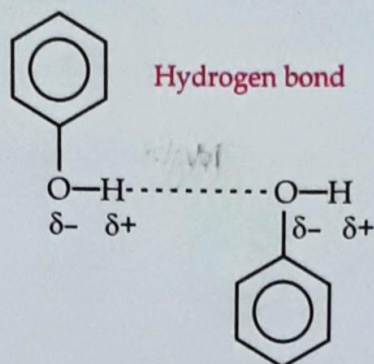


## PHYSICAL PROPERTIES

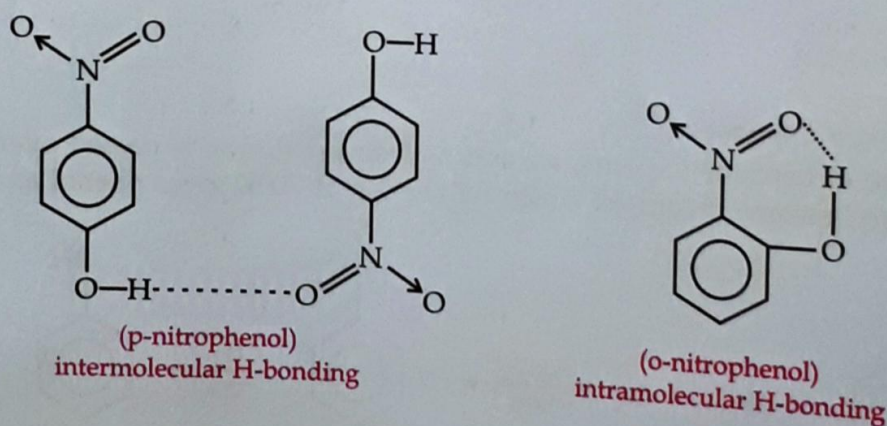
- (i) **Physical state** : Phenols are generally colorless solid or liquid. But they usually turn pink on exposure to air and light as they are hygroscopic in nature.

- (ii) **Boiling points** : Due to the stronger association of molecules by intermolecular hydrogen bonding, phenols have high boiling point than those of corresponding hydrocarbons and aryl halides. For e.g. phenol (m.wt. 94) boils at 455K while toluene (m.wt. 92) boils at 284K only.



- (iii) **Solubility** : Phenol itself and some di and trihydric phenols are somewhat soluble in water since its molecule can form hydrogen bond with water. But the extent of hydrogen bond formation is very small due to the large size of phenyl group which makes the polar character of O-H group. Most other phenols are practically insoluble in water.

It has been noticed that o-nitrophenol has a much lower boiling point and much lower solubility than its meta or para isomer. This can be explained on the basis of the nature of hydrogen bonds and capacity to form hydrogen bonding with water. High boiling point of m- and p- isomers are due to intermolecular hydrogen bonding. Their higher solubility is due to hydrogen bonding with water.



In case of ortho isomer, nearness of  $-\text{NO}_2$  and  $-\text{OH}$  groups leads to the formation of intramolecular hydrogen bonding and not intermolecular hydrogen bonding as shown by m- and p- isomer. So absence of association with other phenol molecules and also absence of hydrogen bonding with water, ortho isomer has a low boiling point and less solubility in water.



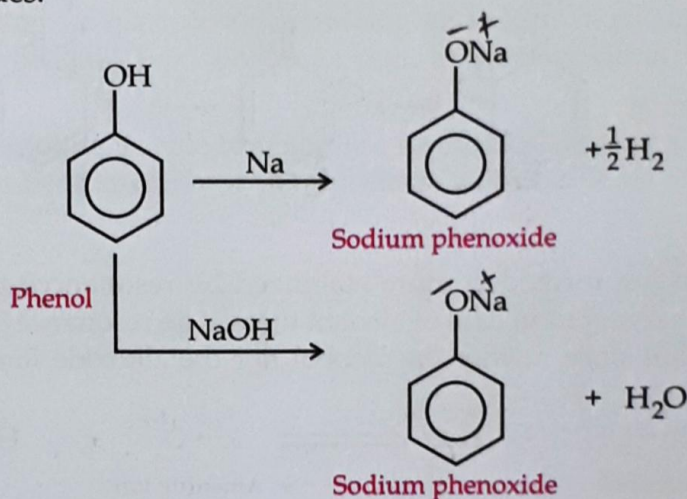
## CHEMICAL PROPERTIES

Reactions of phenol may be divided into following three classes :

- (A) Reactions of the Hydroxyl (phenolic) group (-OH).
- (B) Reactions of the benzene nucleus.
- (C) Special reactions.

