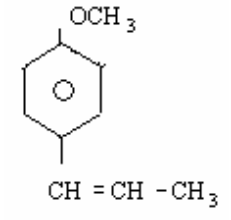
USES : ETHER IS USED IN/AS

1. a solvent for oils, fats, waxes, plastics etc.
2. the extraction of organic compounds from aqueous solutions.
3. an inert medium for various reactions (ex.Wurtz reaction) and preparation of RMgX
4. an anaesthesia in surgery without causing any damage to heart or lungs. (Recently, HALOTHANE is widely used for this purpose since it is harmless and quick in action $CF_3CHClBr$.) (IUPAC name : 2-Bromo-2- chloro-1,1,1-trifluroethane)
5. NATALITE(mixture of Alcohol and Ether), a substitute for petrol
6. Refrigerant along with dry ice (solid CO_2) which produces a temperature around -110°C

i) Enthrane $(CHFCl-CF_2-O-CHF_2)$ and isoflurane $(CF_3CHCl-O-CHF_2)$ are used as anesthetics in place of diethyl ether as the later one has slow effect.

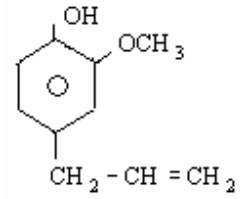
ii) Substituted anisols are used as flavourings and in perfumes due to their pleasant odour.

Eg :



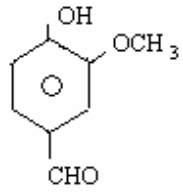
1.ANITHOLE

is a constituent of anise seed.



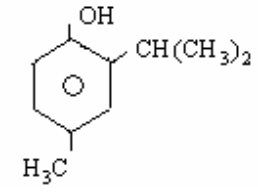
2.EQUGINOL

is present in cloves.



3.VANILLIN

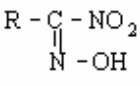
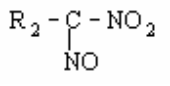
is present in oil of vanilla been



4.THYMOL

is present in thyme and mint are used as flavourings and in perfumes.

Identification of primary , secondary , tertiary alcohols

Test	Primary alcohol	Secondary alcohol	Tertiary alcohol
1) **Lucas test :** The alcohol is treated with Lucas reagent	No reaction (No turbidity)	Reacts with in 5 minutes to give turbidity	Reacts within 30 seconds to give turbidity
2) Victor Meyer's : test : The alcohol is treated with red phosphorous and and the product is treated with and then with nitrous acid $(NaNO_2 + H_2SO_4)$ and finally made alkaline	Red colouration is observed RCH_2OH $\downarrow I_2 / red \quad P$ RCH_2I $\downarrow AgNO_2$ RCH_2NO_2 $\downarrow HNO_2$  (Nitrolic acid) $\downarrow alkali$ red colouration	Blue colouration is observed R_2CHOH $\downarrow I_2 + red \quad P$ R_2CHI $\downarrow AgNO_2$ R_2CHNO_2 $\downarrow HNO_2$  (pseudo nitrol) $\downarrow$ alkali blue colouration	No colour is produced R_3COH $\downarrow I_2 + red \quad P$ R_3CI $\downarrow AgNO_2$ R_3CNO_2 $\downarrow HNO_2 \quad \& \quad alkali$ No reaction.
3) Catalytic dehydrogenation with copper at 300^0c	Aldehyde, $\mathbf{H_2}$ is produced $\underset{\downarrow}{RCH_2OH}$ $RCHO + H_2$	Ketone, H_2 is produced $R_2COH \rightarrow$ $R_2CO + H_2$	Dehydration takes place giving alkene and $\mathbf{H_2O}$ $(CH_3)_3COH \rightarrow$ $CH_3 - \underset{1}{C}(CH_3) = CH_2 + H_2O$
4) Oxidation with acidified $KMnO_4$	$RCH_2OH \xrightarrow{(O)}$ $RCHO$ $\downarrow (O)$ $RCOOH$ same number of carbon atoms in alcohol, aldehyde and acid	$R_2CHOH \xrightarrow{(O)} R_3C-OH \xrightarrow{(O)}$ R_2CO $\downarrow (O)$ Mixture of alcohol and ketone contain same no. of carbons but acids contains lesser no. of carbons	Ketone + acid $\xrightarrow{(O)}$ Mixture of acids ketone contains lesser no. of carbons than . alcohol. Acid contain still lesser no. of carbons than that of ketone.

