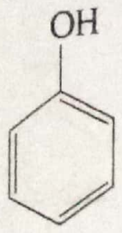
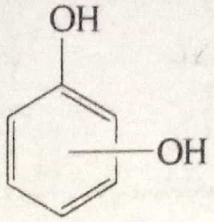
3.1 INTRODUCTION

Compounds in which one or more hydroxy groups are directly attached to a benzene ring are called phenols. The parent compound containing only one hydroxy group attached to benzene ring is called phenol. It is also known as **hydroxybenzene** or **carbolic acid**.



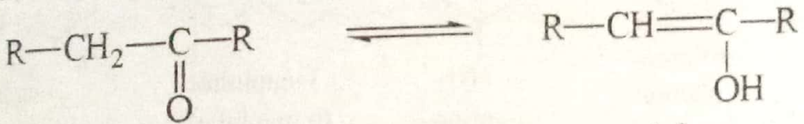
phenol



phenols

3.2 STRUCTURE AND BONDING

(i) As the name suggests, phenols may be regarded as "*enols*". Generally the enol form is unstable as compared to the keto form with respect to the carbonyl compounds.

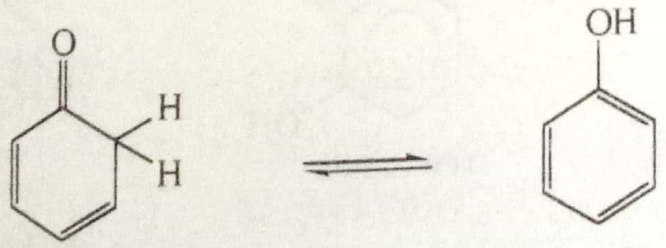


$$R{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}R \rightleftharpoons R{-}CH{=}\underset{\underset{OH}{|}}{C}{-}R$$

keto form
more stable

enol form
less stable

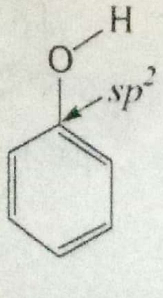
(ii) However, in case of phenols, the enol form is most stable due to aromatic stabilisation as has been discussed in Section 3.6.

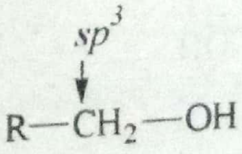


2,4-cyclohexadien-1-one
less stable

Phenol
more stable

(iii) The OH group in phenols is attached to a sp^2 carbon atom, whereas in aliphatic primary alcohols it is attached to a sp^3 carbon atom.





$$R{-}\overset{\overset{sp^3}{\downarrow}}{C}H_2{-}OH$$

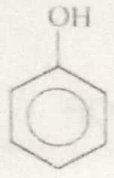
Scanned by CamScanner

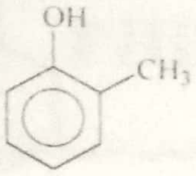
3.3 CLASSIFICATION AND NOMENCLATURE

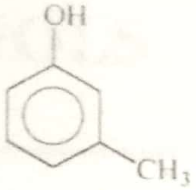
3.3.1 Classification

Depending upon the number of hydroxy groups present on the benzen ring, phenols are classified as :

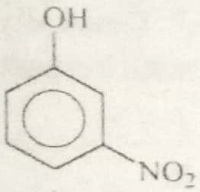
Monohydric phenols : containing one –OH group

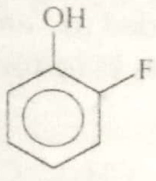

phenol

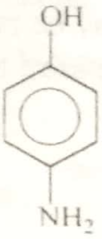

o-cresol

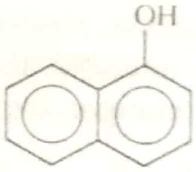

m-cresol

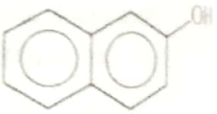

p-cresol


m-nitro-
phenol

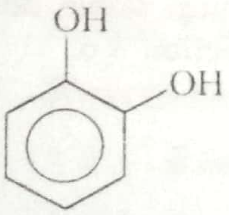

o-fluoro-
phenol

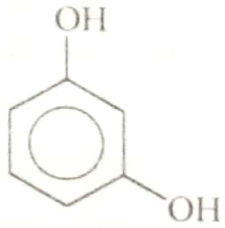

p-amino-
phenol


1-naphthol
(α-naphthol)


2-naphthol
(β-naphthol)

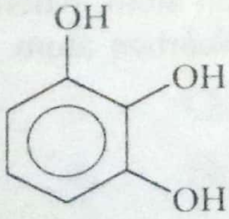
Dihydric phenols : containing two –OH groups.

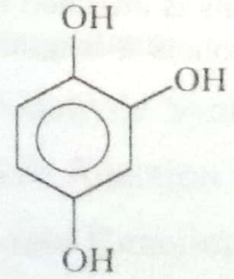

catechol

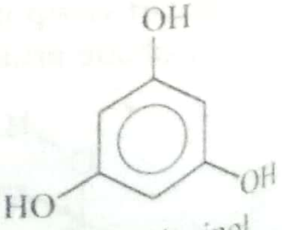

resorcinol


hydroquinone
(quinol)

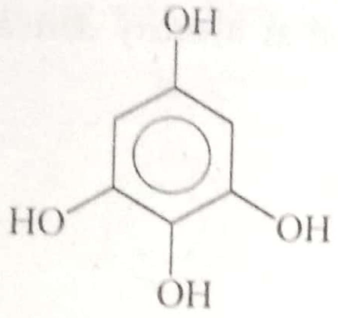
Trihydric phenols : containing three –OH groups.


pyrogallol


hydroxyquinol


phloroglucinol

Polyhydric phenols : containing more than three –OH groups.

