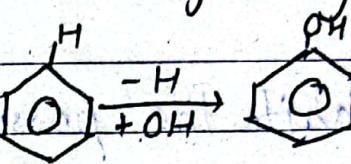


## PHENOLS:

### Q. Define phenols.

Ans: Phenols are the arene derivatives of aromatic hydrocarbons in which hydroxyl group (-OH) is directly attached to an aromatic ring. They are also known as hydroxy benzene or carbolic acid.



General formula: Ar-OH

Molecular formula: C<sub>6</sub>H<sub>5</sub>OH

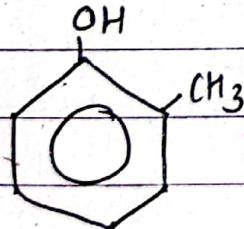
### Q. Classification of phenols.

Ans: Depending upon the no. of hydroxyl group attached to benzene ring, phenols are classified into following types:-

#### a) Monohydric phenols.

→ Phenols containing only one hydroxyl group.

i.e;

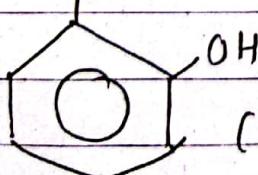


(2-methylphenol)

#### b) Dihydric phenols.

→ Phenols containing two (-OH) hydroxyl groups.

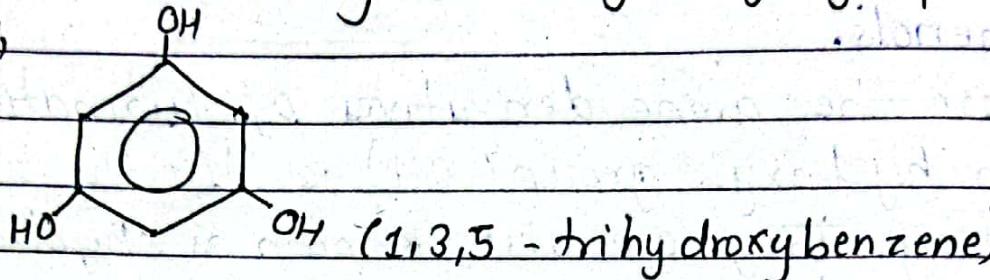
i.e;



(1,2-dihydroxybenzene).

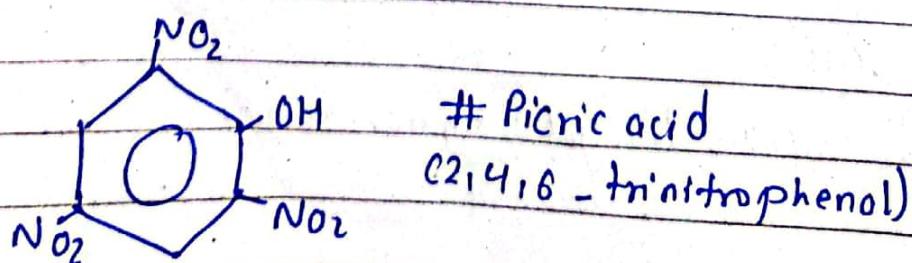
c) Trihydric phenols.

→ Phenols containing three hydroxyl groups.  
i.e;



Q. Write the possible isomers of  $C_7H_8O$  (phenols).

Ans:	Isomers	IUPAC	Common name
		2-methyl phenol	ortho-cresol.
		3-methyl phenol	meta-cresol.
		4-methyl phenol	para-cresol.



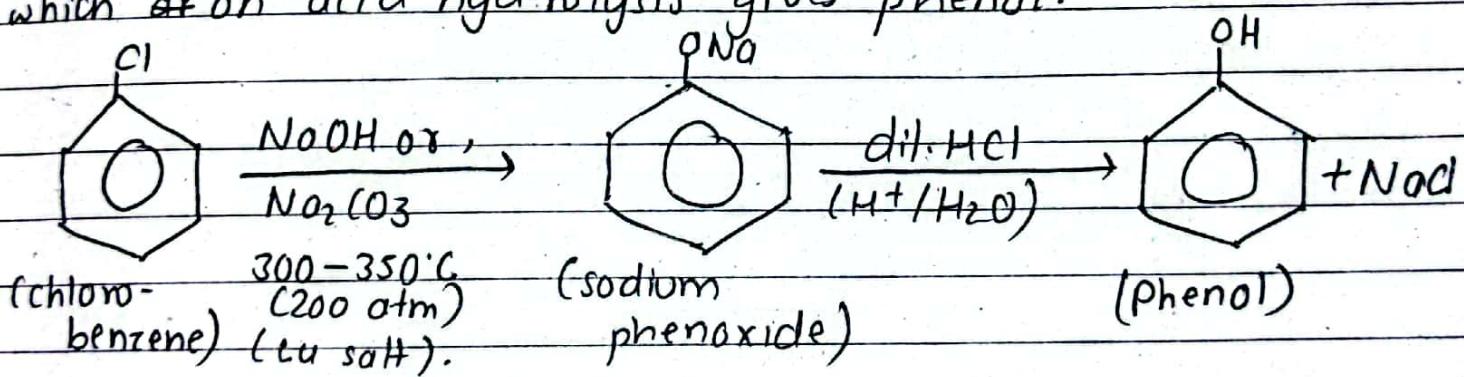
## General methods of preparation.

Phenol can be prepared from:

- i: Chlorobenzene.
  - ii: Benzene diazonium chloride. (BDC).
  - iii: Benzene sulphonic acid.

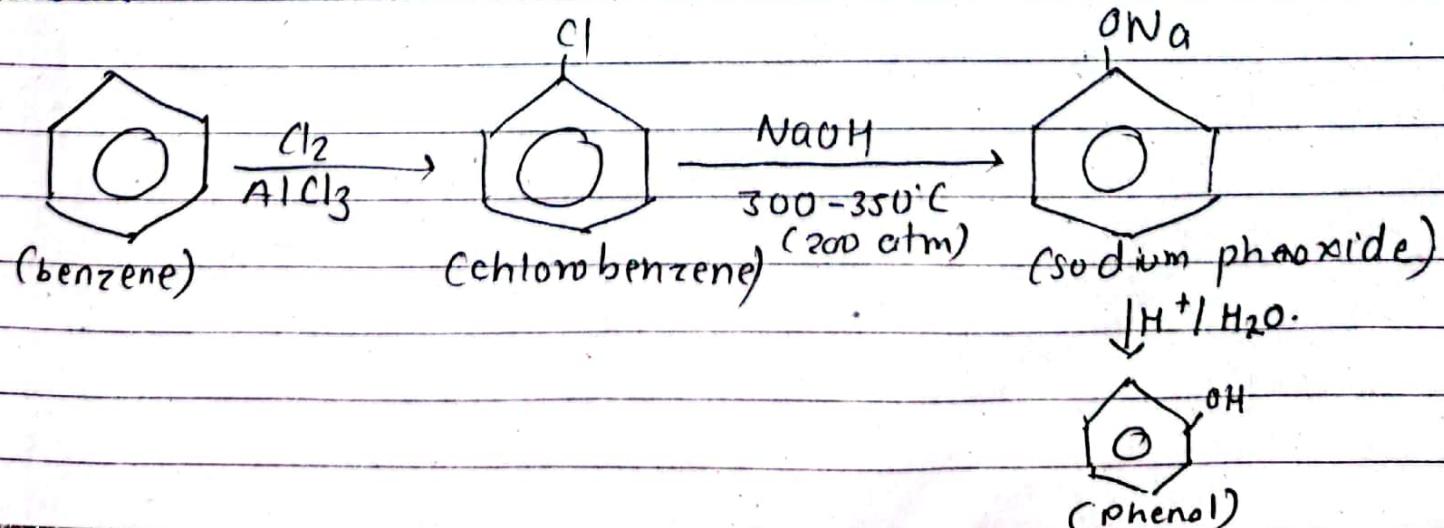
I. From chlorobenzene (Industrial method) (Dow's process);

→ When chlorobenzene is treated with NaOH at a temperature of 300-350°C at 200 atm, sodium phenoxide is obtained which on acid hydrolysis gives phenol.