MECHANISM OF DEHYDRATION :

It takes place in three steps :

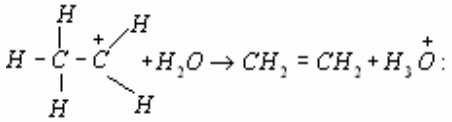
i) $CH_3-CH_3-OH+H_2SO_4 \Leftrightarrow$

$$CH_3-CH_2-{}^{+}\overset{\overset{\cdot\cdot}{}}{\underset{H}{O}}-H+\overline{OSO_3H}$$

ii) Formation of carbonation. It is the slowest step or rate determining step.

$$CH_3-CH_2-{}^{+}\overset{\overset{\cdot\cdot}{}}{\underset{H}{O}}-H \Leftrightarrow CH_3-\overset{+}{C}H_2+H_2\overset{\cdot\cdot}{O}:$$

iii) Elimination of proton to get alkene



Since the rate determining step is the formation of carbocation, the rate of dehydration is directly proportional to the formation of carbocation. Since the stability of carbocation is $3^0>2^0>1^0$, the order of dehydration of alcohols is

$(CH_3)_3COH>(CH_3)_2CHOH>CH_3-CH_2OH$

Dehydration of alcohol requires 95% H_2SO_4 at $H_2SO_4 170^0C$, 2^0 alcohol requires 75% H_2SO_4 at 100^0, where 3^0 as alcohol requires 5% H_2SO_4 at 50^0C .

- The dehydration of 1^o alcohol goes by E_2 mech nism, but that of 2^o and 3^o alcohols go by E_1 mechanism.

  When more than one product is formed, the major product is according to **Zaitsev's** rule. It states that hydrogen is removed from $\beta-carbon$ that is bonded to the least number of hydrogen atoms.(**β-elimination)**

  Eg. Dehydration of 2-butanol predominantly gives 2-butene.

  $CH_3-CH_2-CHOH-CH_3 \xrightarrow[H_2SO_4]{Conc}$

  $CH_3-CH=CH-CH_3+CH_3-CH_2-CH=CH_2$

  2-butene(major) 1-butene (minor)

- **FORMATION OF ADDTION COMPOUNDS :** Ethyl alcohol reacts with anhydrous metal salts to form addition compounds (that is alcohol of crystallisation)

  a) $C_2H_5OH.3CaCl_2, C_2H_5OH.6MgCl_2, C_2H_5OH.3CuSO_4$

USES OF SOME IMPROTANT COMPOUNDS

(Methanol and ethanol)

METHANOL

1. Methanol a colourless liquid with b.pt 67^0C .is used as solvent, paints, varnishes, shellac etc.,
2. Used in the manfacture of HCHO, perfumes and dyes.
3. Used in the preparation of methylated spirt, a mixture of recatified spirit (95.6% ethyl alcohol + 4.4%water) and methyl alcohol making ethyl alcohol unfit for drinking .
4. Two types of methylated spirits:

   a) mineralised spirit = 90% rectified spirit + 9% methyl alcohol + 1% pyridine

b) Surgical spirit = 95% rectified spirit + 5% MeOH

5. In denaturation of ethyl alcohol copper sulphate is added to give colour and pyridine is added to make it a foul smelling liquid. Because of denaturation alcohol becomes unfit for drinking.

USES OF ETHYL ALCOHOL

1. As a solvent for pharmaceutical preparations, paints, perfumes, varnishes, gums etc.,
2. In alcoholic bevarages.
3. As reaction medium, extractant and crystallsing
4. A source for the preparation of acetaldehyde, chloral, chloroform, iodoform, acetic acid ether etc.
5. A preservative for biological specimens, an antifreeze for automobile radiotors, a fuel in spirit lamps, stoves, a petrol substitute known as power alcohol.

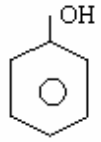
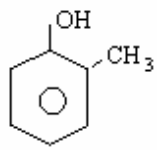
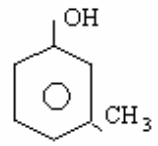
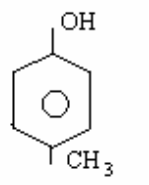
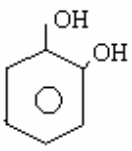
PERPARATION OF WINE

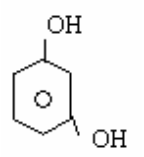
Grapes are the source of sugar and yeast.