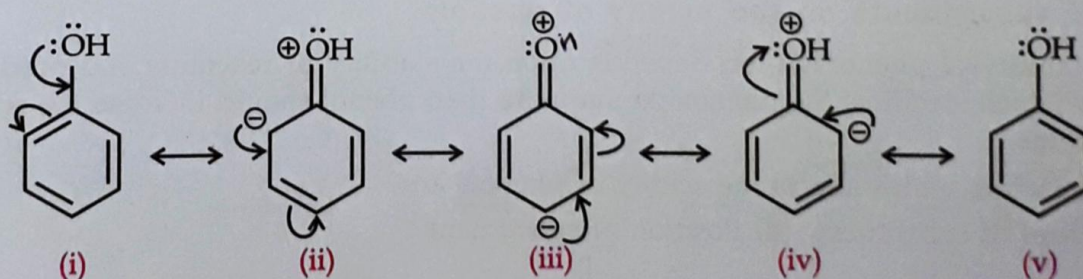
### A. Reactions of the Hydroxyl group

- (i) **Acidic nature** : Phenols are weakly acidic compounds ( $K_a \approx 1 \times 10^{-10}$ ). They turn blue litmus red. They react with sodium metal and aqueous alkali hydroxides to form salt and phenoxides.



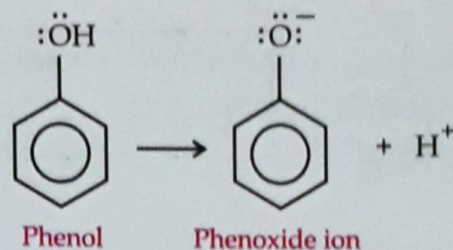
Phenols, however, do not react with carbonate or bicarbonate showing that phenols are weak acids than carbonic acid or carboxylic acid. But **phenols are stronger acids than alcohol** since both are characterised by presence of hydroxyl groups. This can be explained as follows :

Phenols is a resonance hybrid of following canonical structures.

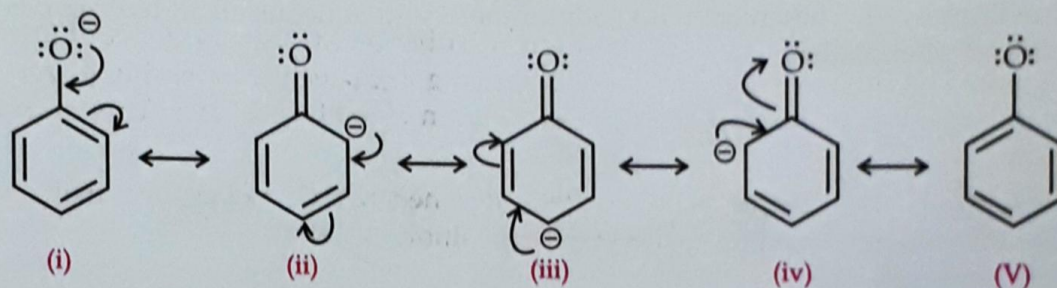


The oxygen atom of phenol acquires a partial positive charge due to resonance contribution of structures (ii), (iii) and (iv). As a result, it attracts the electron pair of the O-H bond, thereby facilitating the release of  $H^+$ .

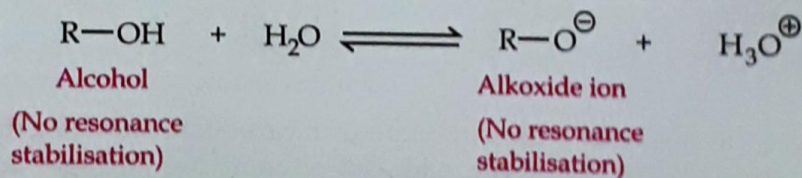




Phenoxide ion is also a resonance hybrid of following contributing structures.



