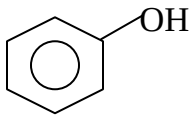
THESE NOTES TO COME AFTER 'BENZENE'

PHENOL

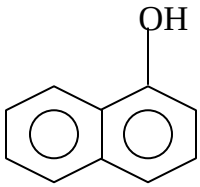
1. Introduction:

Phenols are organic compounds in which a hydroxyl group is directly bonded to an aromatic ring.

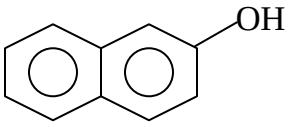
e.g (i) Phenol

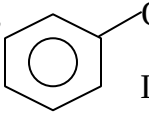


(ii) Naphthalene-1-ol (OR 1-Naphthol)



(ii) Naphthalen-2-ol (OR 2-Naphthol)



Phenol , 

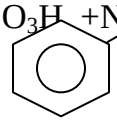
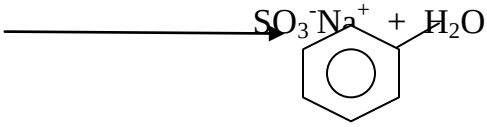
, the simplest of the phenols is a colourless, deliquescent solid. It however turns reddish-brown (or pink) on continued exposure to air, due to formation of complex oxidation products.

It has a characteristic smell and is sparingly soluble in water. It is sparingly soluble because it contains a big proportion of the water-insoluble group (the phenyl group).

2. Methods of Preparation:

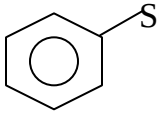
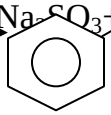
(a)<u>From Benzenesulphonic acid</u>

Benzenesulphonic acid is first converted to sodium benzenesulphonate, by neutralizing it with sodium hydroxide.

i.e SO_3H +NaOH   $SO_3^-Na^+ + H_2O$

Sodium benzenesulphonate

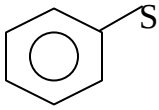
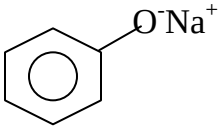
The sodium bezenesulphonate is then fused with solid sodium hydroxide at a temperature of 300ºC , forming sodium phenoxide.

 $SO_3^-Na^+ + 2NaOH(s) \xrightarrow{300ºC} O^-Na^+ + Na_2SO_3 + H_2O$ 

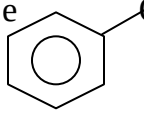
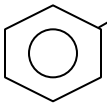
<u>OR</u>

Sodium phenoxide

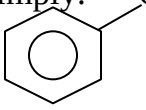
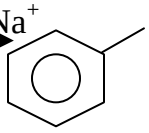
Simply:

 $SO_3^-Na^+ NaOH(s) \xrightarrow{300ºC}$ 

Phenol is then obtained from the sodium phenoxide by addition of a dilute mineral acid (e.g hydrochloric acid)

i.e  $O^-Na^+ + HCl \longrightarrow$  $OH + NaCl$

<u>OR</u>

Simply:  $H^+OH + Na^+ \longrightarrow$ 

<u>Quiz</u>:

Using equations only, show how phenol can be synthesized from benzene.

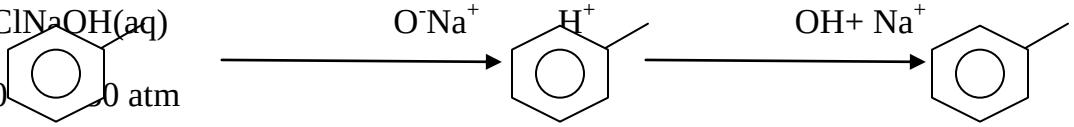
[**Hint**:*Benzene can be converted directly to Benzenesulphonic acid*]

(b) From Chlorobenzene:

At a temperature of 360ºC and a pressure of 150atm, chlorobenzene reacts with aqueous sodium hydroxide solution forming sodium phenoxide. Phenol is then obtained from the sodium phenoxide by addition of a dilute mineral acid.

i.e ClNaOH(aq) O^-Na^+ H^+ OH+ Na^+

360 150 atm



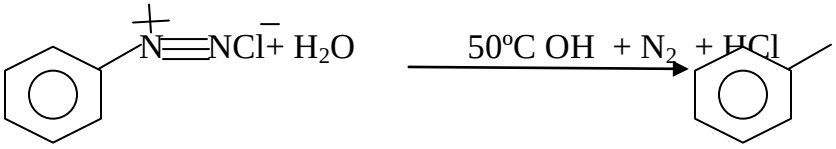
Quiz:

Using equations only, show how phenol can be synthesized from benzene.