Sugar increases in ripe grapes and yeast grows on the outer skin. On crushing the grapes, sugar and enzyme come in contact and fermentation starts in anaerobic conditions. If air is present it oxidises alcohol to acids

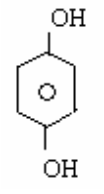
PHENOL

NAMING OF PHENOLS

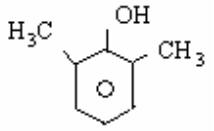
Molecule	Common name	IUPAC name
	Phenol	Phenol
	O-cresol	2-methyl phenol
	m-cresol	3-methyl phenol
	p-cresol	4-methyl phenol
	Catechol	Benzene-1,2-diol



Resorcinol Benzene-1,3-diol



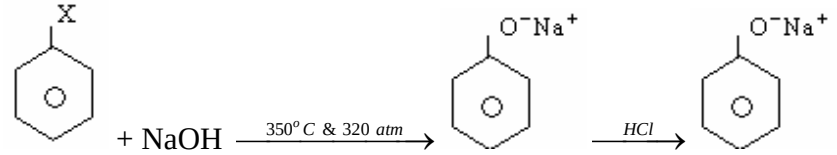
Hydroquinone (or)quinol Benzene-1,4-diol



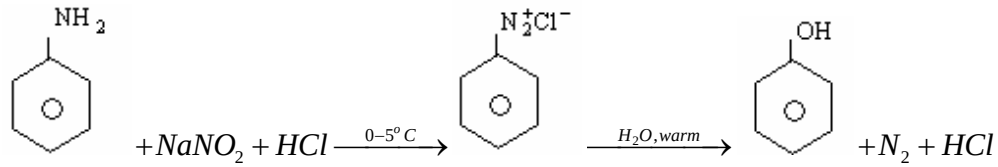
2,6-dimethyl phenol

METHODS OF PREPARATION OF PHENOL :

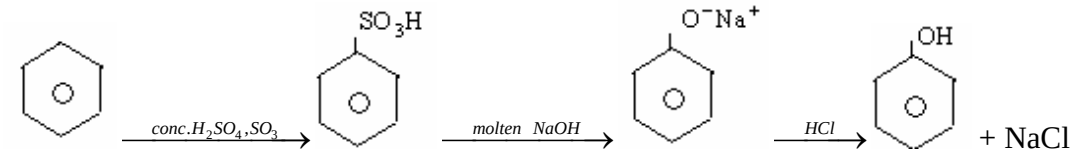
1) Phenol was first isolated from coaltar.
2) From haloarenes



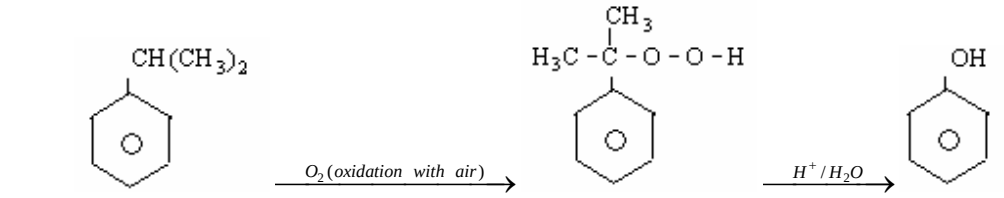
3) From diazonium salt :



4) From benzene sulphonic acid :



5) From cumene : Phenol is manufactured from cumene (isopropyl benzene)