The phenoxide ion formed is more stabilized by resonance than phenol due to dispersal of negative charge. But in case of alcohol there is no resonance stabilization of alkoxide ion relative to alcohol since neither the alcohol nor the alkoxide ion exhibits resonance.



Hence phenols ionise more readily to form phenoxide ion. In other words phenols are more acidic than alcohols.

### Effects of substituents on the acidity of phenols

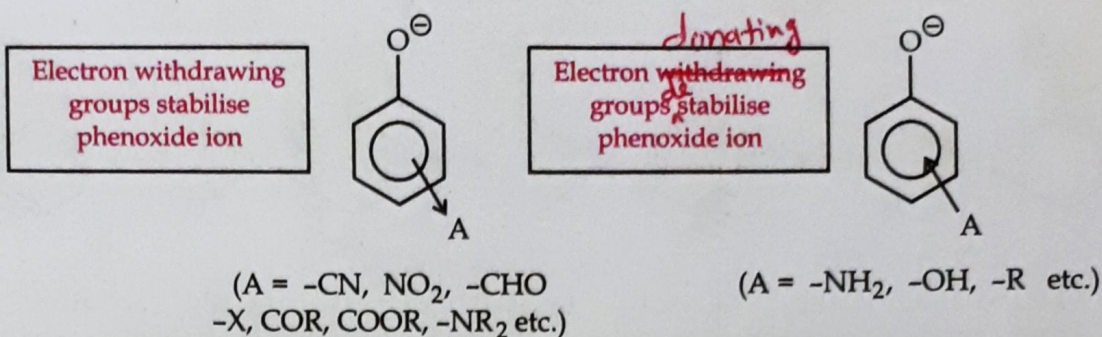
The stability of phenoxide ion depends upon the stability of reactants and products. Any factor which stabilises the phenoxide ion more than phenol should increase the acidity and vice-versa.

So the factors which affects the acidity of phenols are

(i) Nature of substituent (ii) Position of substituent

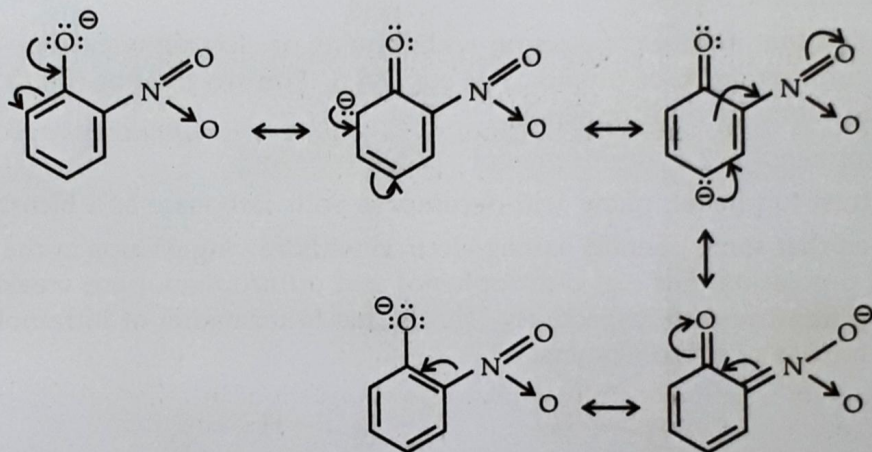
- (i) **Nature of substituent** : Electron withdrawing substituents such as  $-\text{NO}_2$ ,  $-\text{CN}$ ,  $-\text{X}$  (Cl, Br, I) etc. stabilise the phenoxide ion by the dispersal of negative charge on it and thus increase the acidity of phenols. Whereas electron releasing groups such as  $-\text{NH}_2$ ,  $-\text{OH}$ , R etc. destabilise the phenoxide ion by increasing the negative charge on it and thus decrease the acidity of phenols.