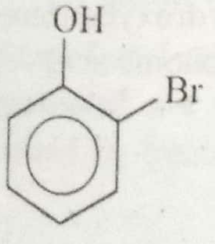


hydroxypyrogallol

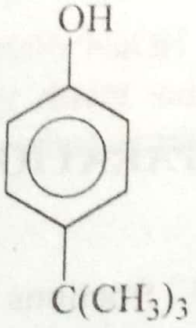
3.3.2 Nomenclature

(i) A number of phenols have been given special names. These names, as mentioned above, have been retained by IUPAC. Other compounds are named as their derivatives.

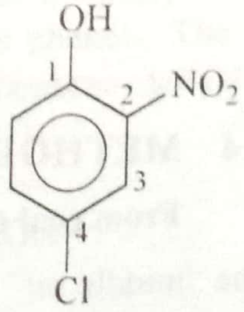
(ii) Substituted phenols are named as derivatives of phenol. Position of the substituent(s) is indicated by prefixes *o*, *m*, *p* or by numbering system. For example –



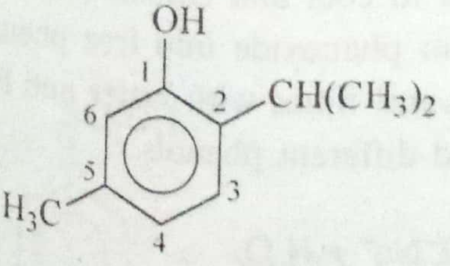
(*o*-bromophenol)
(2-bromophenol)



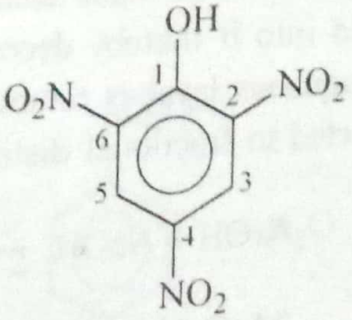
p-*t*-butylphenol
(4-*t*-butylphenol)



4-chloro-2-nitrophenol



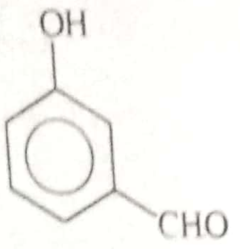
2-isopropyl-5-methylphenol
(thymol)

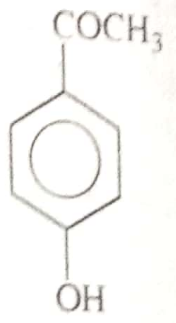


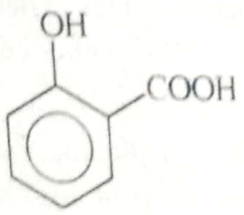
2,4,6-trinitrophenol
(picric acid)

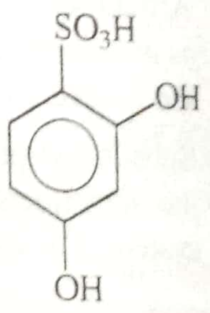
Scanned by CamScanner

(iii) When other functional groups such as $-COOH$, $-CHO$, $-SO_2OH$, etc., which have priority over $-OH$ group, are present on the benzene ring, the phenols are named as hydroxy derivatives of these compounds.


m-hydroxybenzaldehyde


p-hydroxyacetophenone


o-hydroxybenzoic acid
(salicylic acid)


2,4-dihydroxybenzene-sulphonic acid

3.4 METHODS OF PREPARATION

1. From coal tar

The "middle oil" and "heavy oil" fractions of coal-tar distillation contain phenols. These fractions are cooled so that naphthalene crystallises out. The mother liquor is then treated with aqueous sodium hydroxide, phenols being weakly acidic, form salts (sodium phenoxide) and get dissolved in the alkaline solution. This solution is allowed to cool and carbon dioxide is passed into it thereby decomposing sodium phenoxide into free phenols. The aqueous layer is removed, washed several times with water and then subjected to fractional distillation to afford different phenols.

$$ArOH + NaOH \longrightarrow ArO^-Na^+ + H_2O$$

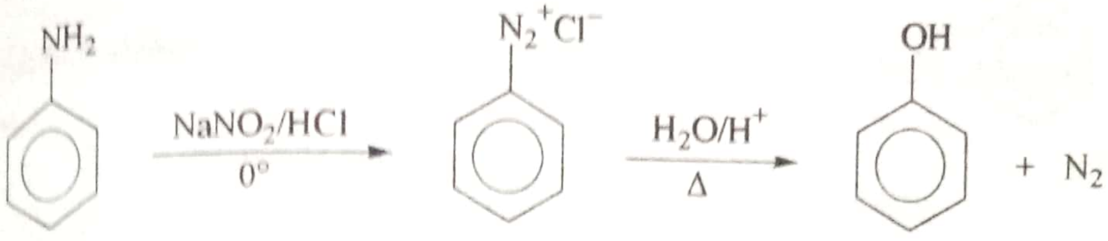
$$2ArO^-Na^+ + CO_2 \longrightarrow 2ArOH + Na_2CO_3$$

Ar = benzene or substituted benzene ring

Scanned by CamScanner

2. By hydrolysis of diazonium salts

Hydrolysis of a diazonium salt with dilute acid produces phenol.

