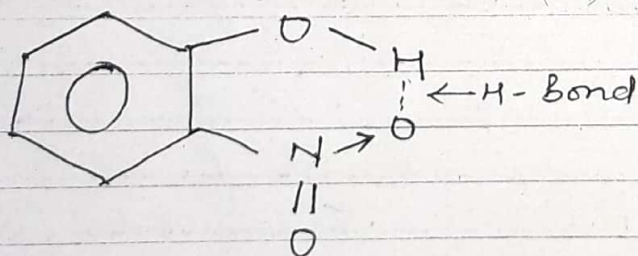
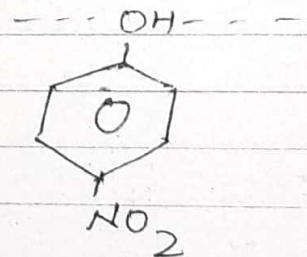


\*Boiling point of ~~ortho~~ Nitro phenol is less than p-Nitro phenol :-

In case of o-nitrophenol Intramolecular hydrogen bond is formed between hydrogen atom of the -OH group and Oxygen atom of the nitro group.



O-nitrophenol  
with intramolecular  
H-bond.



\* Nitrophenols are more acidic than phenols :-

~~Nitro~~ <sup>Nitro</sup> (-NO<sub>2</sub>) group is the strong electron withdrawing group. It causes -M effect when substituted on aromatic ring. In presence of -NO<sub>2</sub> group proton releasing tendency of phenolic hydrogen increases.



and it also helps in stabilising the phenoxide ion. Therefore, nitrophenols are more acidic than phenol.  $\rightarrow$  (Resonating str. on last page)

\* Ortho and Para Nitrophenols are more acidic than meta-nitrophenol.

During Mesomeric transfer of  $\pi$ -electrons, electron deficiency occurs at ortho and para positions in presence of nitro ( $-\text{NO}_2$ ) group while meta positions remain unaffected. Therefore, Ortho and para substituted phenols are more acidic than m-nitrophenol.

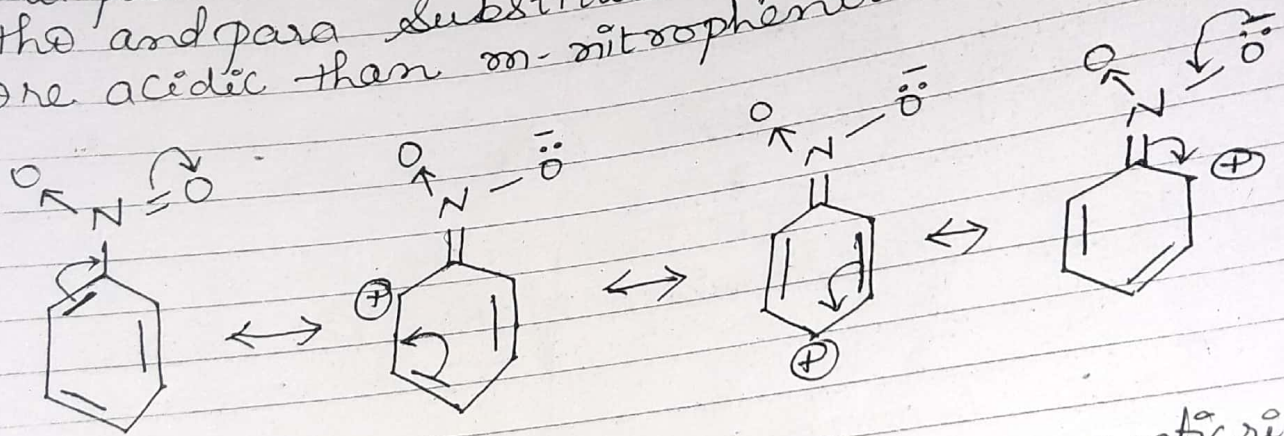


Fig:-  $-\text{M}$  effect of  $-\text{NO}_2$  group on aromatic ring.

\* Phenol is more acidic but Ethanol is Neutral.

Proton releasing tendency of ethanol is much less than phenol in the aqueous solution. (Explain acidic nature of phenol) (previous one)

In the aqueous solution, ethanol prefers to remain unionised because electron-negative oxygen atom of  $-\text{OH}$  group is attached with electron pushing ethyl group ( $+\text{I}$  effect).