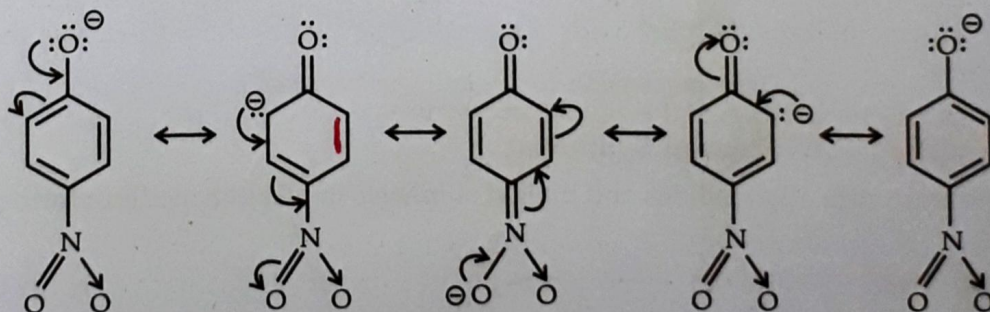


**(ii) Position of substituent :** The position of substituent also influence the acidity of phenol. The presence of electron withdrawing and electron releasing group is more pronounced at ortho and para positions than at meta position. This is due to the resonance effect.

A nitro group, for example, is able to delocalise negative charge on phenoxide ion more effectively. When it is present at ortho or para position as below :-

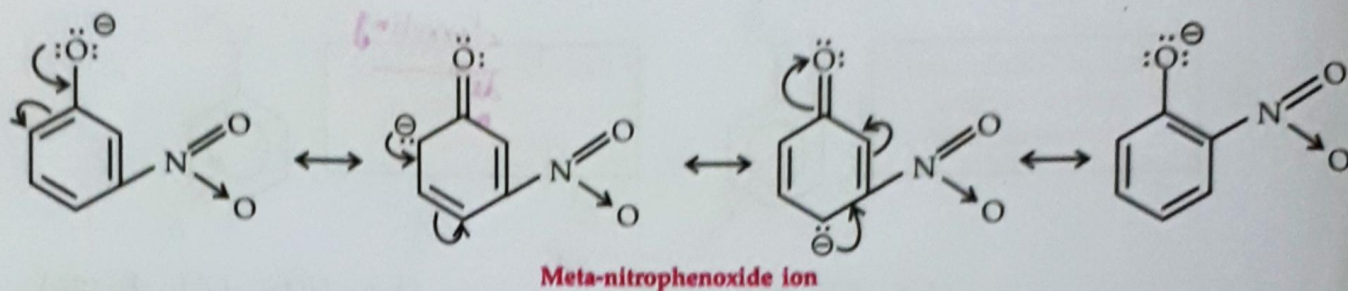


Ortho Nitrophenoxide ion



Para-nitrophenoxide ion





From the above resonating structures, it may be seen that in each of o- and p- nitro phenoxide ions conjugation is extended upto oxygen atom of nitro group. But no such conjugation is possible for m-nitro phenoxide ion, so m-nitrophenoxide ion has only four contributing structures. That's why greater resonance stabilisation occurs in o- and p-anions than the m-isomer. As such o- and p-nitrophenols are much stronger acids than m-nitrophenol.

p-nitrophenol > o-nitrophenol > m-nitrophenol

Similarly in case of cresols the decrease in acidic strength is

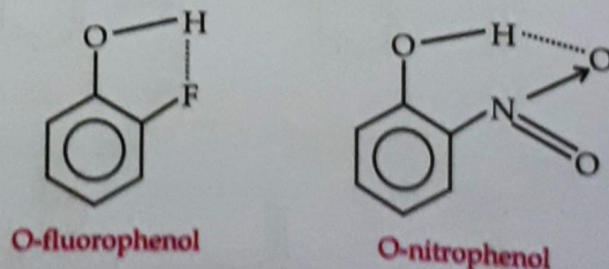
m-cresol > p-cresol > o-cresol

It may be noted that number of electron withdrawing or electron releasing substituents also effect the acidic strength of phenol. For e.g. 2,4,6, Trinitro phenol (Picric acid) is a stronger acid than mono or dinitrophenols.