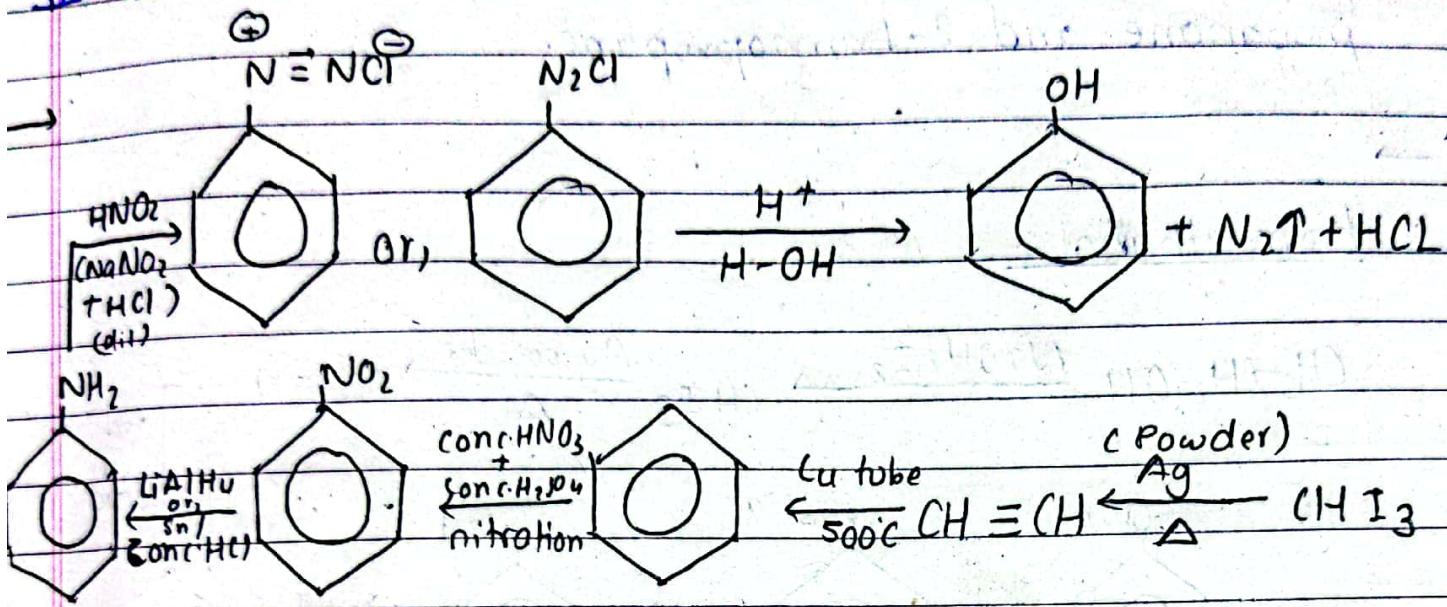


Q. How would you prepare phenol from:-

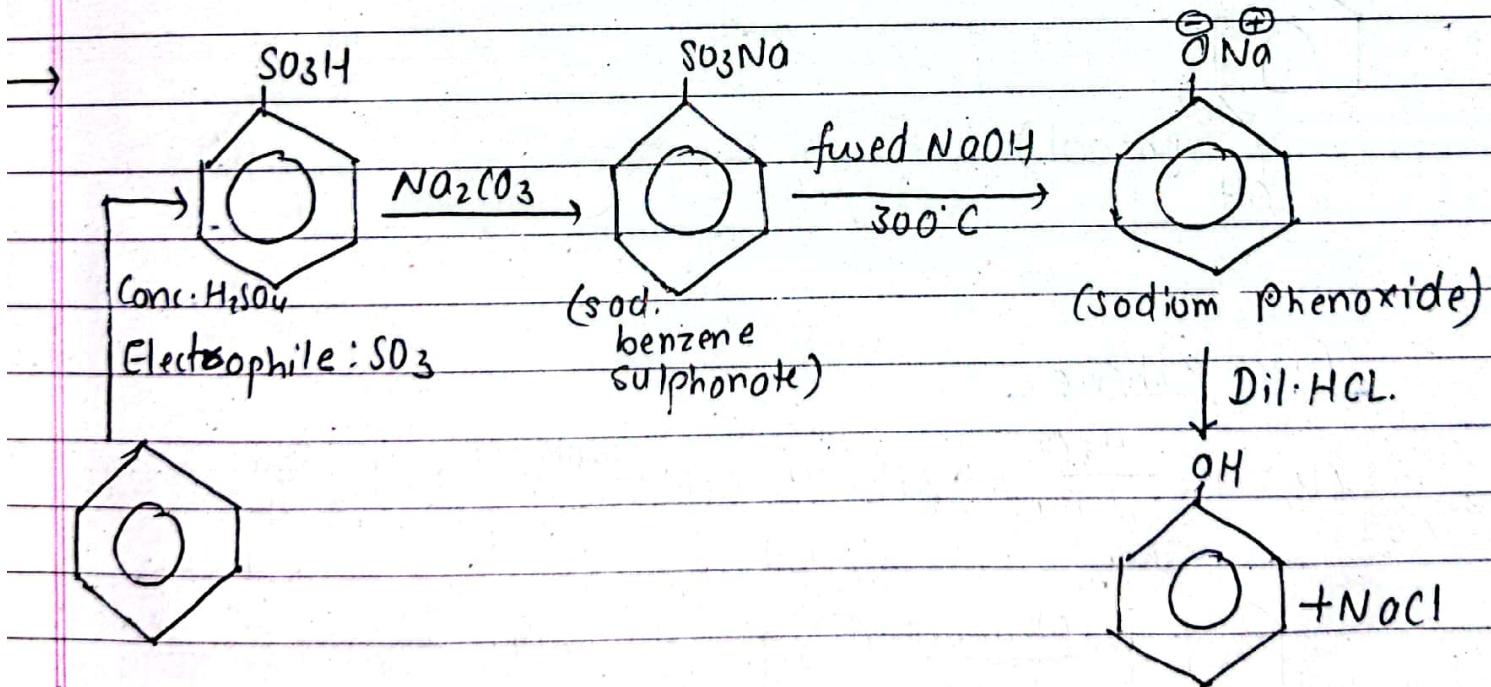
### a. Benzene.



## II: From benzenediazonium chloride (BDC).



## III. Benzene sulphonic acid.



## PHYSICAL PROPERTIES:

### 1. Physical state:

State: liquid or solid.

Odour: Colourless.

Odour: characteristic carbolic smell.

carbolic acid: 95% phenol + 5% water.

### 2. Solubility:

→ Phenol is slightly soluble in water due to formation of intermolecular  $\mu$ -bonding with water.

Intermolecular H-bonding

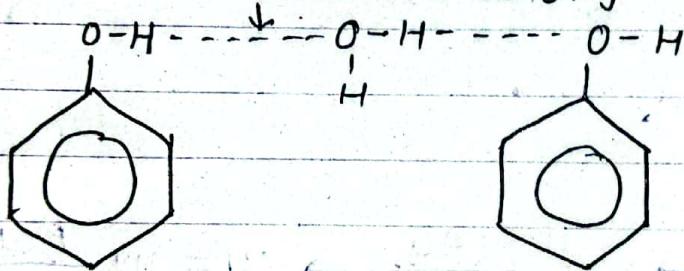


fig: Intermolecular H-bonding of phenol with water

### 3. Boiling point:

→ Phenol has higher boiling point than aromatic hydrocarbons having comparable molecular mass due to presence of molecular H-bonding between phenol molecules.

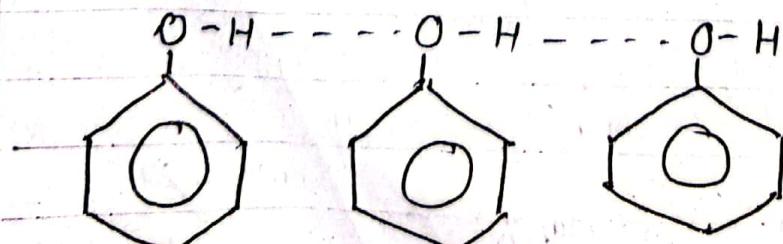
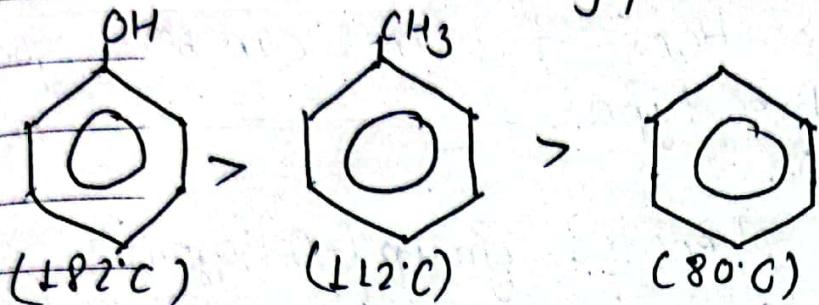


fig: Intermolecular H-bonding of phenol molecules.

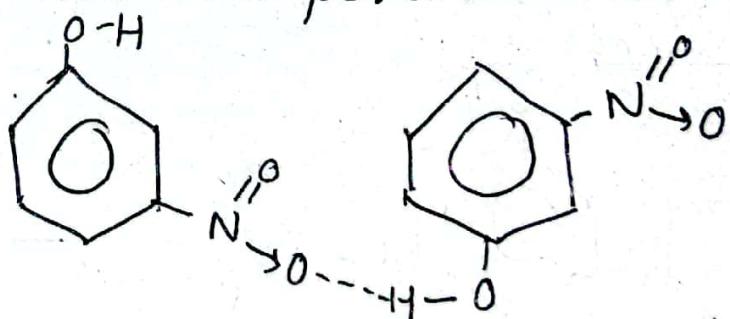
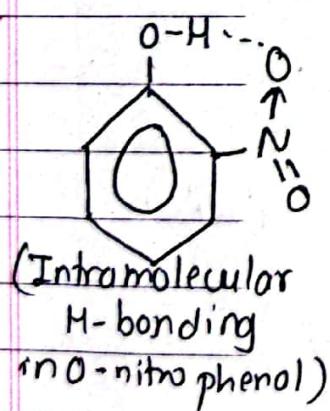
Due to this reason, boiling point decreases as:



(Bpt of nitrophenols)

g. O-nitrophenol has less boiling point (less solubility) than meta and para isomers. Give reason.

→ O-nitrophenol has intermolecular H-bonding and m-nitrophenol and p-nitrophenol form intermolecular H-bonding. Therefore, O-nitrophenol acts as monomer and has less mass whereas, p-nitrophenol or m-nitrophenol acts as polymer having higher mass. Hence, O-nitrophenol has less b.pt. than meta and para isomers.



## (Intermolecular H-bonding in m-nitrophenol molecules)

Since, O-nitrophenol has intra-molecular H-bonding, it cannot form bond with water molecules; P-nitrophenol and m-nitrophenol can form intermolecular H-bonding with water molecules. Hence, O-nitrophenol is sparingly soluble in water.

## CHEMICAL PROPERTIES:

→ The chemical reactions of phenol can be categorized into following three types:

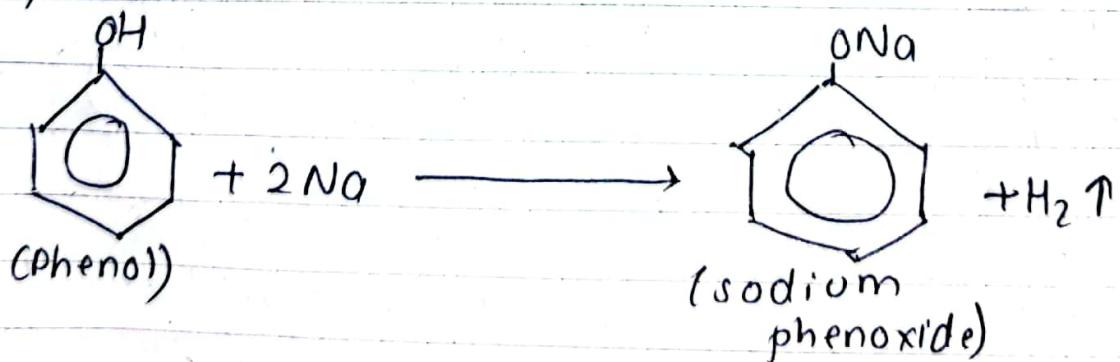
1. Reactions due to phenolic group (-OH group).
2. Reactions due to aromatic ring (electrophilic substitution).
3. Special reactions.