[**Hint**: *Benzene can be converted directly to Chlorobenzene*]

(c) From Benzenediazonium chloride:

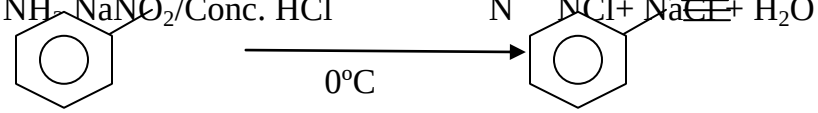
When an aqueous solution of benzenediazonium chloride is warmed at 50ºC, phenol is formed.

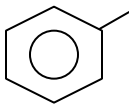
i.e 

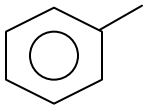
Note:

Benzenediazonium chloride is an important compound in organic synthesis (since it can be used in the synthesis of a variety of organic compounds. It is formed by treating aminobenzene with a solution of sodium nitrite in concentrated hydrochloric acid, at a temperature in the range of 0-5ºC(e.g 0ºC).

i.e NH2 $NaNO_2$/Conc. HCl N NCl + NaCl + H_2O

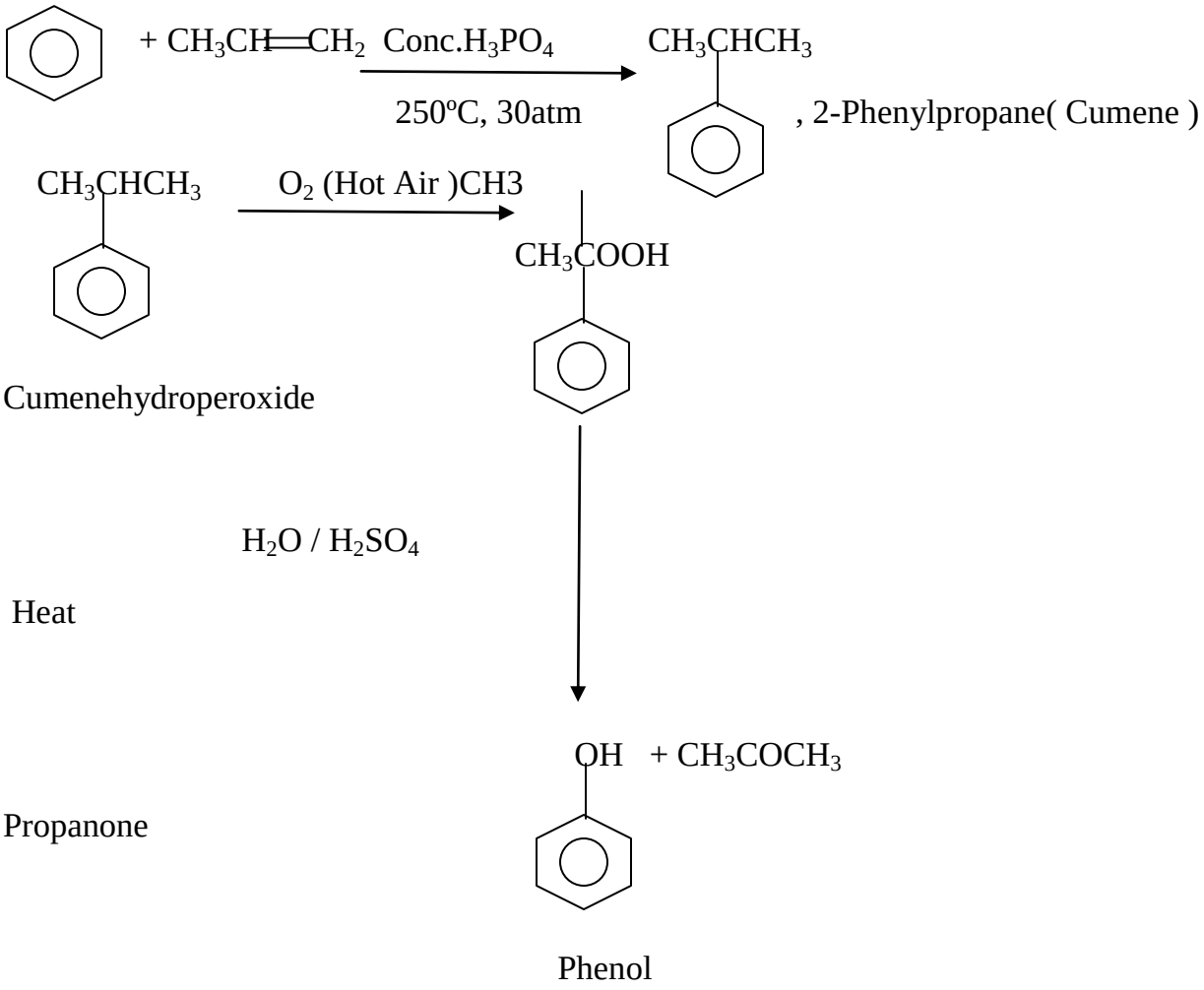


Benzenediazonium chloride may also be written as  $N_2^+Cl^-$

[i.e showing a summarized structure of the cation,  N_2^+ (benzenediazonium ion)]

(d) From Benzene and Propene (using the Cumene Process):

This is an industrial process and is summarized in the reaction scheme below:



3. Chemical Properties of Phenol:

(a) Phenol as a Nucleophile:

Compared to alcohols, phenol is a weaker nucleophile.

Reason:

In phenol, a lone pair of electronson the oxygen atom interacts with the delocalized electrons of the aromatic ring. As a result, the lone pair of electrons is drawn towards the ring and thus not readily available to attack an electrophilic atom.

In an alcohol, the alkyl group, owing to its positive inductive effect, pushes electrons towards the hydroxyl group. As a result, the lone pair of electrons is concentrated on the oxygen atom and thus more readily available to attack an electrophilic atom.

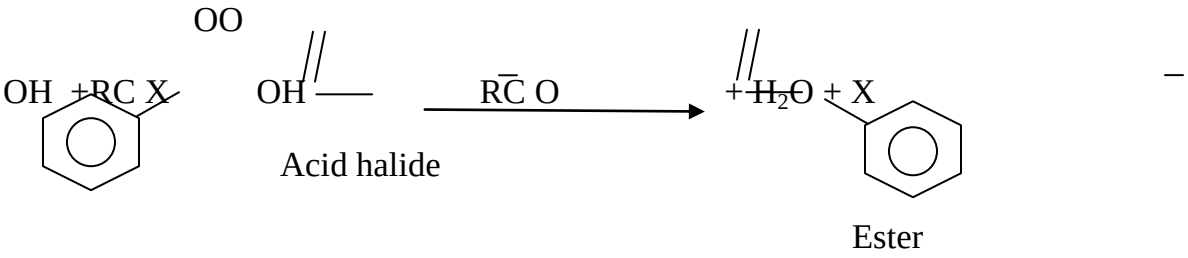
(i) Ester Formation:

Since phenol is a weak nucleophile, it cannotform an ester with carboxylic acids, owing to their low reactivity. It instead forms esters with acid halides and acid anhydrides- which have higher reactivity.

Even then, the reactivity of phenol as a nucleophile has to be enhanced-via conversion to a phenoxide. This is done by including an alkali in the reaction mixture.