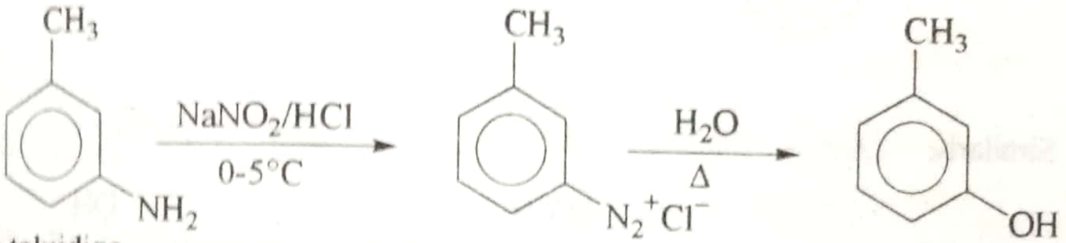


aniline

benzene diazonium chloride

phenol

Similarly

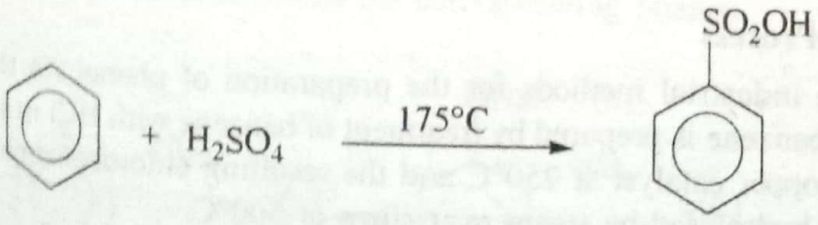


m-toluidine

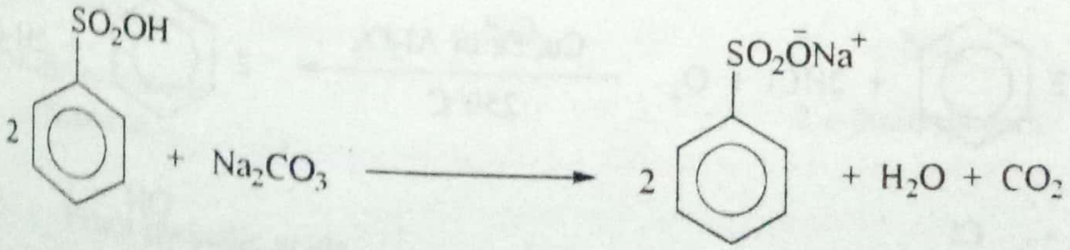
m-cresol

3. By alkali fusion of aryl sulphonates

Fusion of aryl sulphonates with NaOH at 300°C gives phenols. The aryl sulphonates are prepared by direct sulphonation of benzene derivatives followed by treatment with sodium carbonate.