2,4,6- Trinitrophenol > 2,4- dinitrophenol > 2-Nitro-phenol

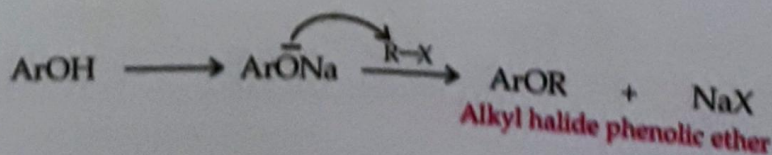
Thus in contrast to phenol, picric acid decompose both carbonate and bicarbonate.

It may be seen that some phenols having electron withdrawing groups in the o-position are weaker than p-position. For e.g. o-nitrophenol and o-fluorophenol are weaker than p-nitrophenol and p-fluorophenol respectively. This is due to formation of intramolecular hydrogen bonding in case of ortho isomers.

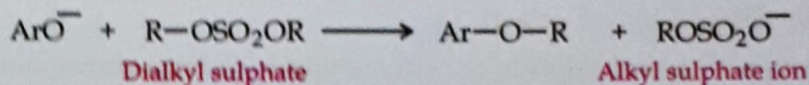


## (2) Alkylation : (Williamson Synthesis)

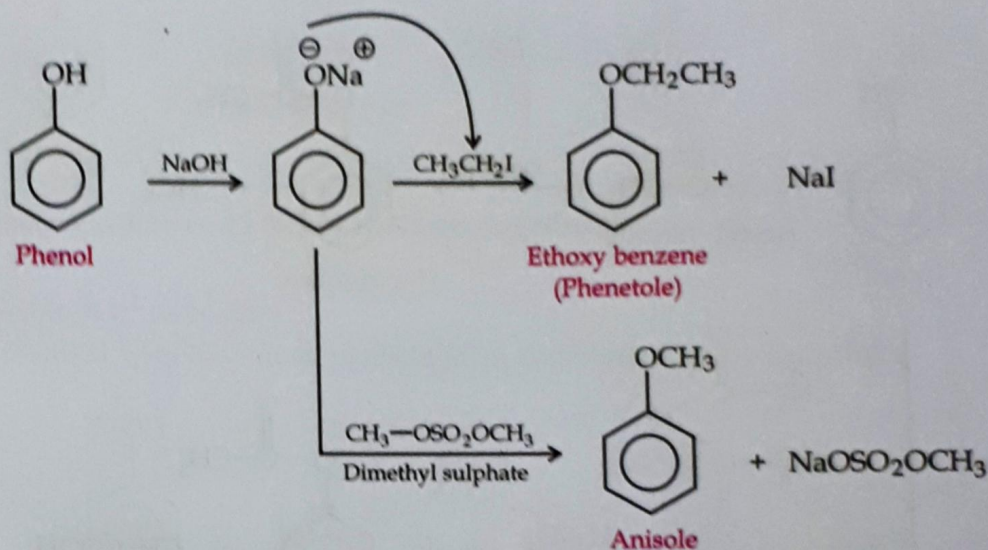
Phenols react with alkyl halides and dialkyl sulphates in alkaline medium form phenolic ethers)