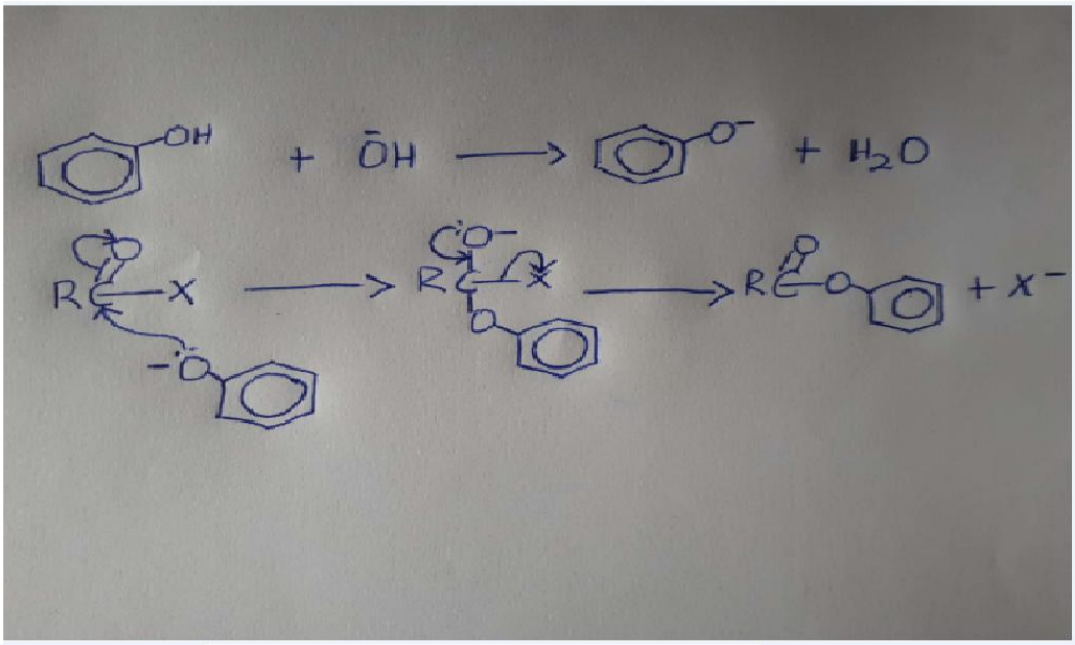
i.e

With acid halide:

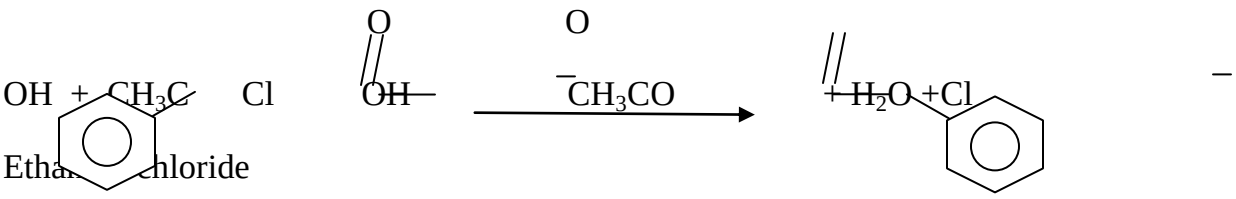


General mechanism:

REFER TO NEXT PAGE



e.g

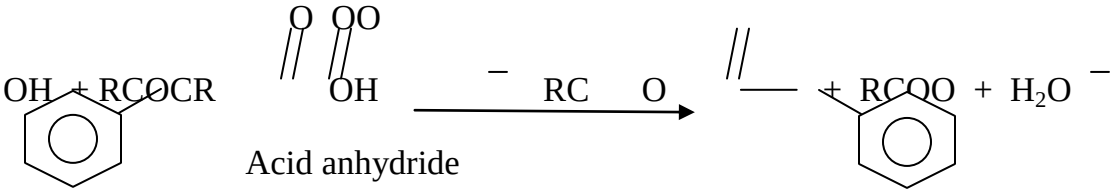


Ethanoyl chloride

Phenyl ethanoate

Mechanism:(Exercise)