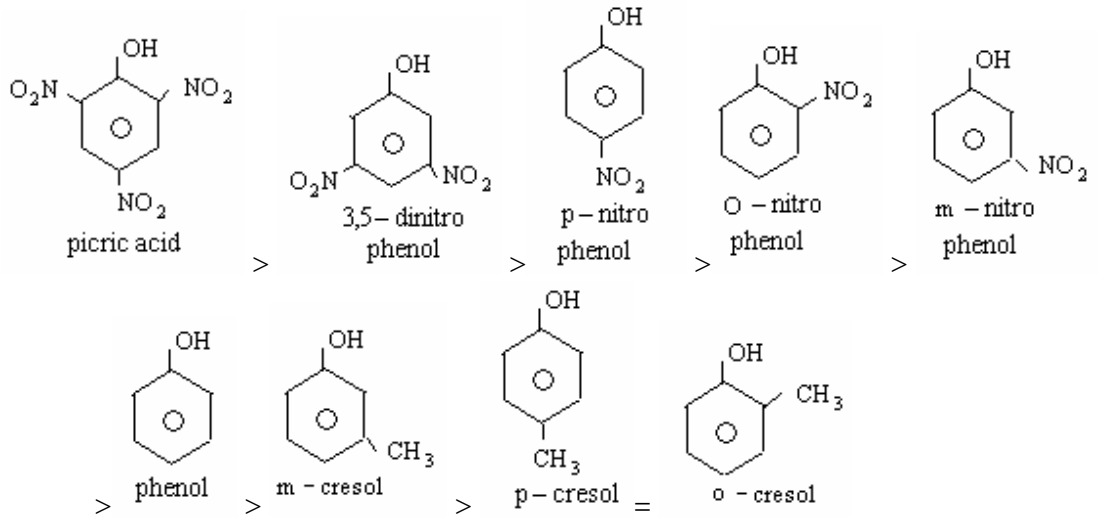
ACIDITY OF PHENOLS : The reactions of phenol with metals as well as NaOH indicate it is relatively more acidic than alcohols and also water. This is explained on the basis of the structure of phenol. The hydroxyl group in phenol is directly attached to sp^2 carbon of benzene ring. The sp^2 carbon attached to 'O' being more electronegative than sp^3 carbon of alcohols, it decreases the electron density on oxygen. Because of this oxygen develops still more electron seeking character and releases proton by taking the shared pair of electrons with it. The acidic nature of phenol can also be explained .On the basis of resonance stabilization of phonoxide ion.

Electron withdrawing groups of phenol increase the acidic nature.

Electron releasing group of phenol decrease the acidity of phenols.

Acidic strength increases with the decrease of the P^{K_a} values.

The order of the strength of phenols is as follows



PHYSICAL AND CHEMICAL PROPERTIES OF PHENOLS

PHYSICAL : 1) Phenol has higher boiling point than the arenes or haloarenes or ethers of same molecular weight. It is due to the formation of intermolecular hydrogen bond.

2) Phenols are relatively more soluble in water due to their ability to form hydrogen bonding with water.

3) As the hydrocarbon part increases in size and mass, the solubility decreases.

CHEMICAL PROPERTIES :

1) Acidic nature of phenol :

Alcohols and phenols react with active metals like Na, K, Al etc to liberate hydrogen gas.

$$2ROH + 2Na \rightarrow 2RONa + H_2$$

$$C_6H_5OH + 2Na \rightarrow 2C_6H_5ONa + H_2$$

Phenols also react with aqueous NaOH solution to produce the salt sodium phenoxide and water.

$$C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O$$

The acidic nature of alcohols is due to the polar nature of O-H group. Electron releasing groups like alkyl groups increase the electron density on oxygen and decrease the polarity of O-H bond. This decreases the acidic strength.

The order of acidic strength is

$$H_2O > RCH_2OH > R_2CHOH > R_3COH$$

Even through the electron releasing groups like $-CH_3, -C_2H_5$ etc decrease the acidic strength of phenol, Phenol does not liberate CO_2 with Na_2CO_3 or $NaHCO_3$ because phenol is weaker acidic than carbonic acid and carboxylic acids.

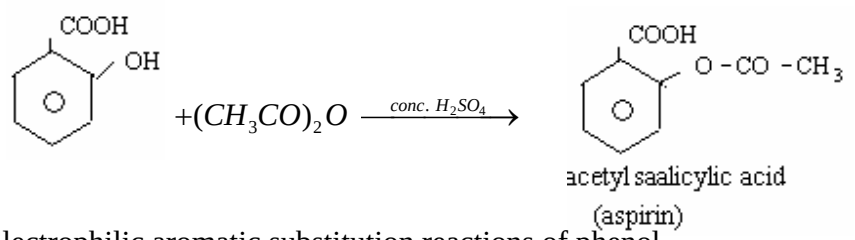
ESTERIFICATION OF PHENOL :

Phenols react with carboxylic acids and their derivatives like acid chlorides and anhydrides to form esters. This reaction (benzoylation) is called Schotten-Baumann reaction.