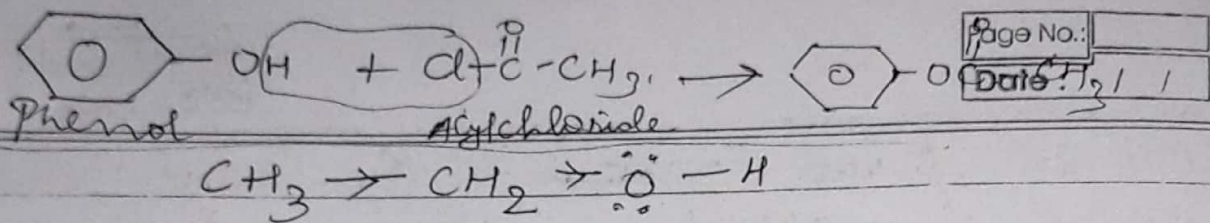


Fig: +I effect in ethanol

The ethoxide ion formed after removal of  $\text{H}^+$  ion becomes unstable due to lack of delocalisation of negative charge from oxygen atom. Ethyl group also pushes electron cloud towards oxygen by +I effect. Therefore, ethanol is neutral.

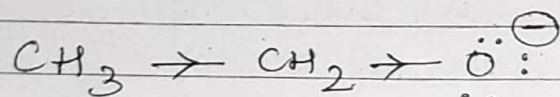


Fig: unstable ethoxide ion

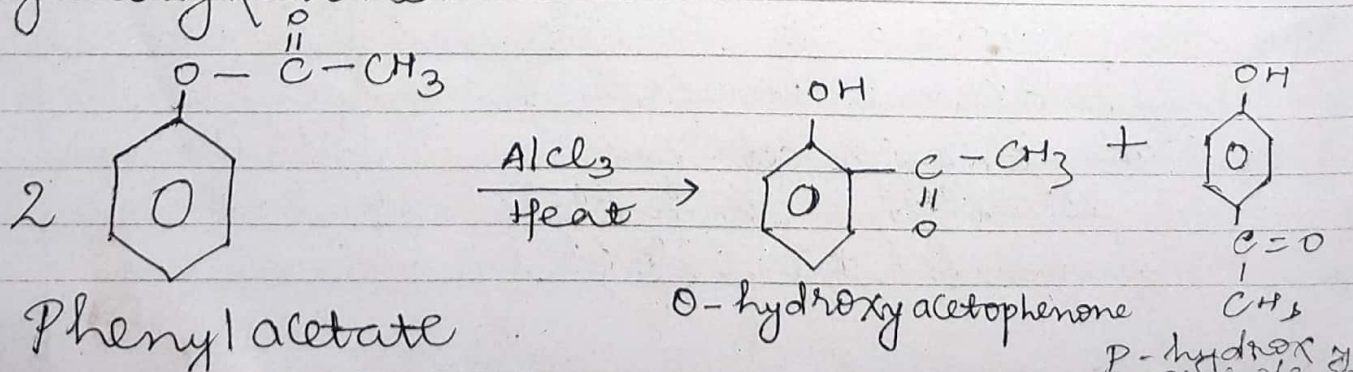
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## Mechanism of the Reactions

### \* Frie's Rearrangement :-

Conversion of phenolic ester into phenolic ketone on heating with  $\text{AlCl}_3$  catalyst is called Frie's Rearrangement.