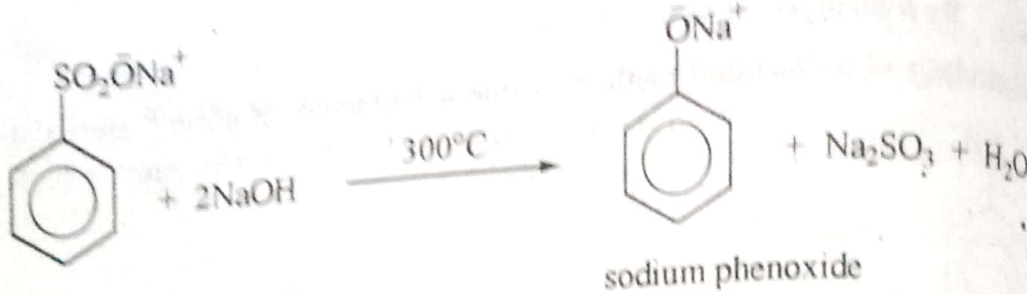


benzene sulphonic acid

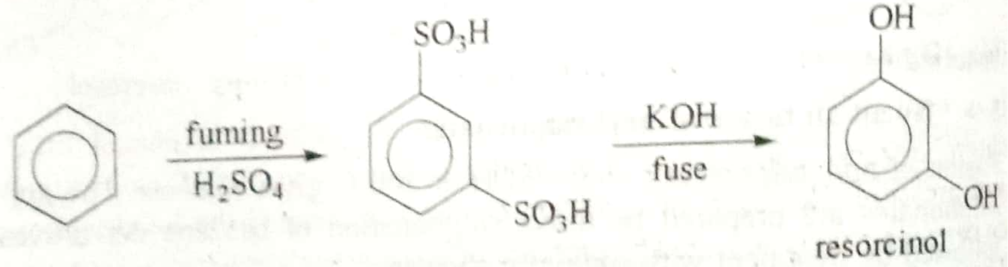


benzene sodium sulphonate

Scanned by CamScanner



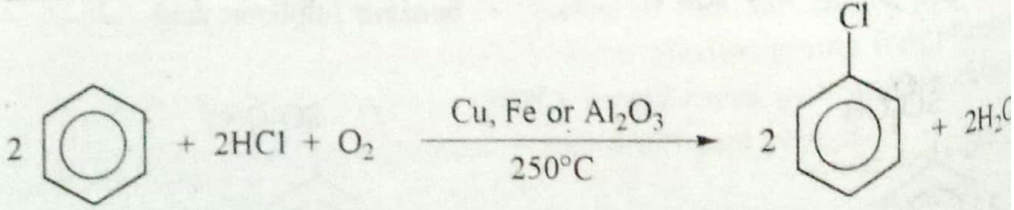
Similarly,

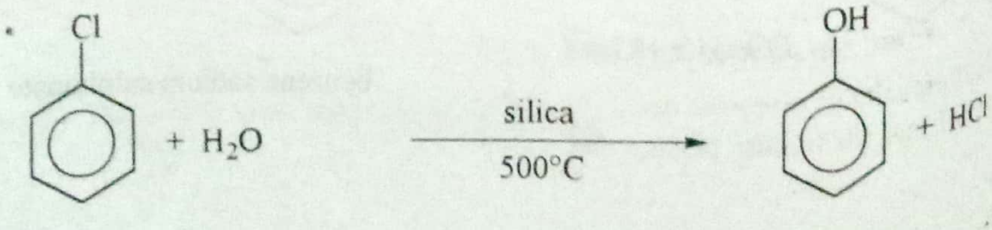


4. **From halobenzenes**

(i) **Raschig Process**

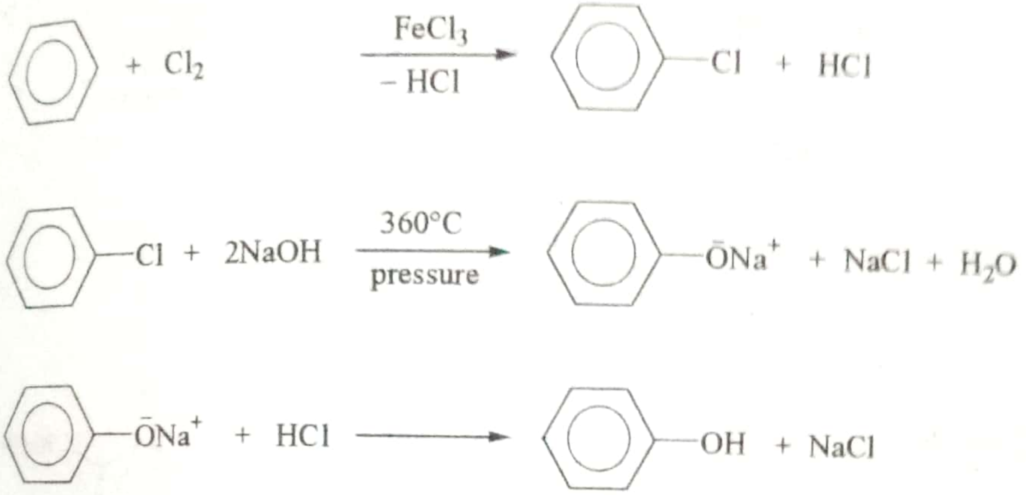
It is one of the industrial methods for the preparation of phenol. In this method, chlorobenzene is prepared by treatment of benzene with HCl in the presence of a copper catalyst at 250°C and the resulting chlorobenzene is simultaneously hydrolysed by steam over silica at 500°C.





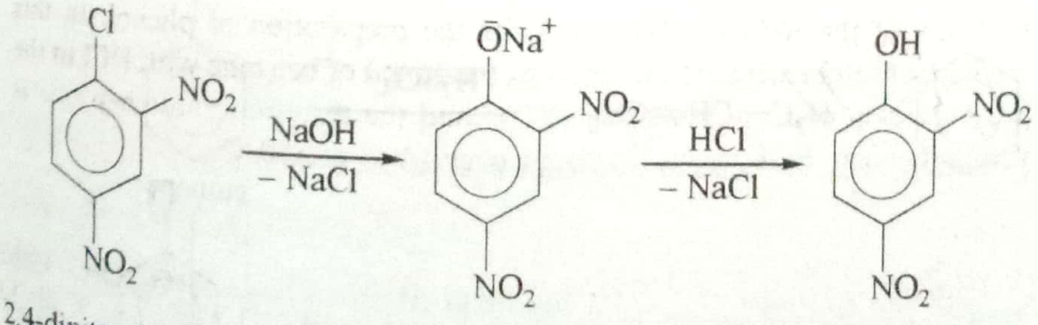
(ii) Dow Process

It is also the commercial method for the manufacture of phenol. Here the chlorobenzene is prepared by direct chlorination of benzene from which phenol is obtained by alkaline hydrolysis at high temperature and pressure.



(iii) By hydrolysis of aryl halides containing – I groups

It is evident from above [(i) and (ii)] that preparation of phenol from chlorobenzene requires hydrolysis under strong conditions of temperature and pressure. However this problem can be overcome if the halide group on benzene ring is activated by presence of electron-withdrawing (–I) groups. Thus 2,4-dinitrochlorobenzene can be easily hydrolysed with dil. NaOH at room temperature to afford the corresponding phenol.