$$C_6H_5OH + RCOOH \rightarrow C_6H_5 - O - CO - R + H_2O$$

$$C_6H_5OH + RCOCl \xrightarrow{pyridine} C_6H_5 - O - CO - R + HCl$$

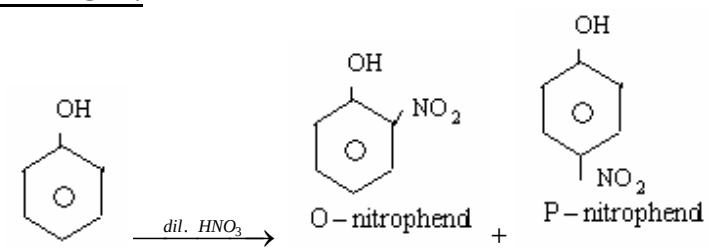
Salicylic acid on acetylation gives acetyl salicylic acid known as Aspirin.



Electrophilic aromatic substitution reactions of phenol

In phenol, -OH group is ring activating and ortho and para directing as these positions get more electron density through resonance structures.

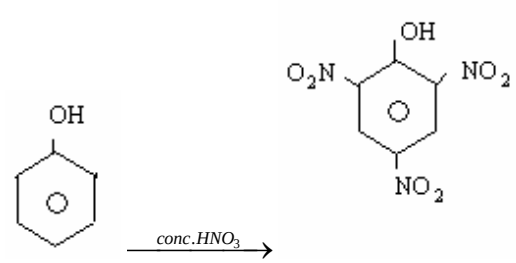
a) NITRATION :



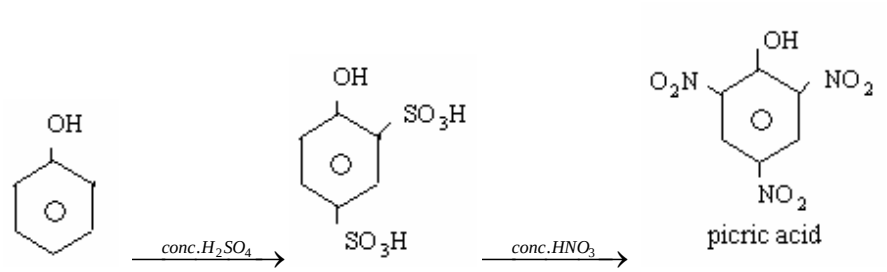
O-nitrophenol is steam volatile due to intramolecular hydrogen bond.

P-nitrophenol is less volatile due intermolecular hydrogen bond.

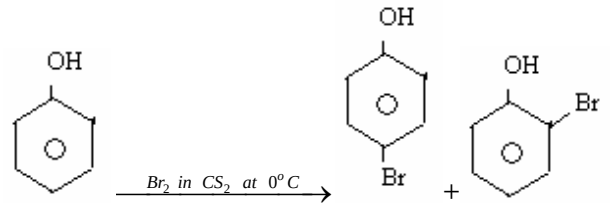
Phenol when treated with conc. HNO_3 gives 2,4,6-trinitrophenol known as picric acid



Now a days picric acid is prepared by treating phenol with conc. H_2SO_4 and then with conc. HNO_3 .

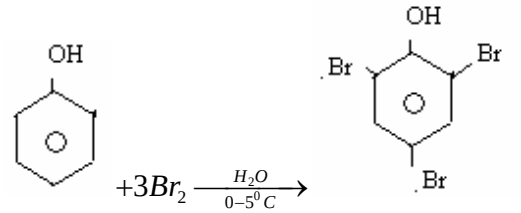


b) HALOGENATION :



Here no Lewis acids like are required because highly activating effect of -OH group polarises bromine quickly.

Phenol reacts with bromine water and gives 2,4,6-tribromo phenol (white precipitate)



c) REIMER-TIEMANN REACTION :