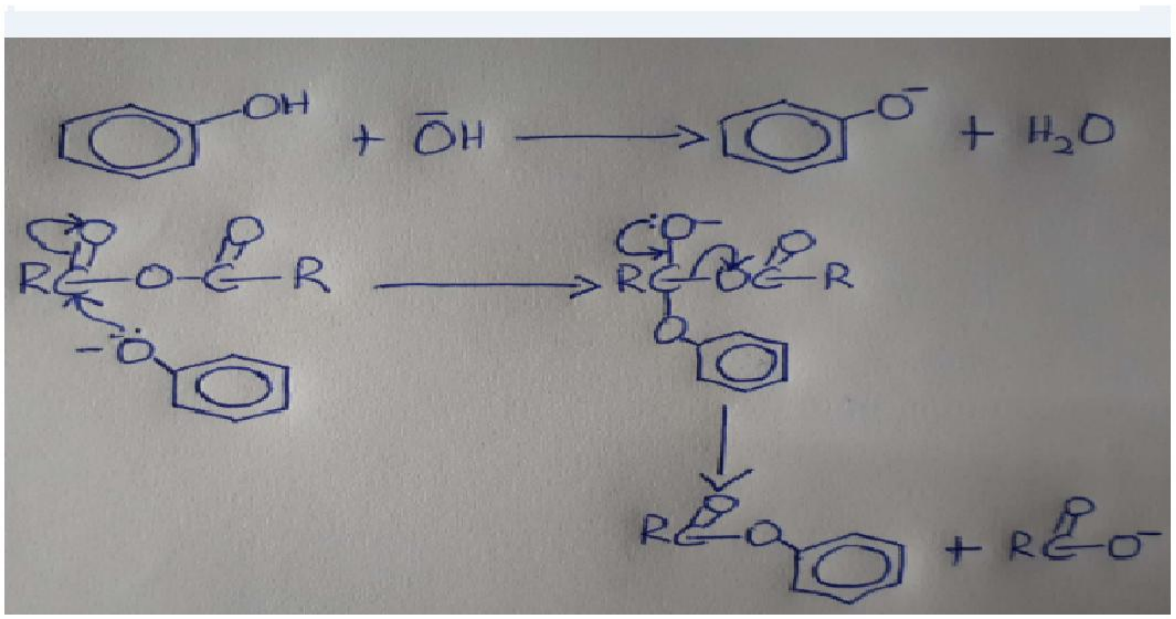
With Acid anhydride:



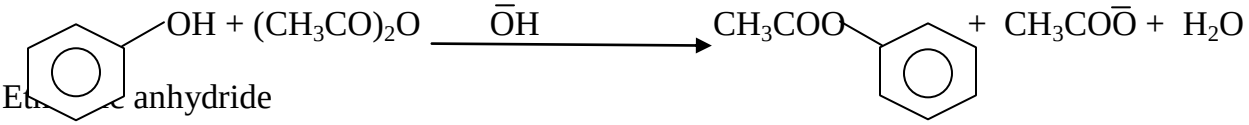
Acid anhydride

Ester

General mechanism:



e.g



Et[illegible] anhydride

Phenyl ethanoate

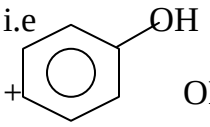
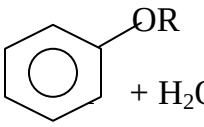
Mechanism:(Exercise)

Quiz:

Using equations only, show how aminobenzene can be converted to phenyl ethanoate

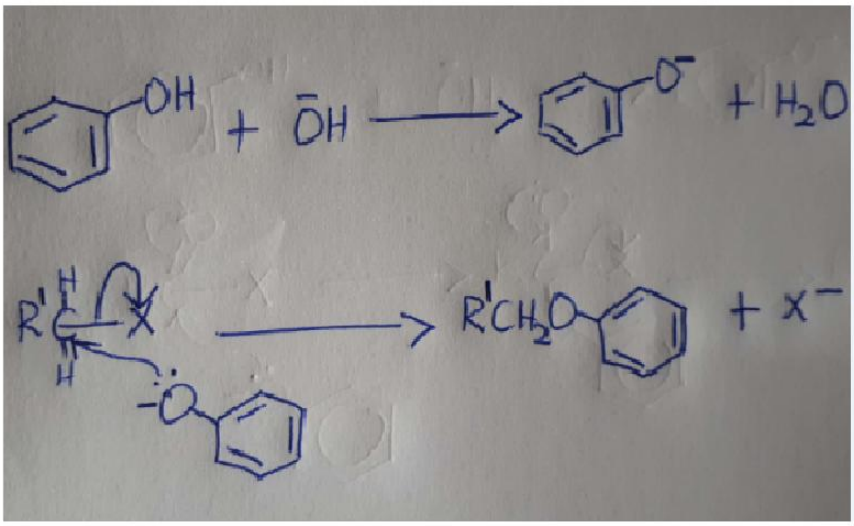
(ii) Ether Formation:

When phenol is heated with an alkylhalide in alkaline medium, an aromatic ether is formed.