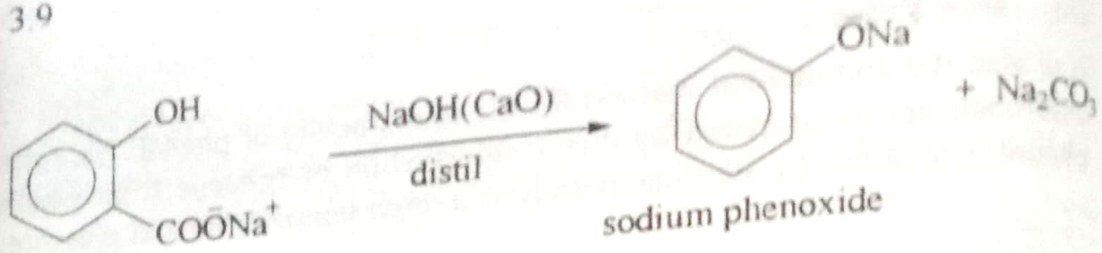


2,4-dinitrochloro-benzene

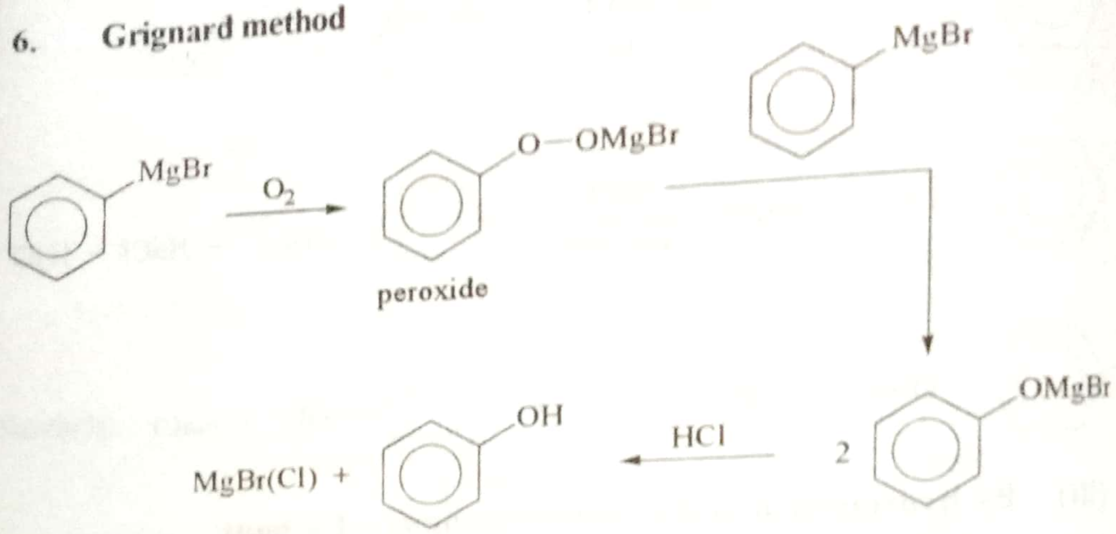
2,4-dinitrophenol

5. From phenolic acids

Sodium salts of phenolic acids like sodium salicylate, upon distillation with soda lime, form salts of phenols.