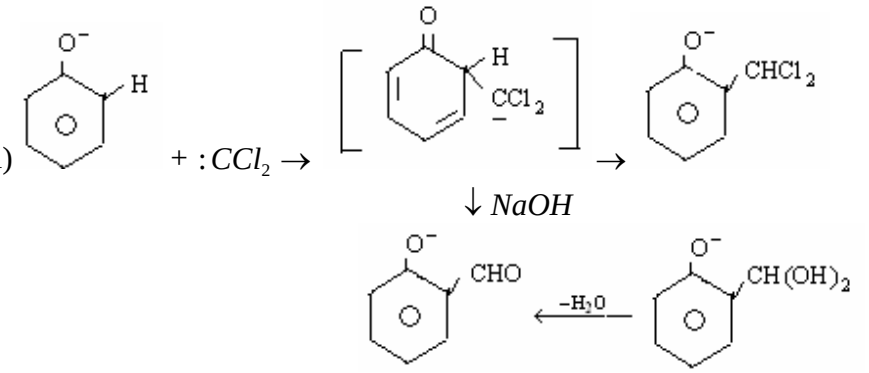
Phenol when treated with chloroform in the presence of NaOH give salicylaldehyde.

Mechanism :

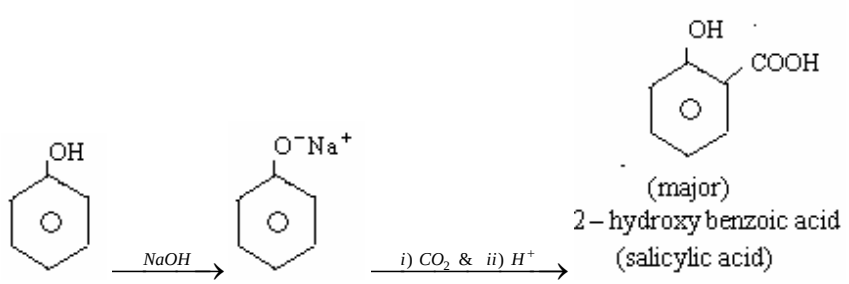
i) $CHCl_3 + OH^- \Leftrightarrow H_2O + CCl_3^- \rightarrow :CCl_2 + Cl^-$

Dichloro carbene ($:CCl_2$) is the attacking electrophile in this reaction :

ii)

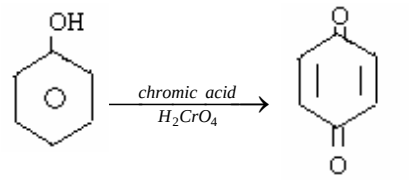


d) KOLBE'S REACTION :

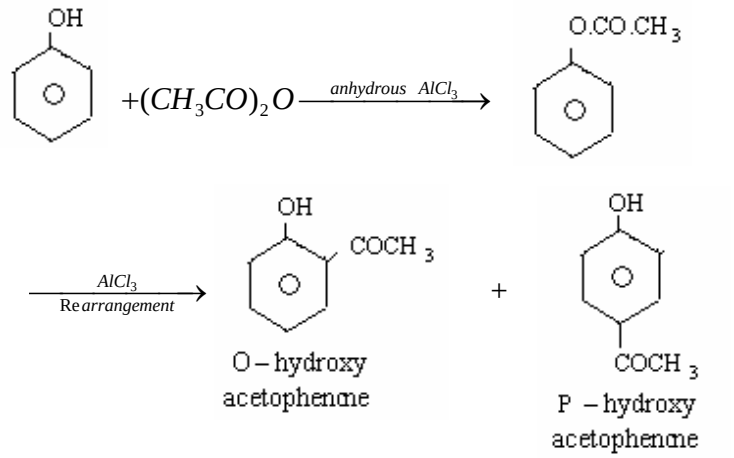


e) <u>ACTION OF ZINC DUST :</u> Phenol on heating with zinc dust produces benzene.

<u>f) OXIDATION</u> : Phenol oxidation with chromic acid $(Na_2Cr_2O_7 + H_2SO_4)$ produces benzoquinone, which is a conjugate diketone.



<u>g) FRIES REARRANGEMENT :</u>



<u>USES OF PHENOL</u> :

1) It is raw material for the manufacture of important dyes, drugs, pharmaceuticals, polymers and several other compounds.
2) It is strong antiseptic. 2,4-dichloro-3,5 dimethyl phenol is used as powerful antiseptic under the name Dettol.
3) It is used as a preservative for ink.
4) It is used in the manufacture of drugs like Aspirin, Salol etc.
5) It is used for causterising wounds caused by the bite of mad dogs.

Tests of Phenol :

i) Aqueous solution of phenol gives violet colour with a drop a $FeCl_3$.

ii) Aqueous phenol gives white precipitate with bromine water.

iii) Phenol gives blue colour with ammonia and sodium hypochlorite.