### 1. Reactions due to phenolic group (-OH group)-

Q. What happens when phenol is treated with:

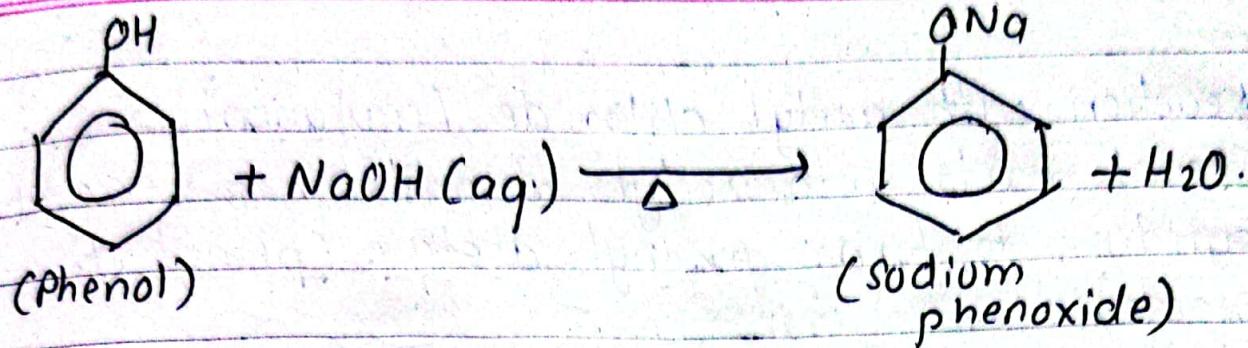
a. Active metals like Na.

→ When phenol reacts with active metal like Na, sodium phenoxide is formed along with hydrogen gas.  
i.e;



b. Reaction with  $NaOH$ .

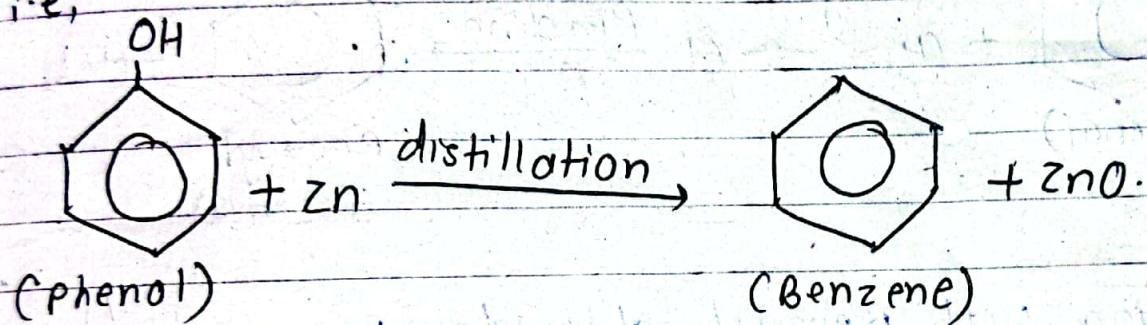
→ Phenol reacts with aqueous alkali to give sodium phenoxide salt and water.  
i.e;



#### c. Reaction with Zn.

→ Phenol reacts with distilled with Zn, benzene is formed.

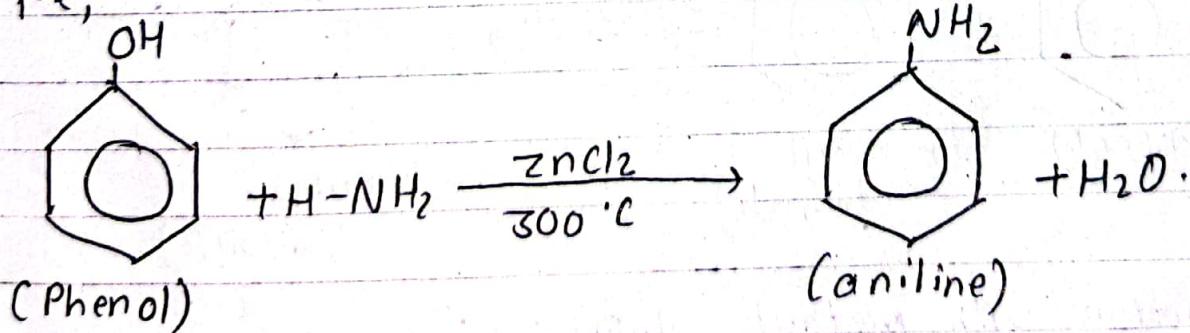
i.e;



#### d. Reaction with ammonia.

→ When phenol reacts with ammonia at about  $300^\circ\text{C}$  in presence of  $\text{ZnCl}_2$ , aniline is formed.

i.e;

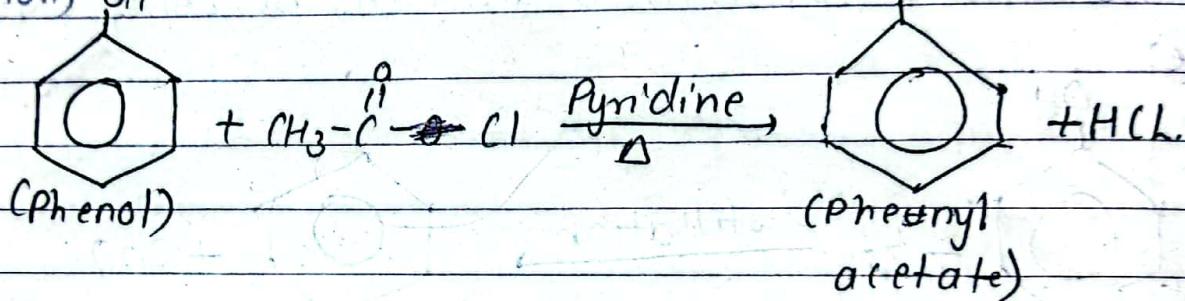


e. Reaction with acetyl chloride (Acylation)

→ Phenol reacts with acetyl chloride in presence of pyridine to form phenyl acetate (phenyl ethanoate).

Example:

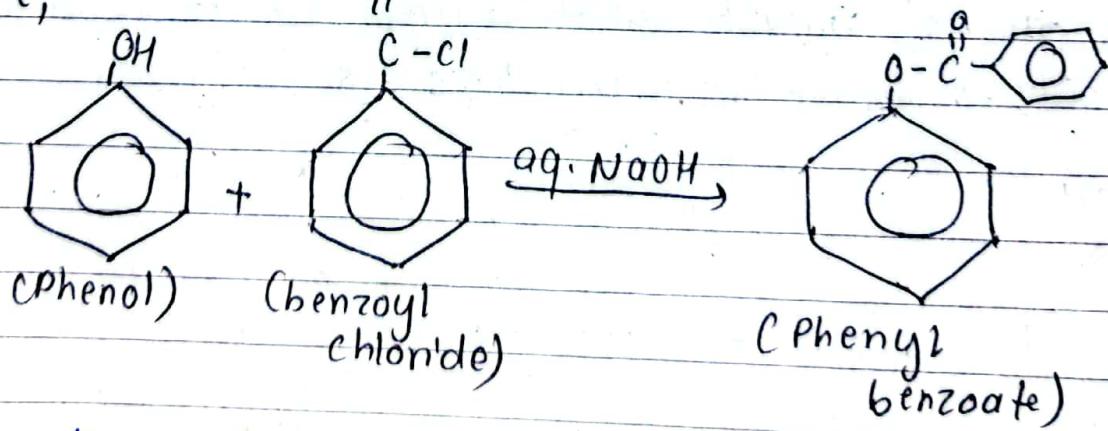
(Esterification) OH



f. Reaction with Benzoyl chloride (Benzoylation)

→ Phenol reacts with benzoyl chloride in presence of 9g. NaOH to give phenyl benzoate.

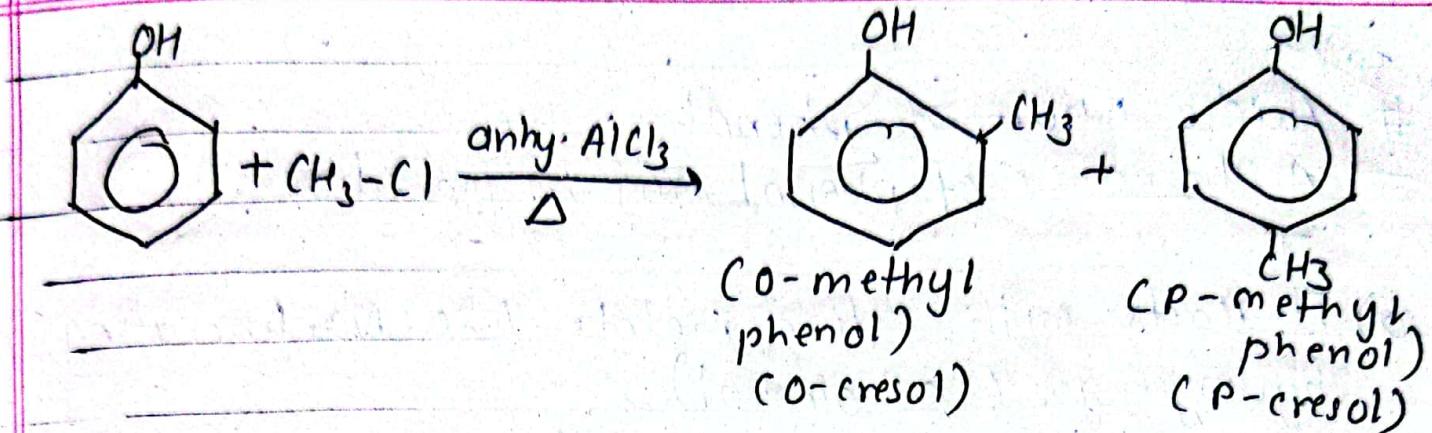
i.e;



g. Reaction with methyl chloride.