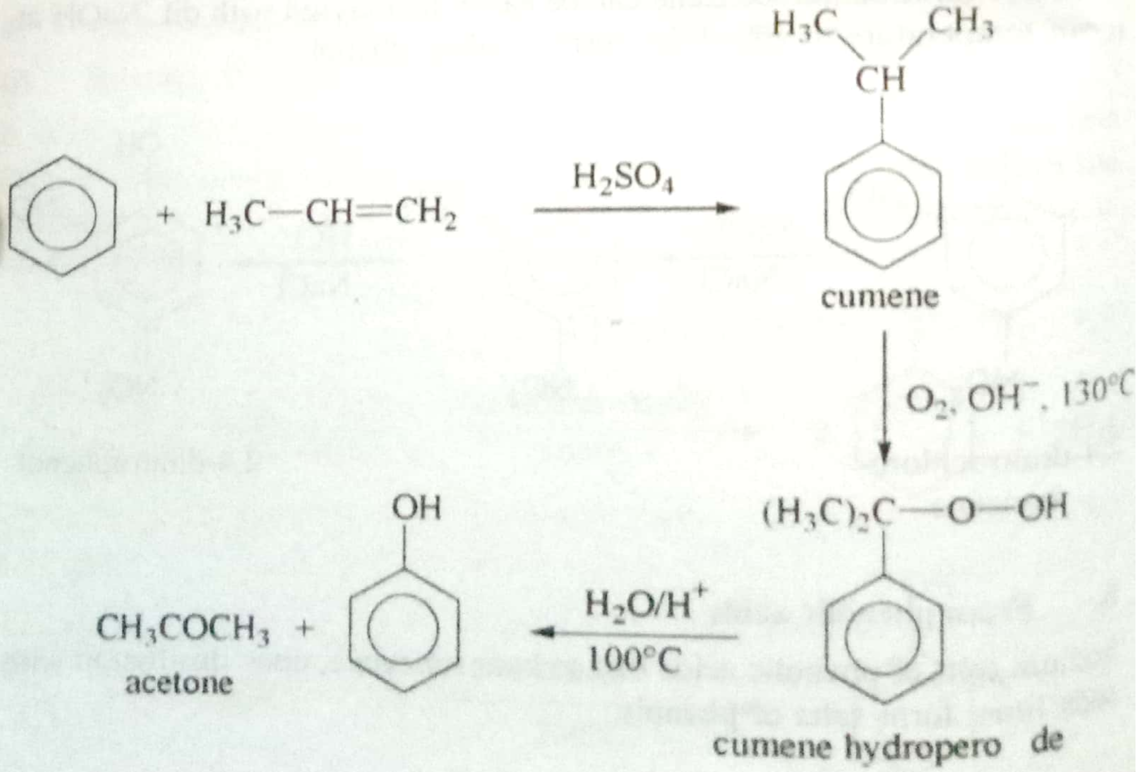


6. Grignard method



7. From cumene

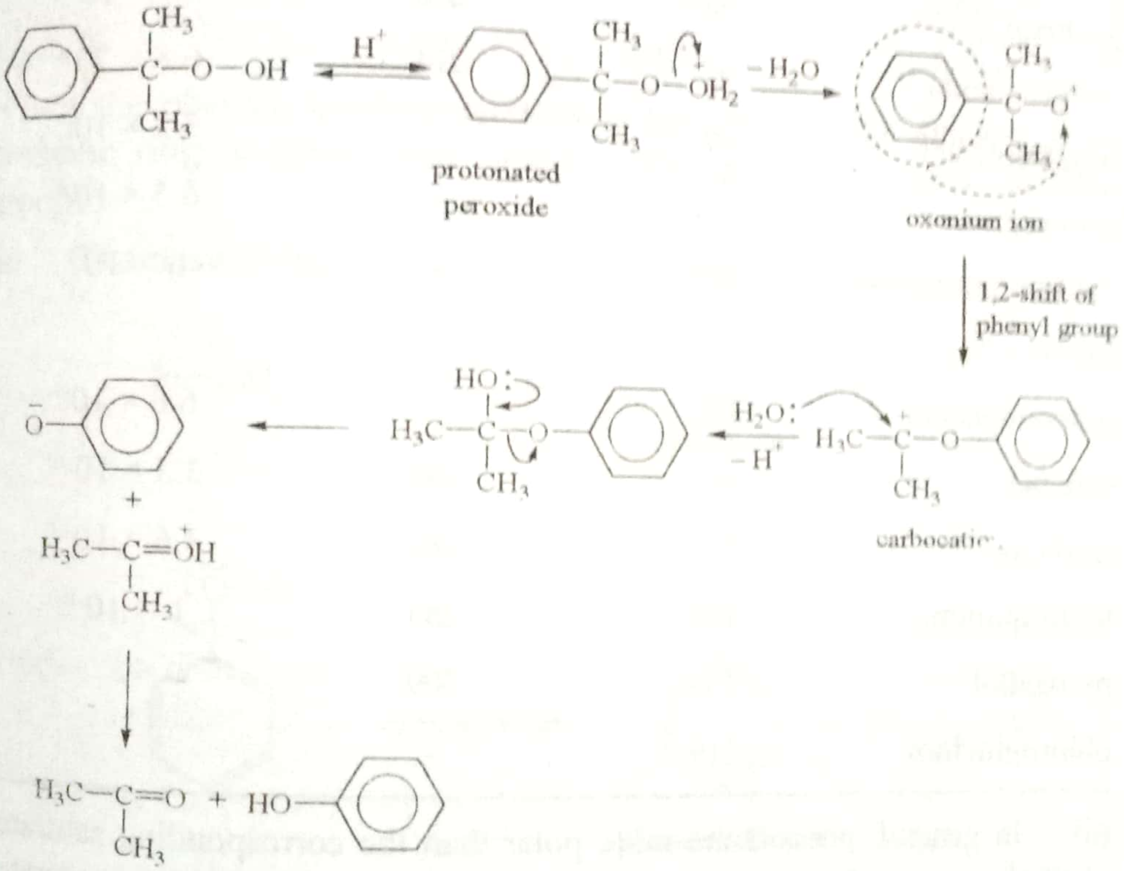
It is the most important industrial method. In this method cumene (isopropylbenzene) is oxidised to hydroperoxide which is then decomposed by acid to phenol and acetone (another commercial by product).



Scanned by CamScanner

Mechanism of rearrangement of hydroperoxide

It is interesting to note that phenyl group attached to carbon in hydroperoxide gets detached to oxygen in phenol. It means that some kind of rearrangement takes place. It is called "**1,2-shift**" of phenyl group and can be explained by the following mechanism (Scheme 3.1).



Scheme 3.1 : Mechanism of 1,2-phenyl shift in cumene hydroperoxide

It may be noted that phenyl group migrates in preference to methyl group.

3.5. PHYSICAL PROPERTIES

(i) The parent compound phenol, is a colourless crystalline solid which turns pink on exposure to air and light due to oxidation. It has phenolic odour, boiling point 182°C, melting point 43°C and is moderately soluble in water. Other phenols are colourless solids or thick viscous liquids. Their melting points, boiling points and K_a (acid dissociation constants) values are summarised in Table 3.1.

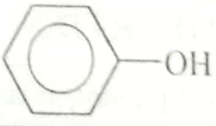
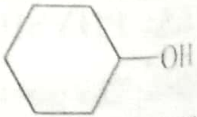
Scanned by CamScanner

Table 3.1 : Physical constants of various phenols

Phenol	**m.p. (°C)**	**b.p. (°C)**	**K_a (H_2O, 25°)**
phenol	43	182	1.3×10^{-10}
o-cresol	31	191	6.3×10^{-11}
m-cresol	12	203	9.8×10^{-11}
p-cresol	34	202	1.5×10^{-10}
o-nitrophenol	45	214	6.8×10^{-8}
m-nitrophneol	97	-	5.3×10^{-9}
p-nitrophenol	114	-	6.5×10^{-8}
2,4,6-trinitrophenol (picric acid)	123	-	6×10^{-1}
p-aminophenol	186	-	6.6×10^{-9}
catechol	105	246	3.3×10^{-10}
resorcinol	110	280	3.6×10^{-10}
hydroquinone	170	285	1×10^{-10}
pyrogallol	139	309	-
phloroglucinol	219	-	-

(ii) In general, phenols are more polar than the corresponding saturated alcohols due to the greater acidity of phenols as compared to saturated alcohols. A comparison of the physical properties of the phenol and the cyclohexanol is shown in Table 3.2.

Table 3.2 : Physical properties of phenol and cyclohexanol

Properties		
Melting point (°C)	43	25.5
Boiling point (°C)	182	161
Solubility in water (g/100 ml at 20°)	9.3	3.6
K_a	1.3×10^{-10}	$\sim 10^{-18}$

Scanned by CamScanner

3.6 ACIDIC CHARACTER

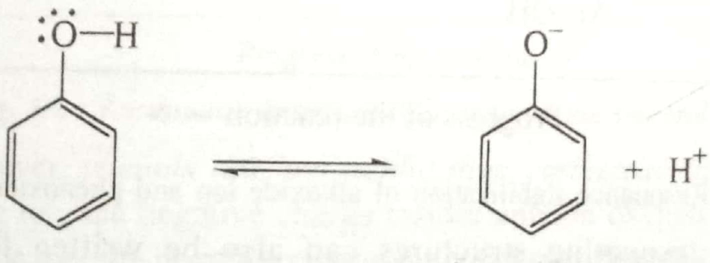
(i) Phenols are less acidic than carboxylic acids, but are more acidic than alcohols.