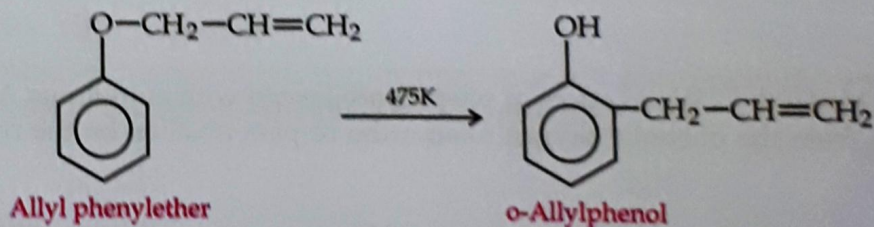




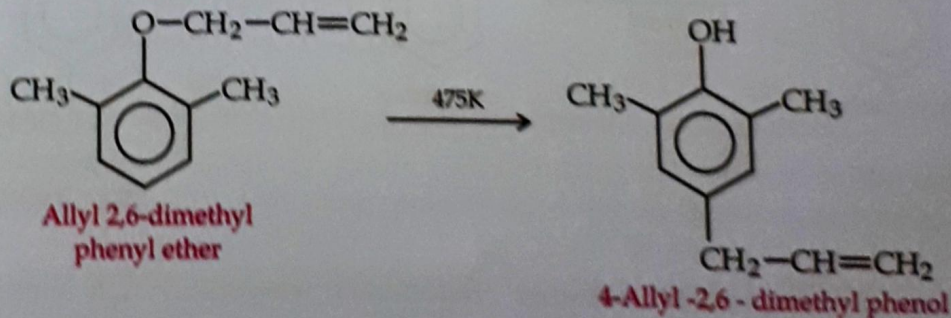
For example



**Claisen rearrangement** : When aryl allyl ether heated to 475K the allyl group of the ether migrates from ether oxygen to the ring carbon at ortho position. For e.g.



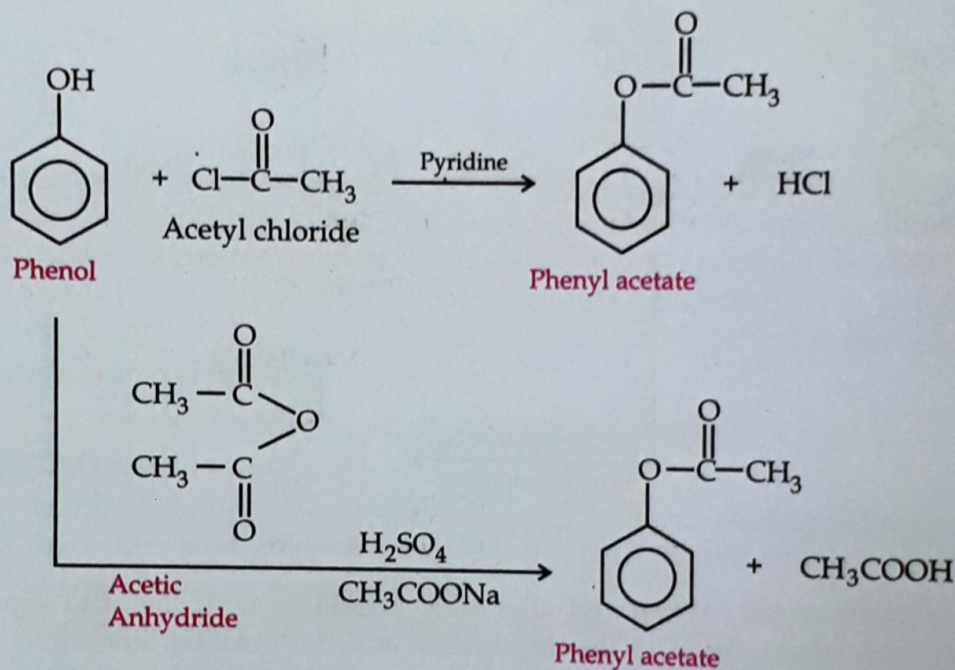
If both ortho position are already occupied, the allyl group migrates to para-position. For e.g.



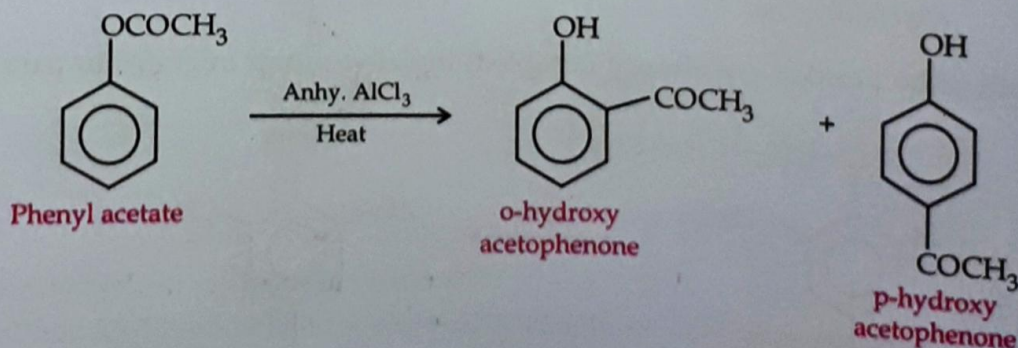


**(3) Acylation (Formation of esters)**

Phenols reacts with acetyl chloride or acid anhydride to form corresponding esters. The hydrogen atom of the hydroxyl group is replaced by the corresponding acyl group (RCO-) in this reaction.