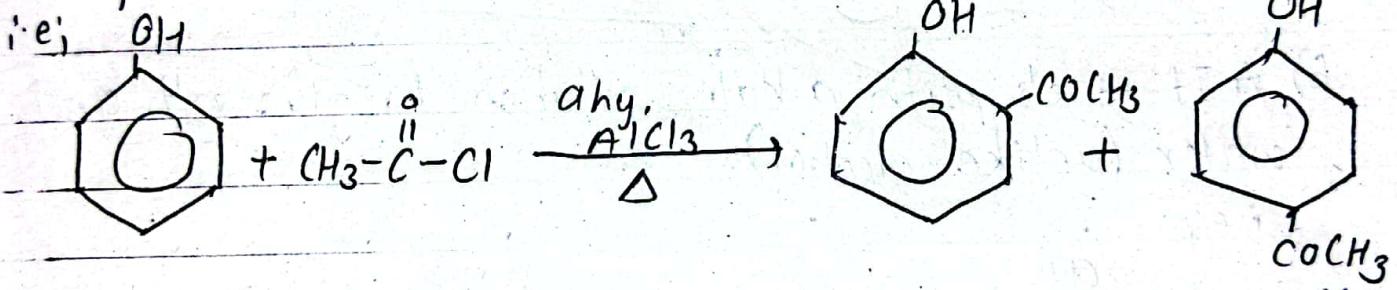
→ When phenol reacts with methyl chloride in presence of anhy.  $\text{AlCl}_3$ , ortho and para-methyl phenol are formed.

i.e;

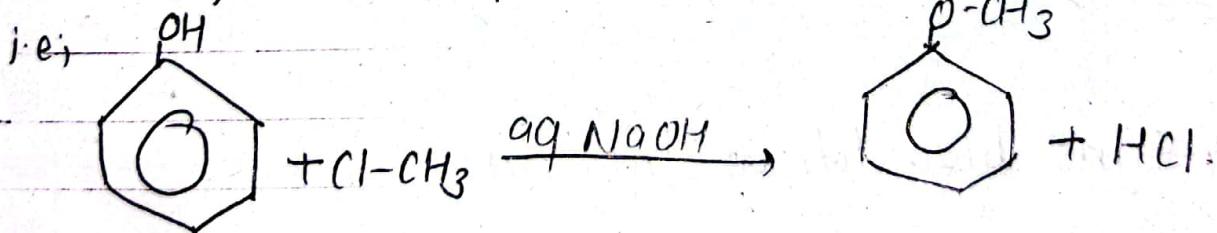


### NOTE:

- \* Phenol reacts with acetyl chloride in presence of anhy.  $\text{AlCl}_3$  to form  $\alpha$ -hydroxy acetophenone and  $\rho$ -hydroxy acetophenone.



- \* When phenol reacts with chloromethane; methyl phenyl ether is formed in presence of alkaline solution.



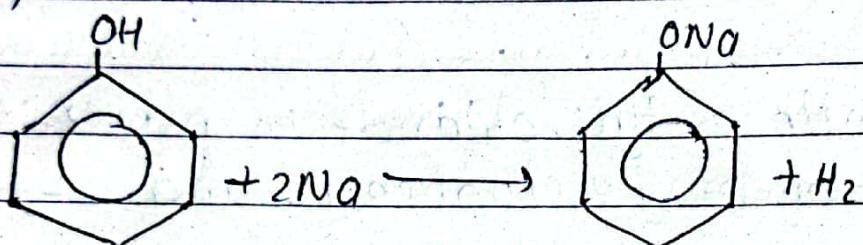
~~V.V.T.M.P.~~

# Acidic nature of phenol.

→ Acidic nature of phenol can be proved as:

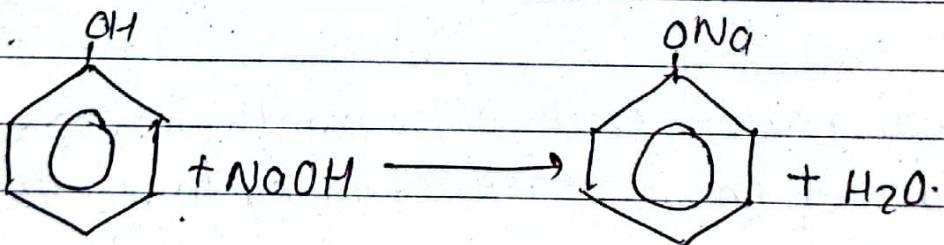
a) It reacts with active metals like; Na, liberating hydrogen gas (like alcohol).

i.e;



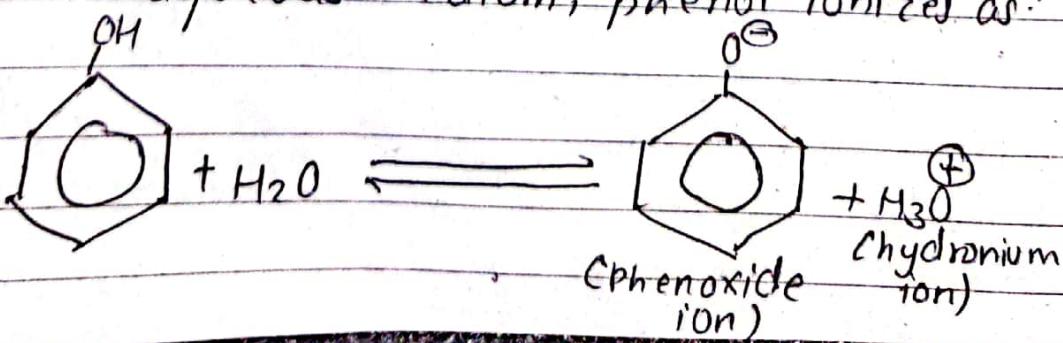
b) It reacts with alkali solution to give salt and water (unlike alcohol).

i.e;

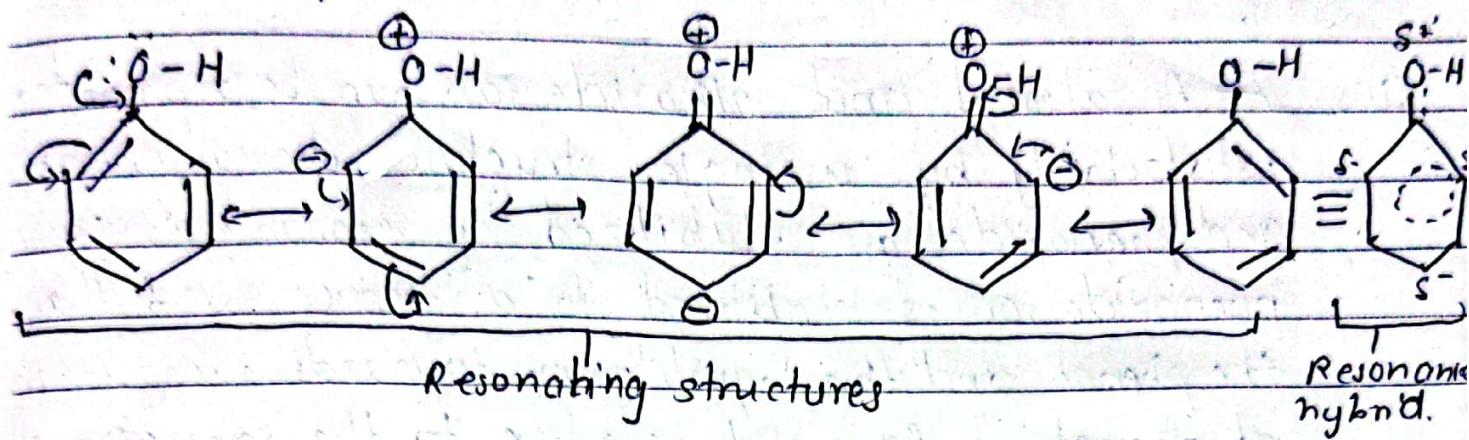


c) It turns blue litmus into red.

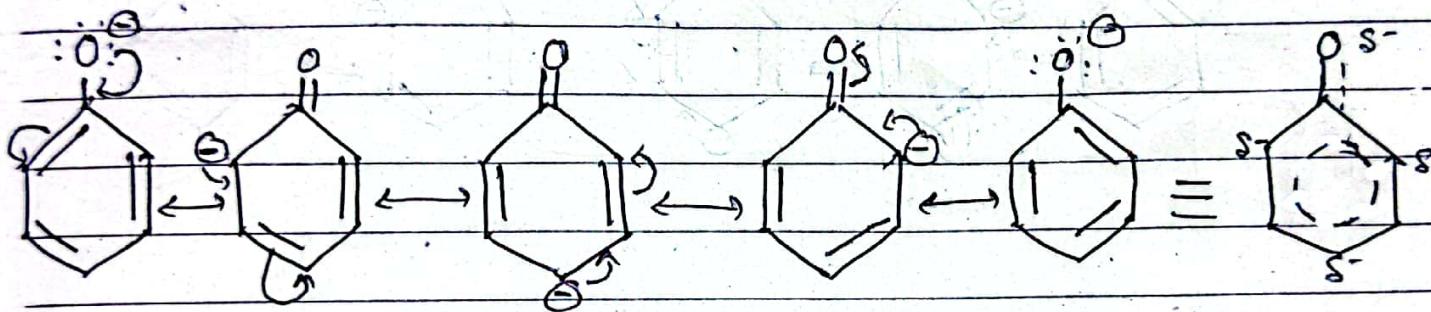
The acidic nature of phenol can be explained on the basis of resonance of phenol and phenoxide ion. In aqueous medium, phenol ionizes as:



d) Resonance in phenol :-



Resonance in phenoxide ion :-



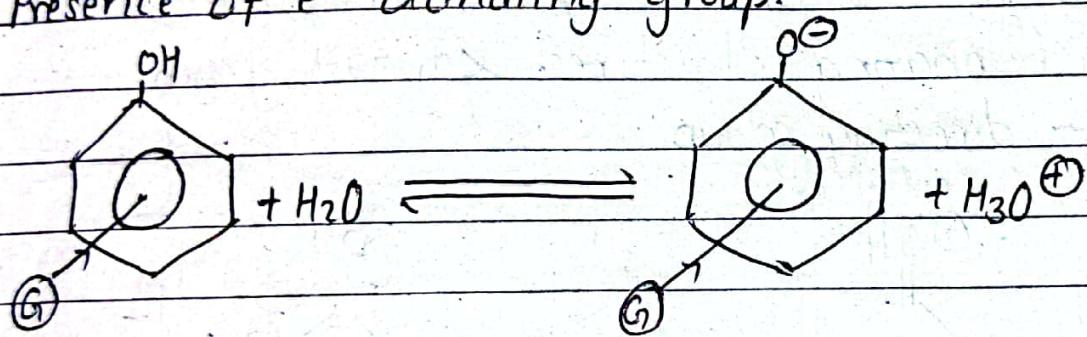
Since, there is charge separation of phenol which makes it less stable than phenoxide ion as there is no charge separation in phenoxide ion. It means phenol has tendency to release  $H^+$  ion showing acidic nature.