	RCOOH	ArOH	ROH
k_a	$\sim 10^{-5}$	$\sim 10^{-10}$	10^{-16}–10^{-18}

Hence the obvious question is "why is that –OH group attached to an aromatic ring is more acidic than the –OH group attached to an alkyl group?"

(ii) The answer lies in the resonating structures of resulting anions.

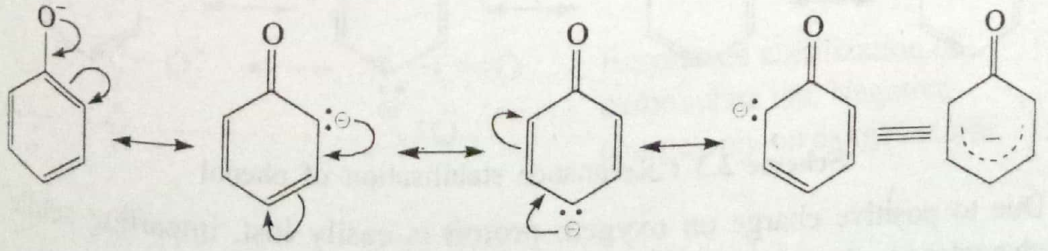
$$R{-}OH \rightleftharpoons \underset{\text{alkoxide ion}}{RO^-} + H^+$$



phenoxide ion

(iii) **Resonance stabilization of phenoxide ion**

Alkoxide ion has no other resonating structure whereas phenoxide ion can be stabilized by the following resonating structures (Scheme 3.2).



Scheme 3.2 : Resonance stabilization of phenoxide ion

It means resonance stabilises the phenoxide ion to a greater extent than alkoxide ion, and therefore, phenols are more acidic than alcohols.

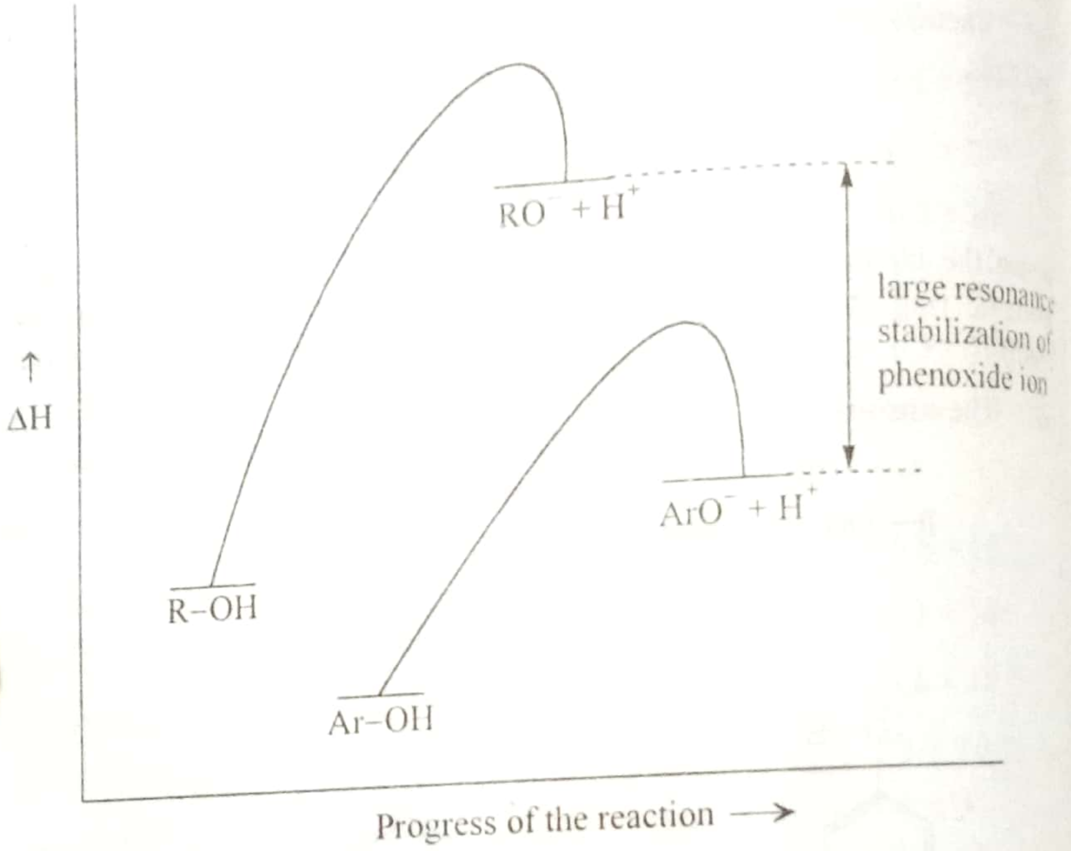
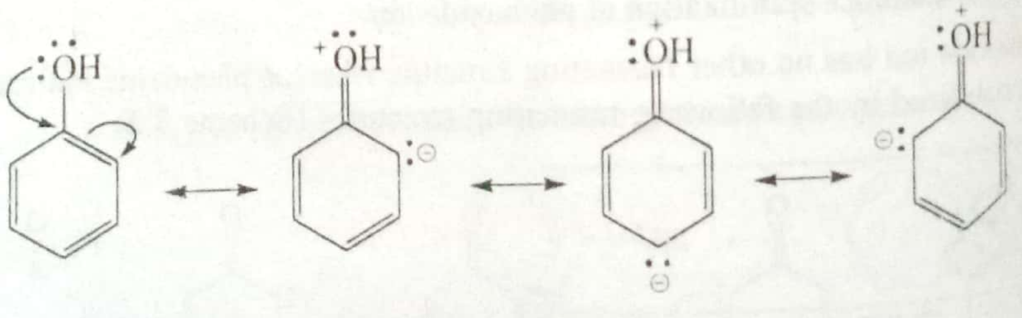


Fig. 3.1: Resonance stabilization of alkoxide ion and phenoxide ion

(iv) Various resonating structures can also be written for phenol (Scheme 3.3).