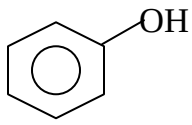
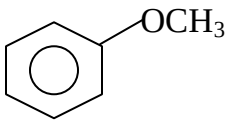
i.e  + OH / Heat $\xrightarrow{-}$  + H_2O $^{-}$

Alkylhalie Aromatic ether

General Mechanism:



e.g

 $\xrightarrow[\text{Heat}]{CH_3Cl / NaOH}$  + NaCl + H_2O

Methoxy benzene

Mechanism:(Exercise)

Quiz:

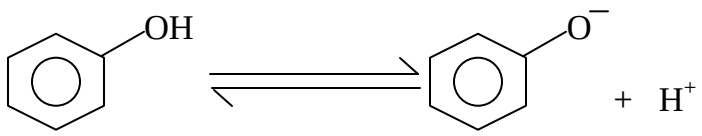
Using equations only, show how ethoxybenzene can be obtained from benzene.

(b) Phenol as an acid:

Compared to alcohols, phenol is a stronger acid.

Reason:

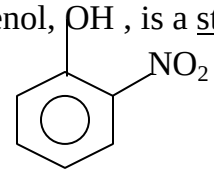
In phenol, a lone pair of electrons on the oxygen atom interacts with the delocalized electrons of the aromatic ring. As a result, the carbon-oxygen bond is strengthened(due to formation of a partial double bond between the two atoms) while the oxygen-hydrogen bond is weakened (due to increased polarity). The weakened oxygen-hydrogen bond therefore breaks more easily, releasing a proton.

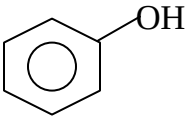
i.e 

In an alcohol, the alkyl group, owing to its positive inductive effect, pushes electrons towards the hydroxyl group. The effect of electron push in the direction of the hydroxyl group is to reduce bond polarity of the oxygen-hydrogen bond. Hence the bond is made stronger and thus more difficult to beak to release a proton.

Note:

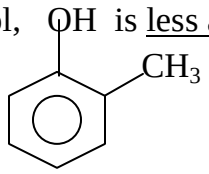
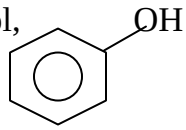
- Presence of electron-withdrawing groups on the aromatic ring of phenol has the effect of increasing the acid strength of phenol and the higher the number of such groups on the ring, the greater the acid strength.

  e.g 2-Nitrophenol, 

, is a stronger acid than phenol, 

  Reason:
  In 2-nitrophenol, the nitro group, owing to its negative inductive effect, tends to pull electrons away from the ring. This makes the aromatic ring to in turn pull electrons of the hydroxyl group more. Thus the oxygen-hydrogen bond is made more polar and weaker than that in phenol. Hence the oxygen-hydrogen bond in 2-nitrophenol breaks more easily to release a proton.

- Presence of electron-releasing groups on the aromatic ring of phenol has the effect of decreasing the acid strength of phenol and the higher the number of such groups on the ring, the lower the acid strength.

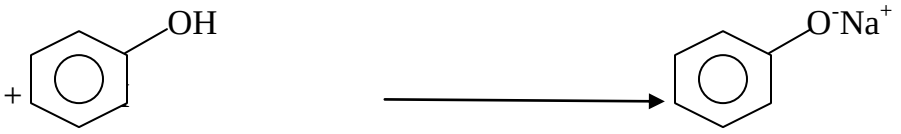
e.g 2-methylphenol,  is less acidic than phenol, 

Reason:

In 2-methylphenol, the methyl group, owing to its positive inductive effect, tends to push electrons towards the ring. This makes the aromatic ring to in turn pull electrons of the hydroxyl group less. Thus the oxygen-hydrogen bond is made less polar and stronger than that in phenol. Hence the oxygen-hydrogen bond in 2-methylphenol breaks less easily to release a proton.

(i) Reaction With Sodium hydroxide:

Phenol reacts with sodium hydroxide (in a neutralization reaction) forming sodium phenoxide and water.



Sodium phenoxide

(ii) Reaction With Sodium Metal:

Phenol reacts with sodium metal forming sodium phenoxide and hydrogen gas.