## # Effects of substituents on acidity of phenols.

→ Ionic factor which stabilizes the phenoxide ion will increase the acidity of phenolic compounds and vice-versa.

The effect of substituents on acidity of phenols can be explained on the basis of following factors:-

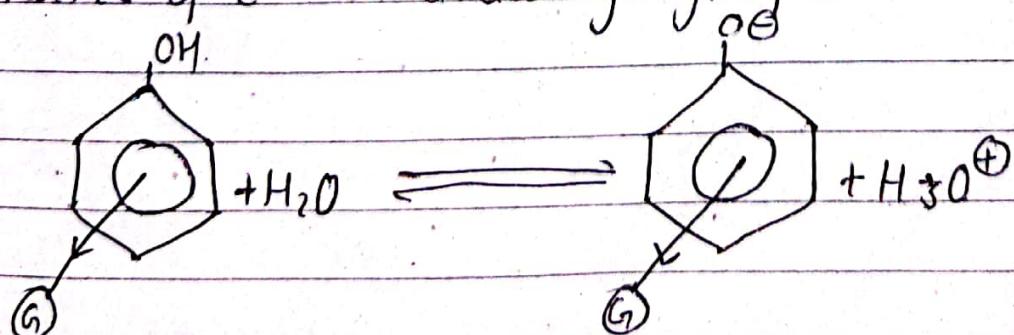
i) Presence of  $e^-$  donating group.



$\textcircled{G}$  =  $e^-$  donating group  
= destabilizes the phenoxide ion }  $d^3$ .  
= decreases acidity

Thus, phenol is more acidic than cresol.

ii) Presence of  $e^-$  withdrawing group.



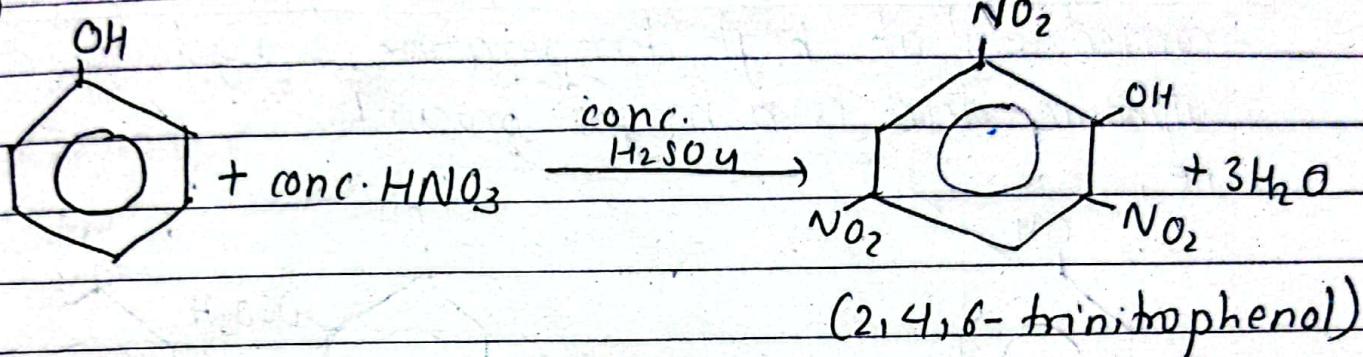
$\textcircled{G}$  =  $e^-$  withdrawing group = increases acidity } WIS  
= stabilizes the phenoxide ion

## # Electrophilic substitution reaction of phenol:

y. IMP

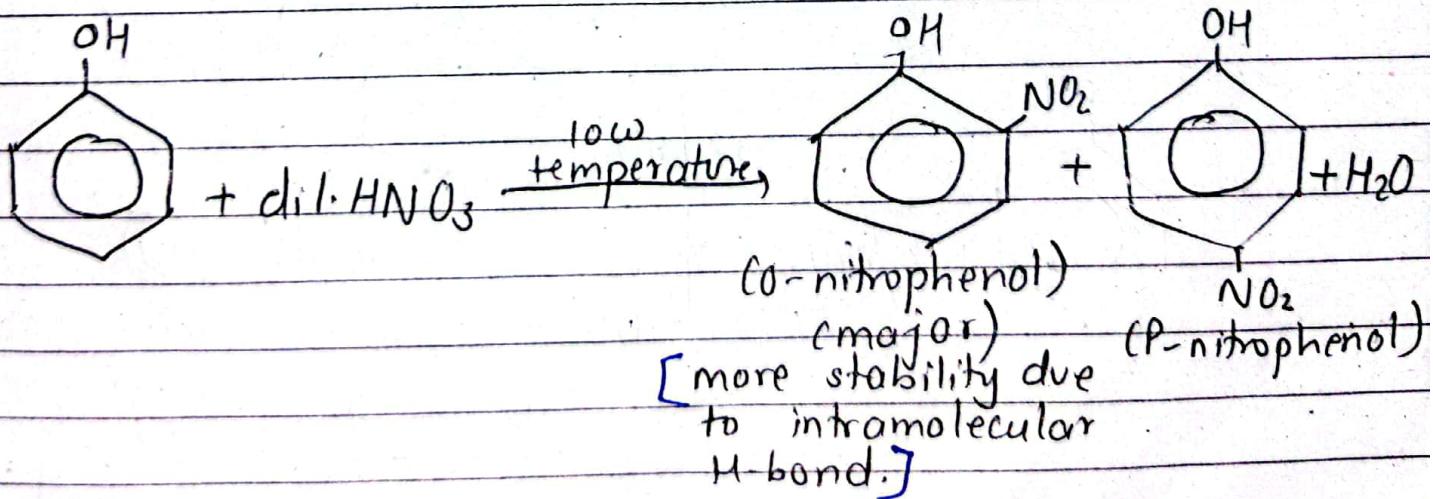
### i. Nitration.

→ When phenol is treated with conc.  $\text{HNO}_3$  in presence of conc.  $\text{H}_2\text{SO}_4$  2,4,6-trinitrophenol (Picnic acid) is formed.  
i.e;



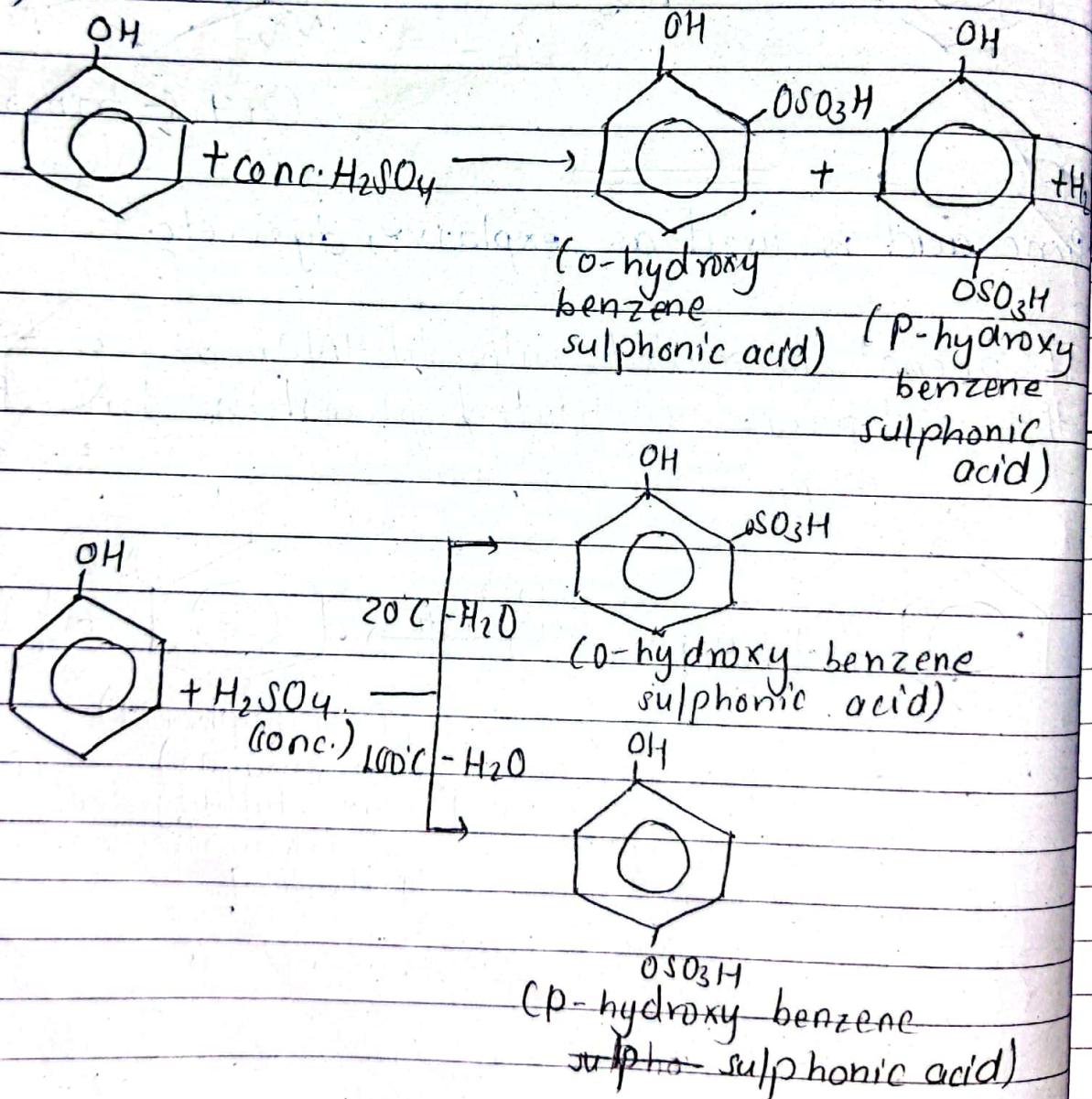
\* Picnic acid is used as explosive, dyes, etc.