Scheme 3.3 : Resonance stabilisation of phenol

Due to positive charge on oxygen, proton is easily lost, imparting acidic character to phenols.

(v) However, in comparison to phenol, phenoxide ion is more resonance stabilized because phenoxide ion contains only negative charge whereas phenol has high energy charge separated species. Therefore, *resonance stabilises phenoxide ion to a greater extent than phenol (Fig. 4.2).*

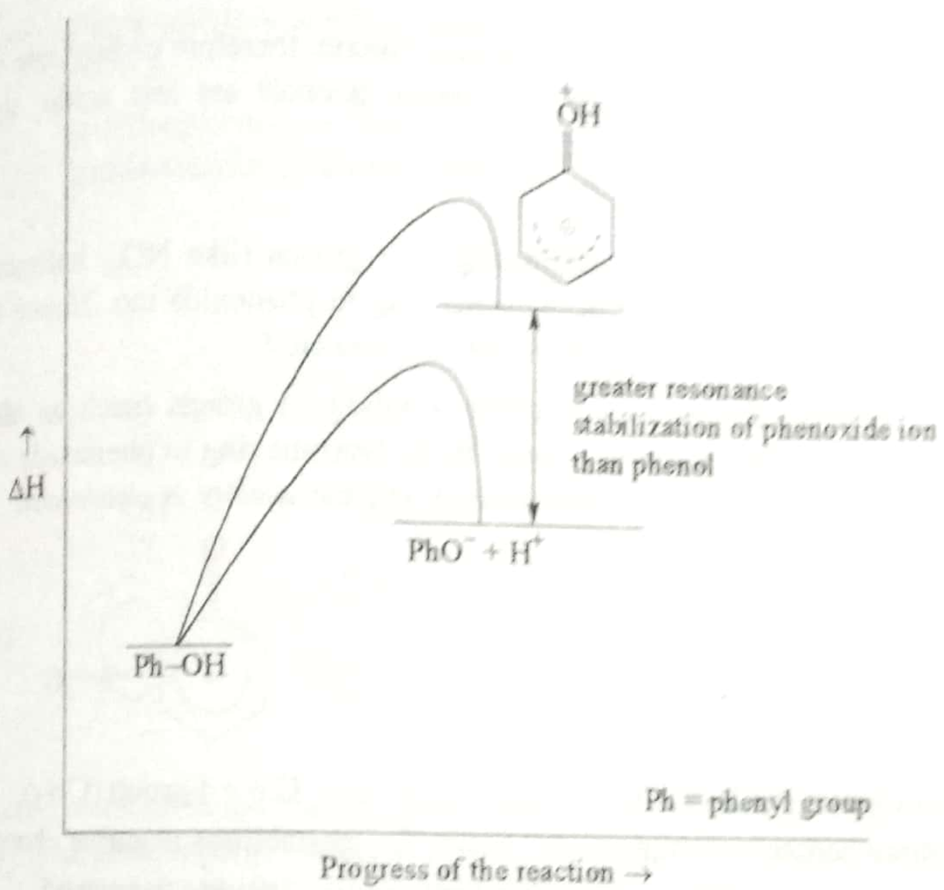
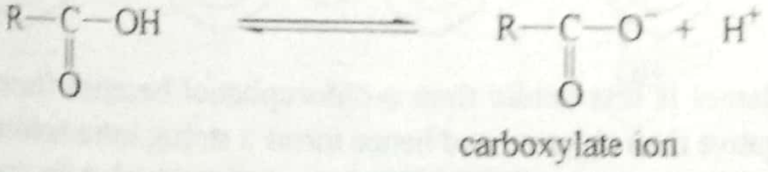
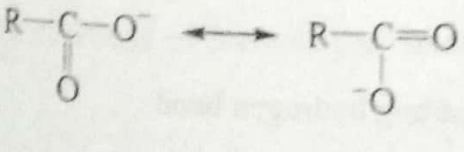


Fig. 3.2 : Resonance stabilization of phenoxide ion and phenol

(vi) However, *phenols are less acidic than carboxylic acids* because in carboxylate ion, the negative charge resides only on oxygen atoms whereas in phenoxide ion, the negative charge is spread over benzene ring and hence lies on carbon also.

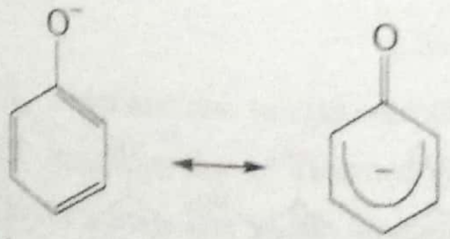


$$\mathrm{R{-}\underset{\underset{O}{\|}}{C}{-}OH} \rightleftharpoons \mathrm{R{-}\underset{\underset{O}{\|}}{C}{-}O^-} + H^+$$



$$\mathrm{R{-}\underset{\underset{O}{\|}}{C}{-}O^-} \longleftrightarrow \mathrm{R{-}\underset{\underset{{}^-O}{|}}{C}{=}O}$$

Resonance stabilization of carboxylate ion. Negative charge only on oxygen atoms.



Negative charge on carbon