**Fries rearrangement :** When esters of phenols are heated with anhydrous  $\text{AlCl}_3$ , the acyl group migrates from the phenolic oxygen to an ortho or para position on the ring and gives a ketone.

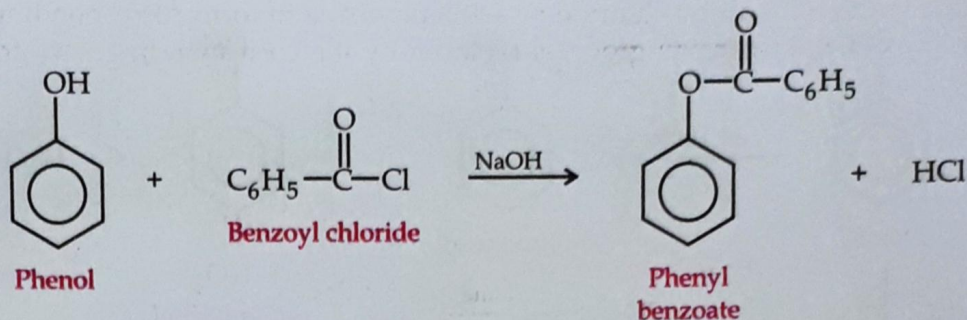


Generally at low temperature p-isomer predominate whereas at high temperature o-isomer predominate.

**(4) Benzoylation**

Phenols react with benzoyl chloride in the presence of sodium hydroxide to form a benzoyl derivative.

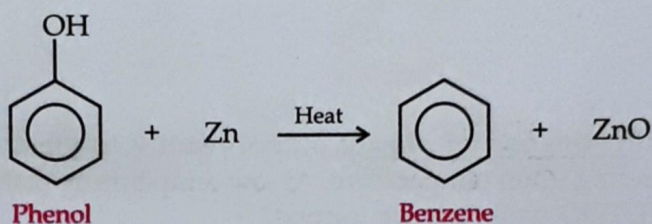




This reaction is known as **Schotten Baumann** reaction.

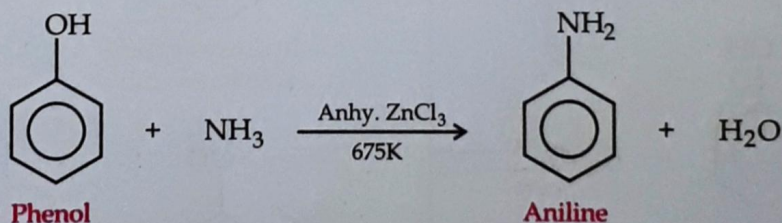
#### (5) Reaction with zinc dust

When distilled with zinc dust, phenols form corresponding hydrocarbons.



#### (6) Reaction with ammonia

When heated with ammonia at high temperature and pressure in the presence of catalysts,  $-\text{OH}$  group of phenols is replaced by  $-\text{NH}_2$  group.



### B. Reactions of Benzene Nucleus : Electrophillic substitution

Due to presence of hydroxyl group ( $-\text{OH}$ ), further substitution in the benzene ring is very much facilitated. The  $-\text{OH}$  group powerfully activates the benzene ring to electrophillic substitution at ortho and para positions. In fact the  $-\text{OH}$  group is very powerful activator and unless precautions are taken polysubstitution takes place. Thus phenol undergoes following electrophillic substitution reactions readily as compared to benzene ring to form ortho and para derivatives.

**(i) Nitration :** Phenol when react with dilute nitric acid it gives a mixture of ortho and para nitrophenol, whereas with conc. nitric acid, it forms 2, 4, 6-trinitro phenol (picric acid) but the yield of picric acid is poor due to oxidation of benzene ring by Nitric acid.