If phenol is treated with dil.  $\text{HNO}_3$  at low temperature ortho- and para- substituted phenol are formed.



## 2. Sulphonation.

→ When phenol is treated with conc.  $H_2SO_4$ , a mixture of ortho- and para-hydroxybenzene sulphonic acid is formed. If sulphonation is carried out at low temperature  $O$ -hydroxybenzene sulphonic acid is major product and if sulphonation is carried out at high temperature,  $p$ -hydroxybenzene sulphonic acid is a major product.  
ie;

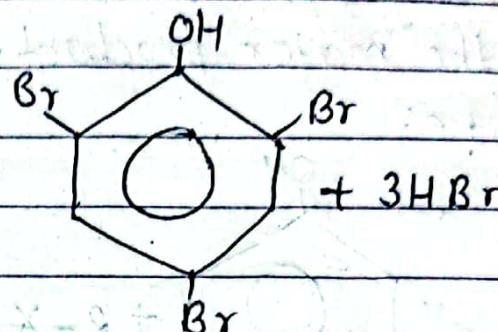
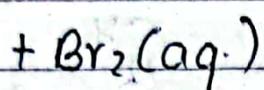
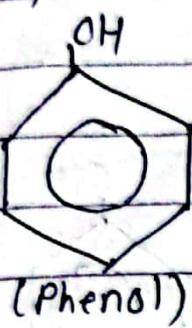


V. Imp

### 3. Halogenation.

→ When phenol is treated with bromine water (i.e; aq. bromine) 2,4,6-tribromophenol is formed.

i.e)

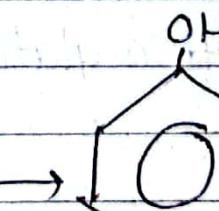
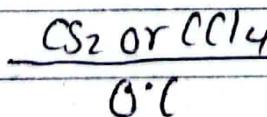
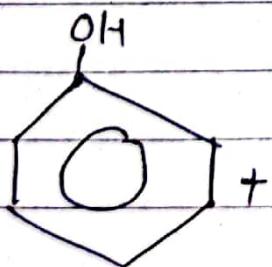


(2,4,6-tribromophenol)  
(white ppt.)

→ Phenol reacts with aqueous chlorine to produce 2,4,6-trichlorophenol.

→ If less polar solvents like:  $\text{CCl}_4$  or  $\text{CS}_2$  are used at low temperature, ortho- and para- substituted halo products are formed.

i.e;

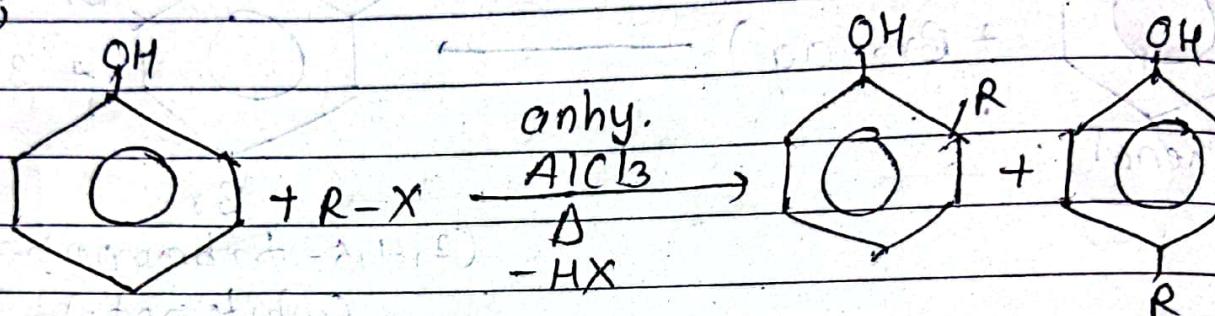


(major)

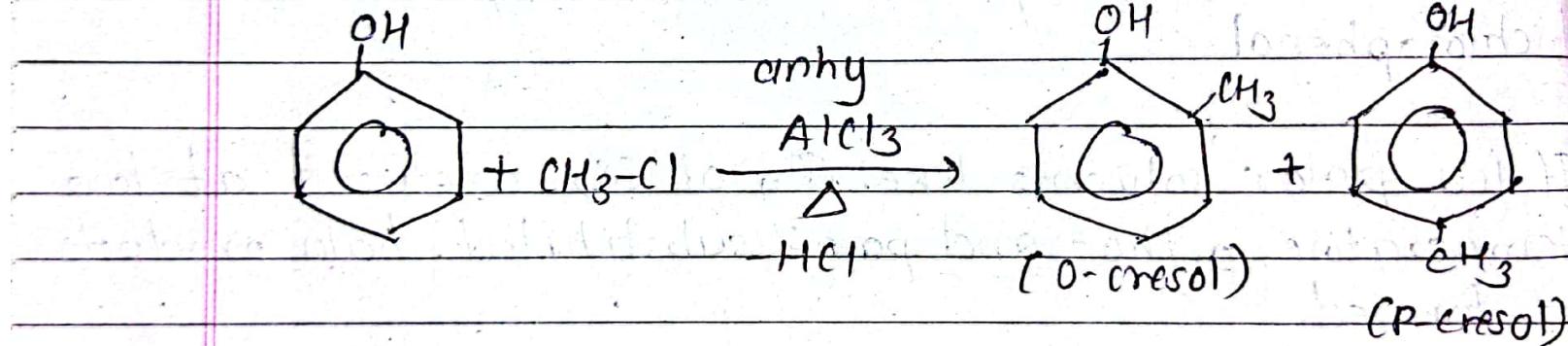
#### 4. Friedel-Crafts alkylation.

→ When phenol is treated with alkyl halide in presence of anhydrous  $\text{AlCl}_3$ , ortho- and para-alkyl phenol are formed. Usually, p-isomers are the major product.

i.e;

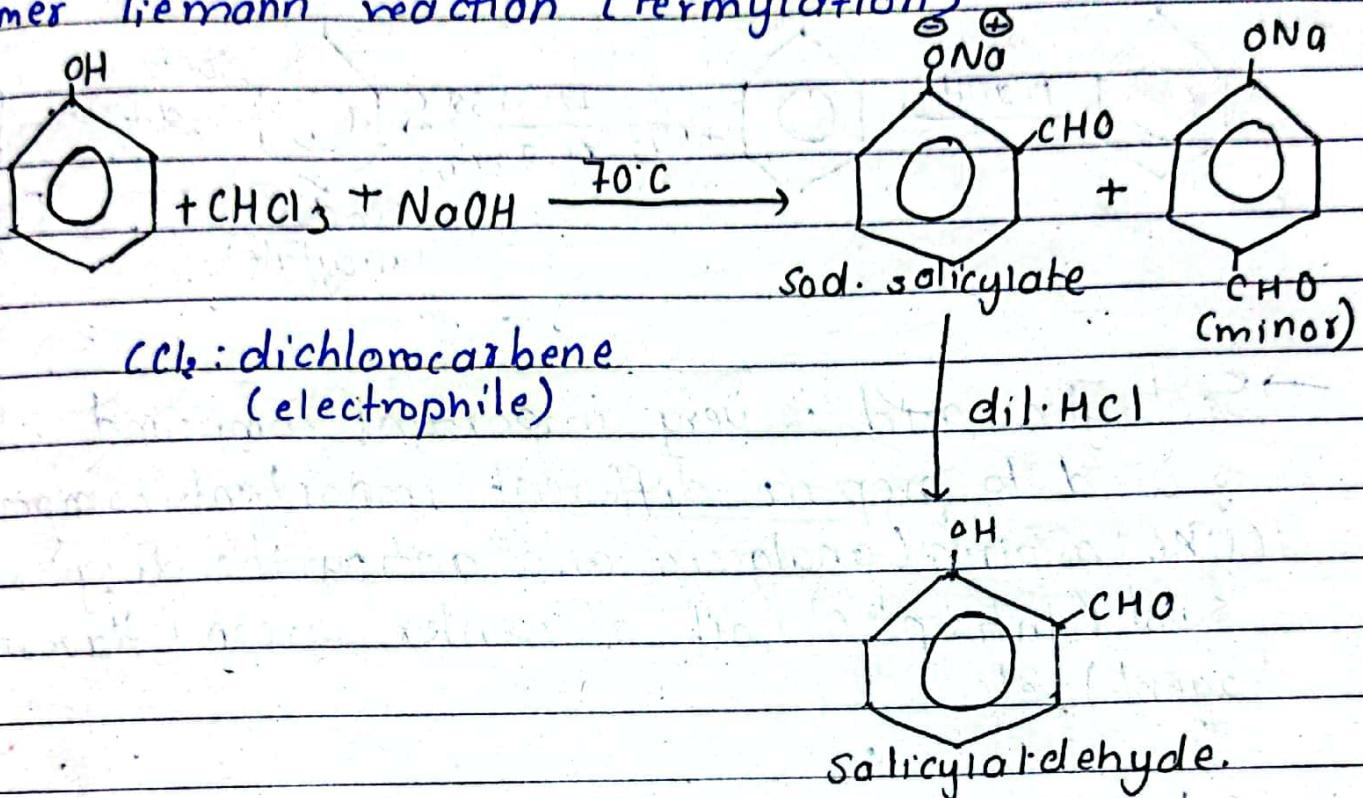


Example:



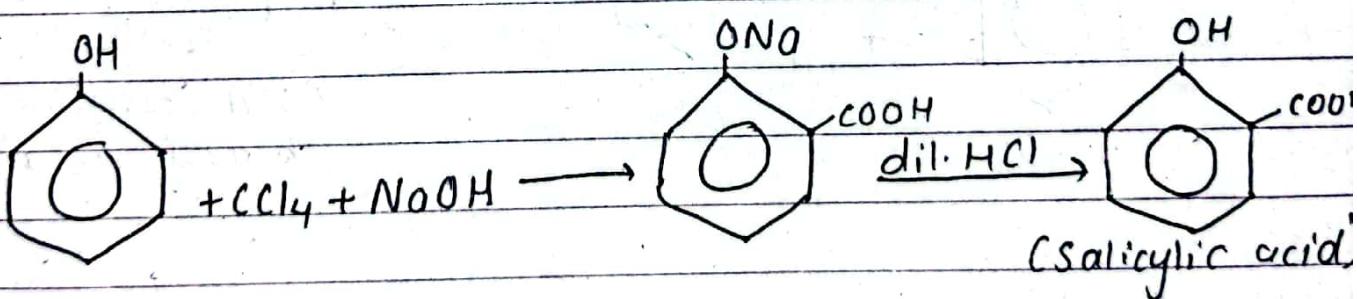
### 3. Special reactions.