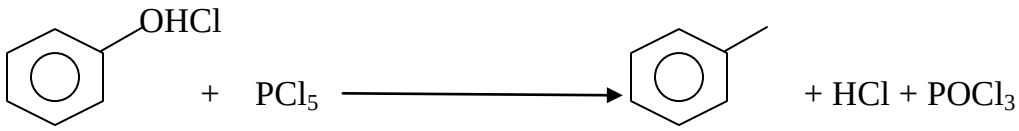
Note:

The above two reactions are characteristic of phenol reacting as an acid.

However, unlike carboxylic acids, phenol is not acidic enough to liberate carbon dioxide from a carbonate or a hydrogencarbonate.

(c) Reaction With Phosphorus(V) chloride:

Phenol reacts with phosphorus(V) chloride (phosphorus pentachloride) forming chlorobenzene.

i.e 

(d) Electrophilic substitution Reactions:

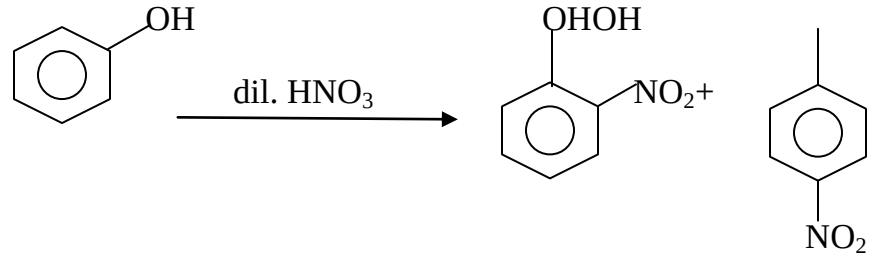
Phenol is a benzene derivative, in which the hydroxyl group is the substituent. It should be remembered that the hydroxyl group is ortho-para directing with activation.

Hence, phenol undergoes electrophilic substitution reactions more readily than benzene forming ortho and para-substituted products and in certain cases forming a single organic product-in which all the extra-activated sites have been substituted.

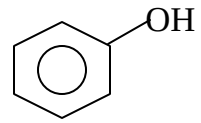
e.g

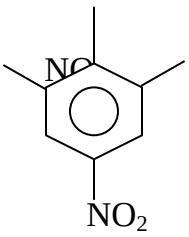
(i) Nitration:

When phenol is reacted with dilute nitric acid forming 2-nitrophenol and 4-nitrophenol, the ortho- and para-substituted products respectively.

i.e 

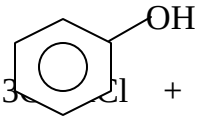
When phenol is reacted with a mixture of concentrated nitric and sulphuric acids (nitrating mixture) 2,4,6-trinitrophenol (single product in which all the extra-activated sites have been substituted) is formed.

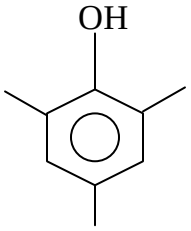
i.e  Conc. HNO_3 OH

Conc. H_2SO_4 O_2N 

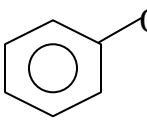
+ $3H_2O$

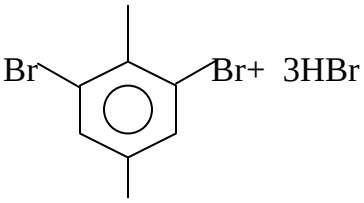
(ii) Halogenation:

i.e 

+ 3Cl Cl + 3HCl 

Cl 2,4,6-trichlorophenol



+ $3Br_2$ 

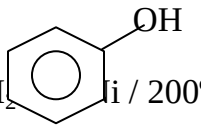
Br 2,4,6-tribromophenol

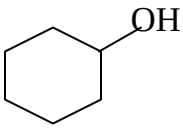
Note:

2,4,6-tribromophenol is an insoluble white solid. This explains why, when bromine water is added to phenol, the reddish-brown colour of the reagent is discharged and a white precipitate is formed.

(e) Addition reaction:

When phenol is reacted with hydrogen gas in the presence of nickel catalyst and at a temperature of 200ºC, the aromatic ring is converted to a cyclohexane ring forming cyclohexanol.

i.e 

+ $3H_2$ Ni / 200ºC 

Quiz:

Using equations only, show how Chlorobenzene can be converted to Cyclohexene.