#### a. Reimer Tiemann reaction [Fermylation]



VOTE: If  $\text{CCl}_4$  is used instead of  $\text{CHCl}_3$ , salicylic acid is obtained as major product (Carboxylation).

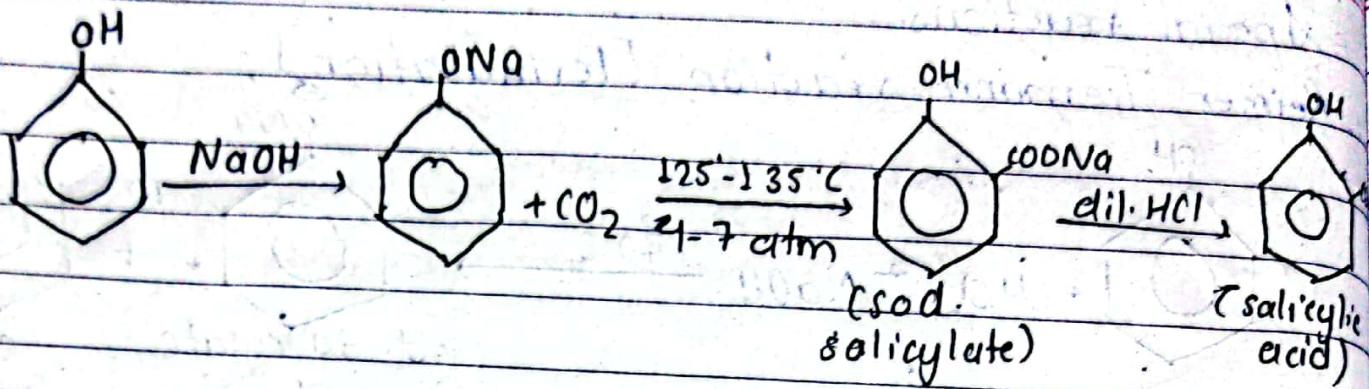
i.e;



#### b. Kolbe's carboxylation.

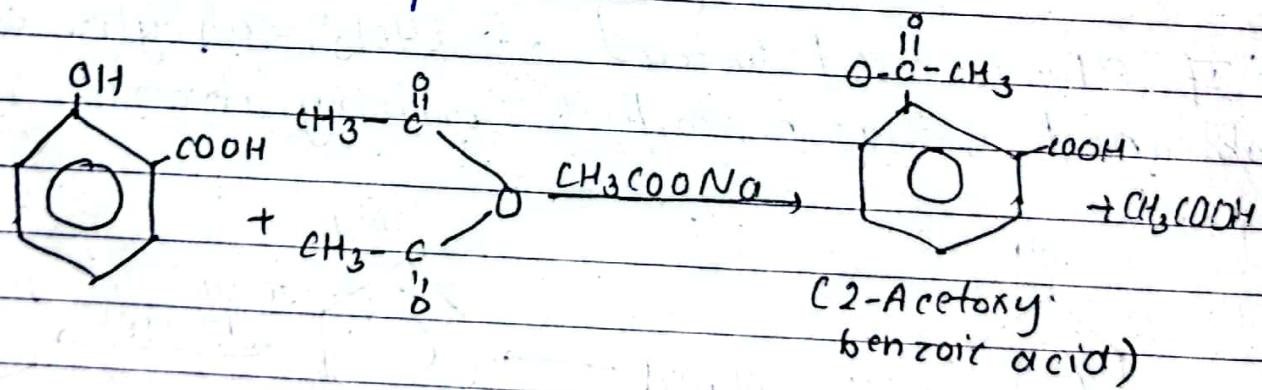
$\rightarrow$  When sodium phenoxide is treated with carbon dioxide at  $125 - 135^\circ\text{C}$  under 4-7 atm pressure, sodium salicylate is obtained which on treating with dil. HCl, salicylic acid is obtained as the major product.

i.e,

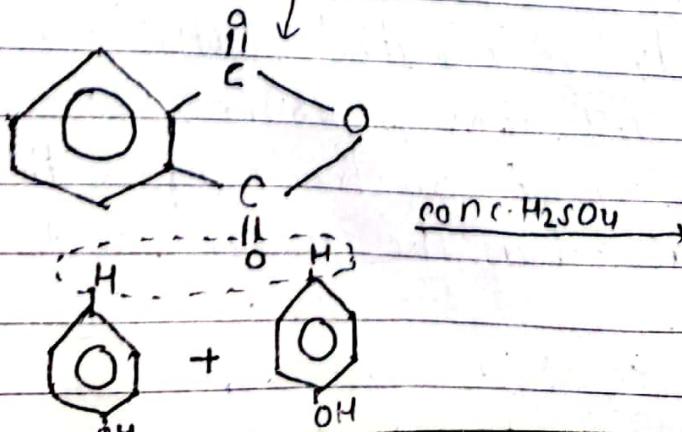


→ Salicylic acid is very important compound which is used to prepare different important compounds like: aspirin (analgesic and antipyretic drug), salol (antiseptic), oil of winter green (flavoring agent), etc.

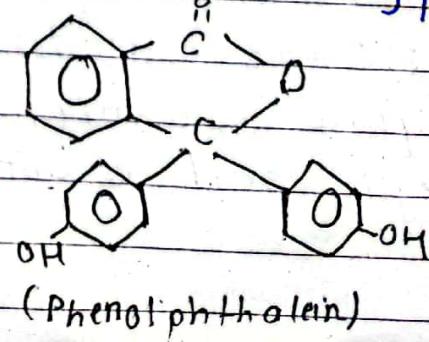
### # Preparation of aspirin.



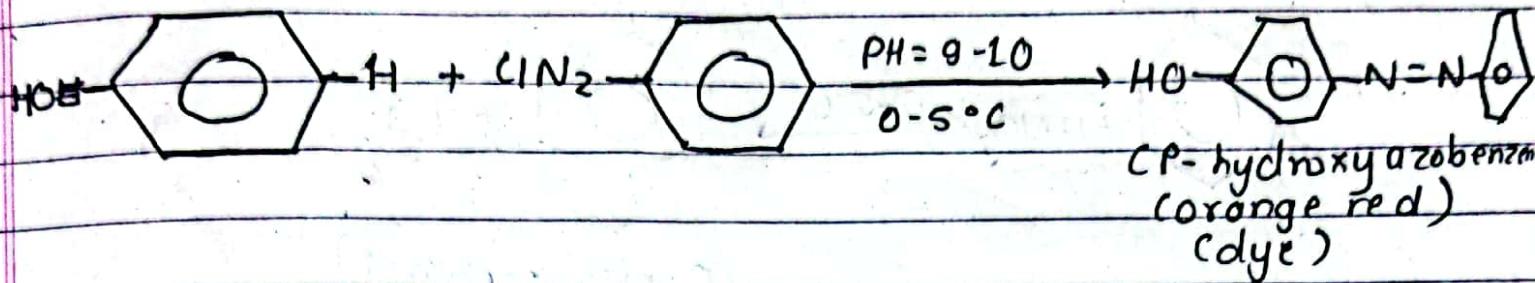
### c. Condensation reaction, (Phthalic anhydride)



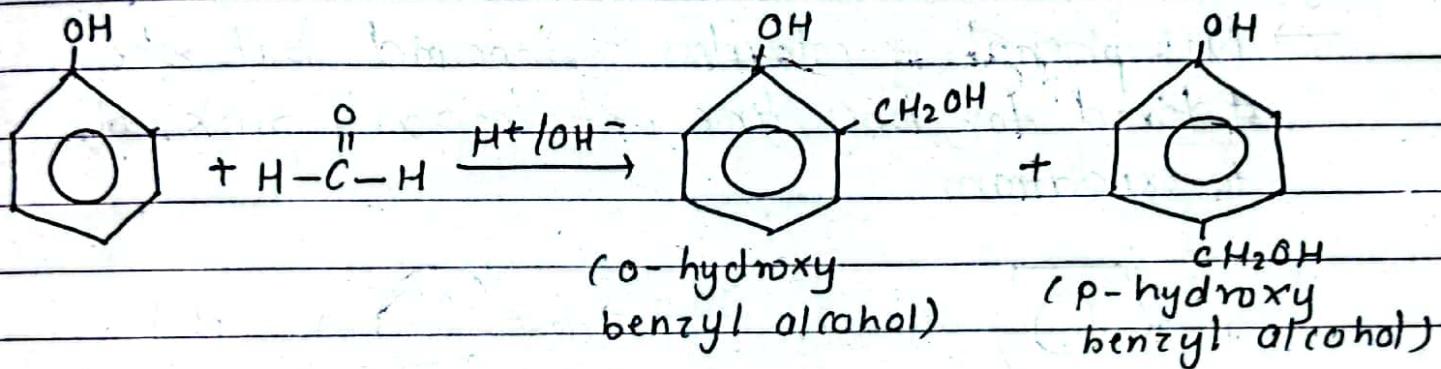
Q. Phenolphthalein is an indicator used in acid base titration. How would you prepare phenolphthalein using phenol?