[**Hint**: Cyclohexene can be directly obtained from cyclohexanol, via dehydration]

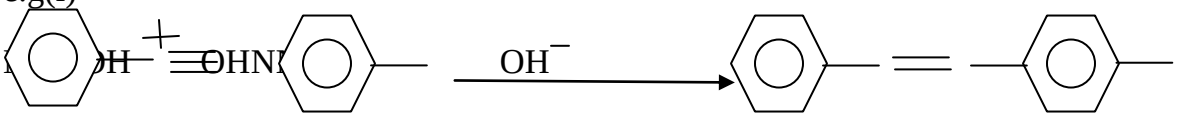
(f) Formation of Azodyes:

Phenols react with benzenediazonium chloride in alkaline medium forming brightly coloured insoluble compounds, commonly referred to as azo dyes (azo compounds)

These compounds contain the azo group, N═N .and their general formula is

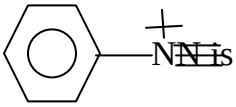
Ar—N═N—Ar^1; Where Ar and Ar^1 are aromatic rings.

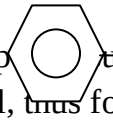
e.g(i)



4-Phenylazophenol

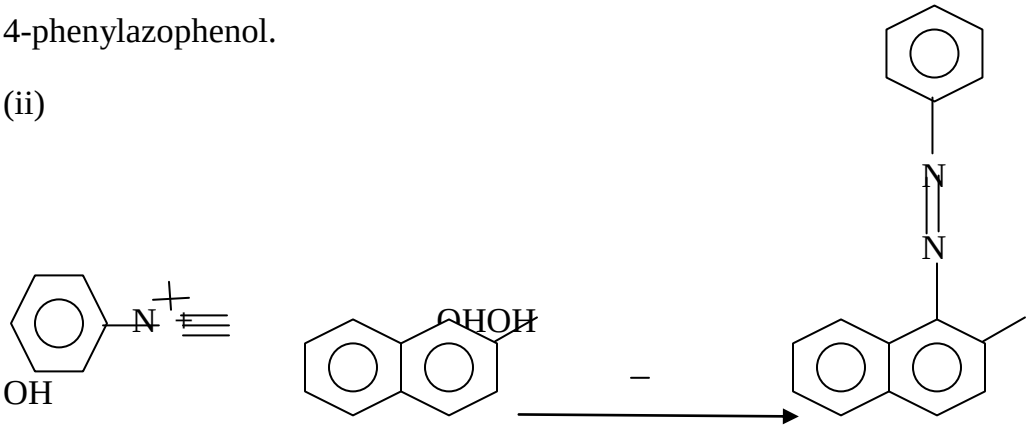
(Bright yellow in colour)

In the above reaction, the benzenediazonium ion,  is first converted to the phenylazo group,

 . This group substitutes a hydrogen atom in the paraposition of the aromatic ring of phenol, thus forming

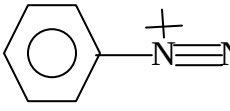
4-phenylazophenol.

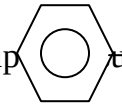
(ii)



1-Phenylazonaphthalen-2-ol

(Bright red in colour)

In the above reaction, the benzenediazonium ion,  is first converted to the phenylazo group,

 . This group substitutes a hydrogen

atom in the alpha position (first carbon atom from the carbon atom joining the two rings) , thus forming 1-Phenylazonaphthalen-2-ol.

Note:

The reaction in (ii) above is the basis for a qualitative test for aminobenzene.

Procedure:

An ice-cold (i.eat 0ºC) solution of sodium nitrite in concentrated hydrochloricacid is added to the unknown (i.eaminobenzene) [*thus generating benzene diazonium chloride*] and then the resulting mixture is poured into alkaline naphthalen-2-ol solution.

Observation:

A red precipitate(due to the insoluble 1-phenylazonaphthalen-2-ol) is formed.

4. Confirmatory Test For Phenol:

(Also, Test for *distinguishing between Phenol and another Organic Compound*)

Reagent: Neutral Iron(III) chloride solution.

Observation: A violet (or purple) colouration

5. Significance:

- In low concentrations, phenol is used as a disinfectant in house hold cleaners and mouthwash.
- In ancient days, phenol was used as a surgical antiseptic.