### d. Coupling reaction.

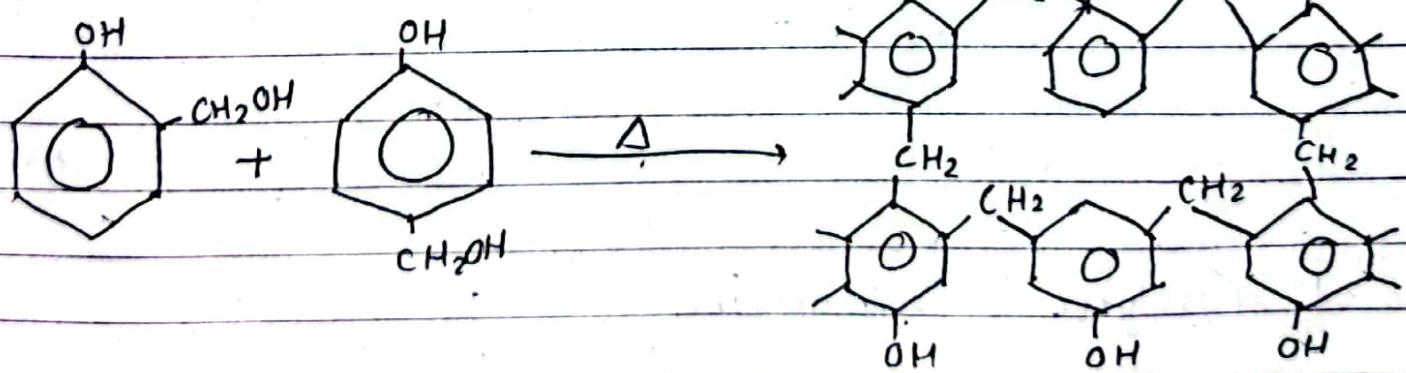


### e. Reaction with formaldehyde.



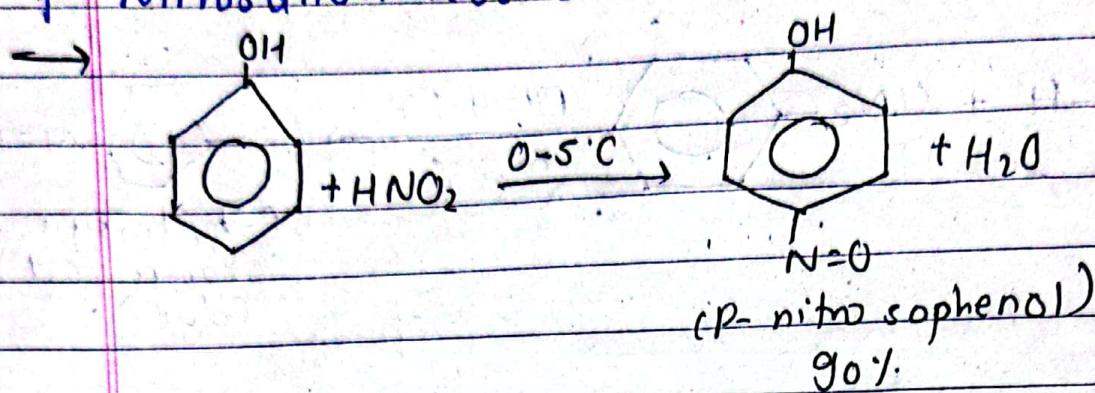
Thus, obtained benzyl alcohol undergoes polymerization to form bakelite i.e; thermosetting plastic at elevated temperature.

i.e;



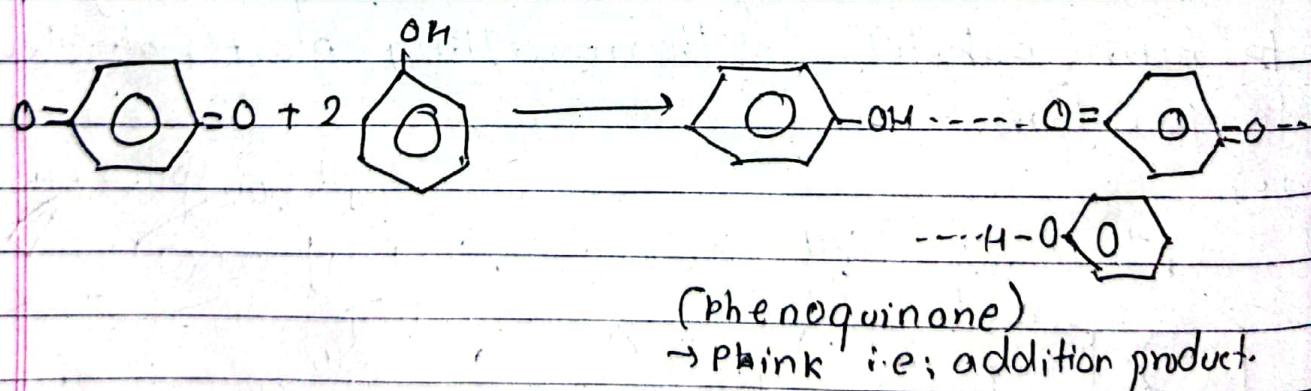
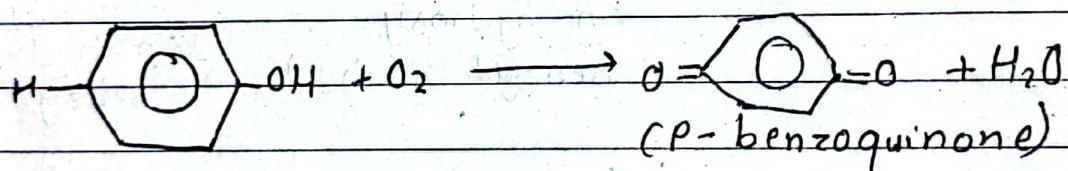
Q. Bakelite is a thermosetting plastic which has wide application. How can you prepare bakelite from phenol?

### f. Nitrosation reaction.

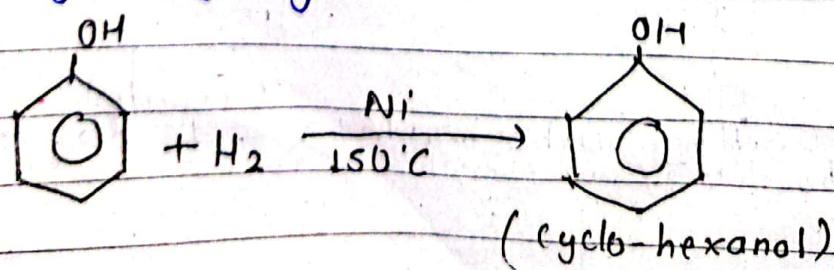


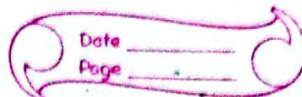
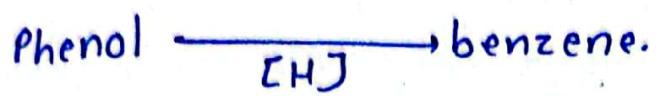
### g. Oxidation.

→ Pure phenol is colourless compound but when it is stored for long time, it imparts pink color due to oxidation.



### h. Catalytic hydrogenation.





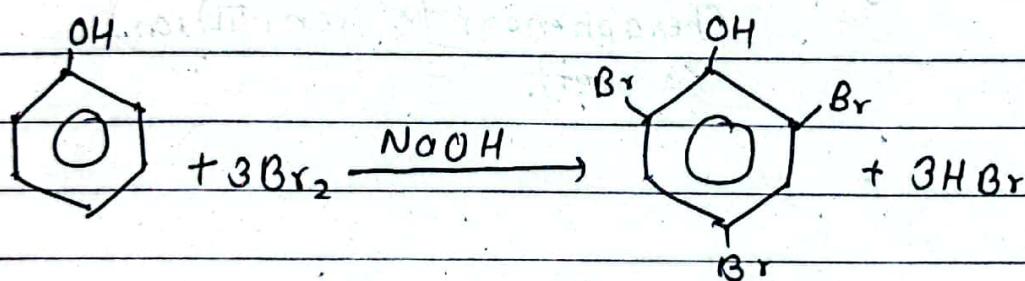
## # Test of phenol.

→ Phenol can be tested in lab by any of the following methods:

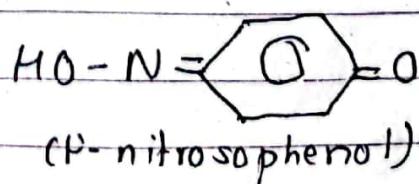
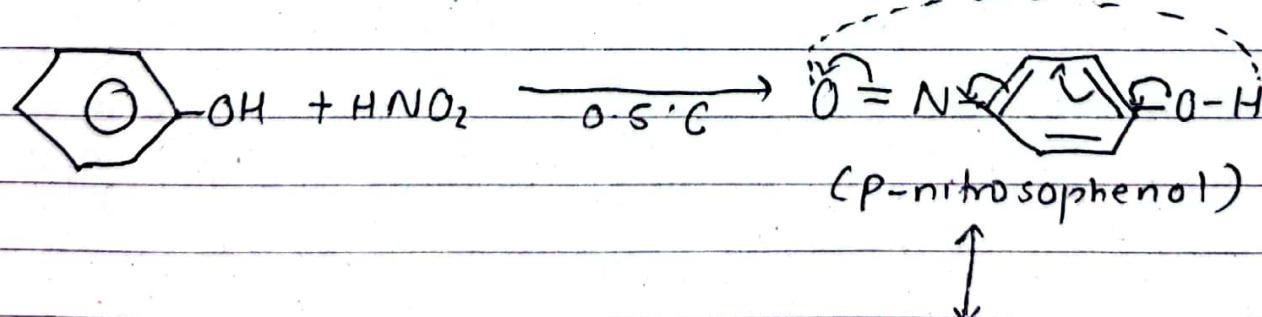
- i.  $\text{Br}_2$  (aq.)
- ii. Libermann's test
- iii. FeCl<sub>3</sub> solution.

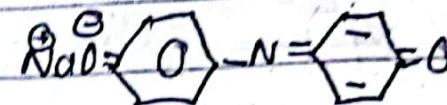
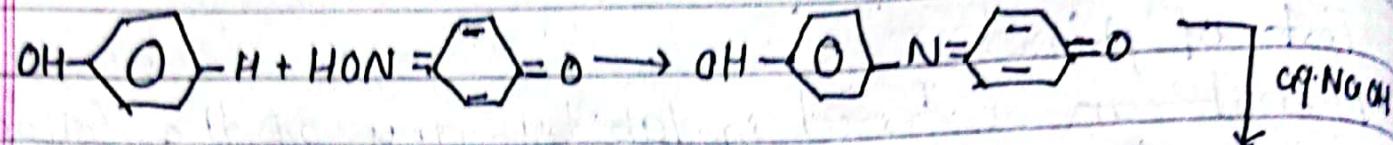
### I. $\text{Br}_2$ (aq.) test.

→ When phenol is heated with aq. bromine, it gives white ppt.



### II. Libermann's test.





(sod. salt of indophenol)  
(blue-green)

### III. FeCl<sub>3</sub> test.