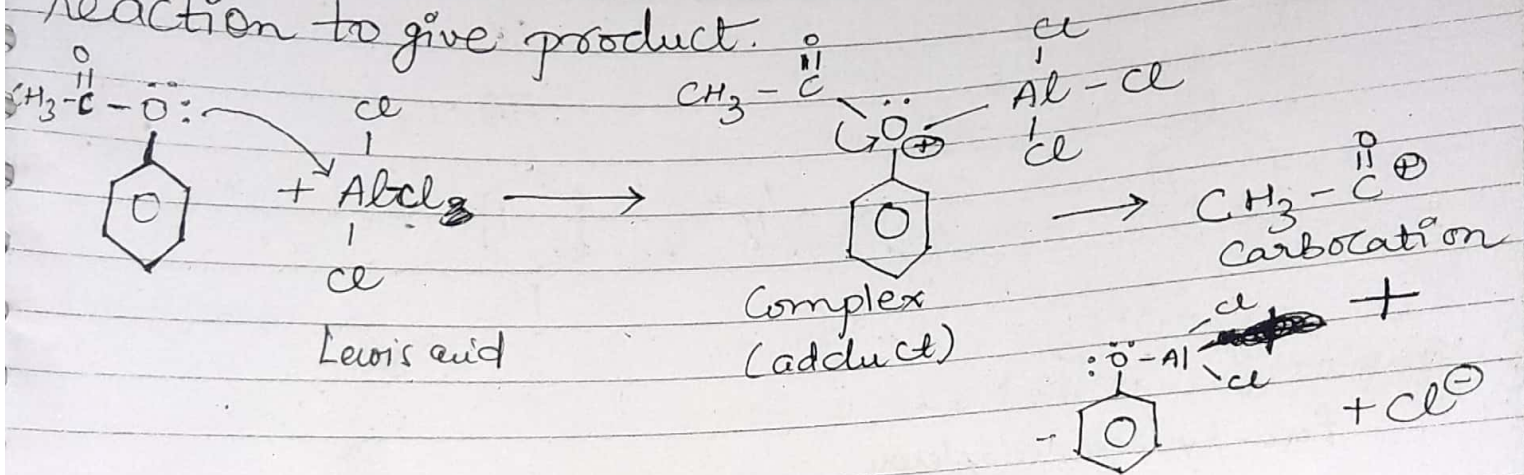
In its simplest form it may be represented by the reaction of phenyl acetate with Aluminium chloride to yield o- and p-hydroxy ketone.



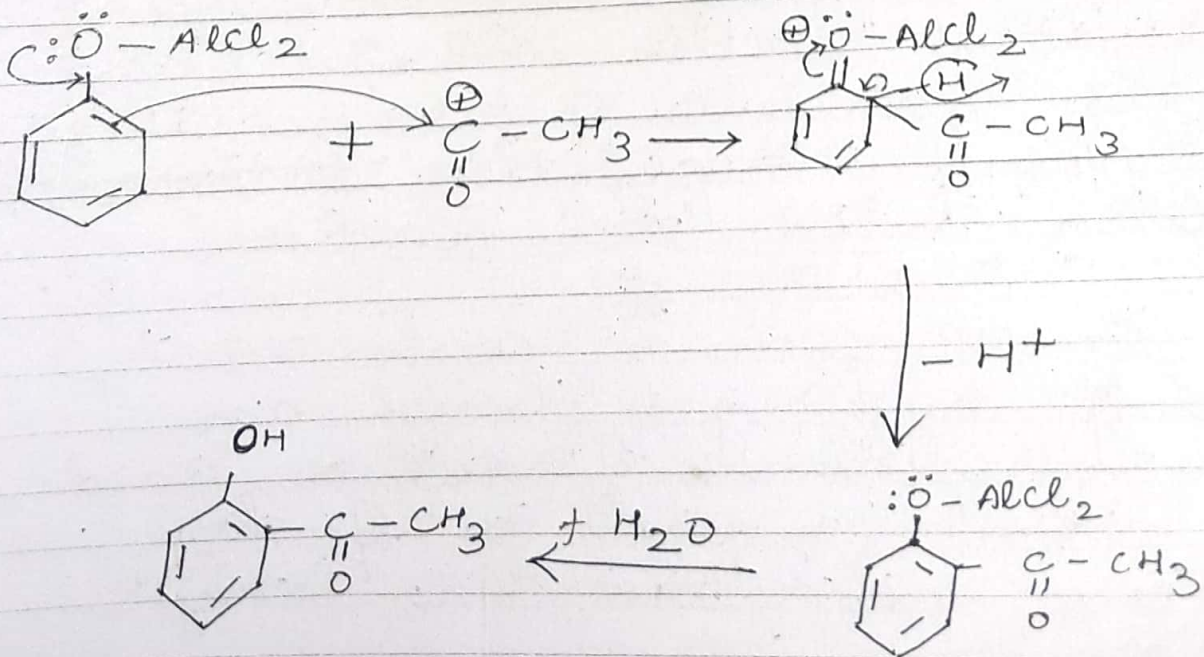


At  $25^{\circ}\text{C}$ , Para-isomer is the major product while at high temp. ( $165^{\circ}\text{C}$ ) Ortho-isomer is the major product.

Mechanism of the reaction :- Initially, a complex is formed between Lewis acid catalyst and ester. This complex undergoes to ~~rearrangement~~ both intra and intermolecular rearrangement reaction to give product.

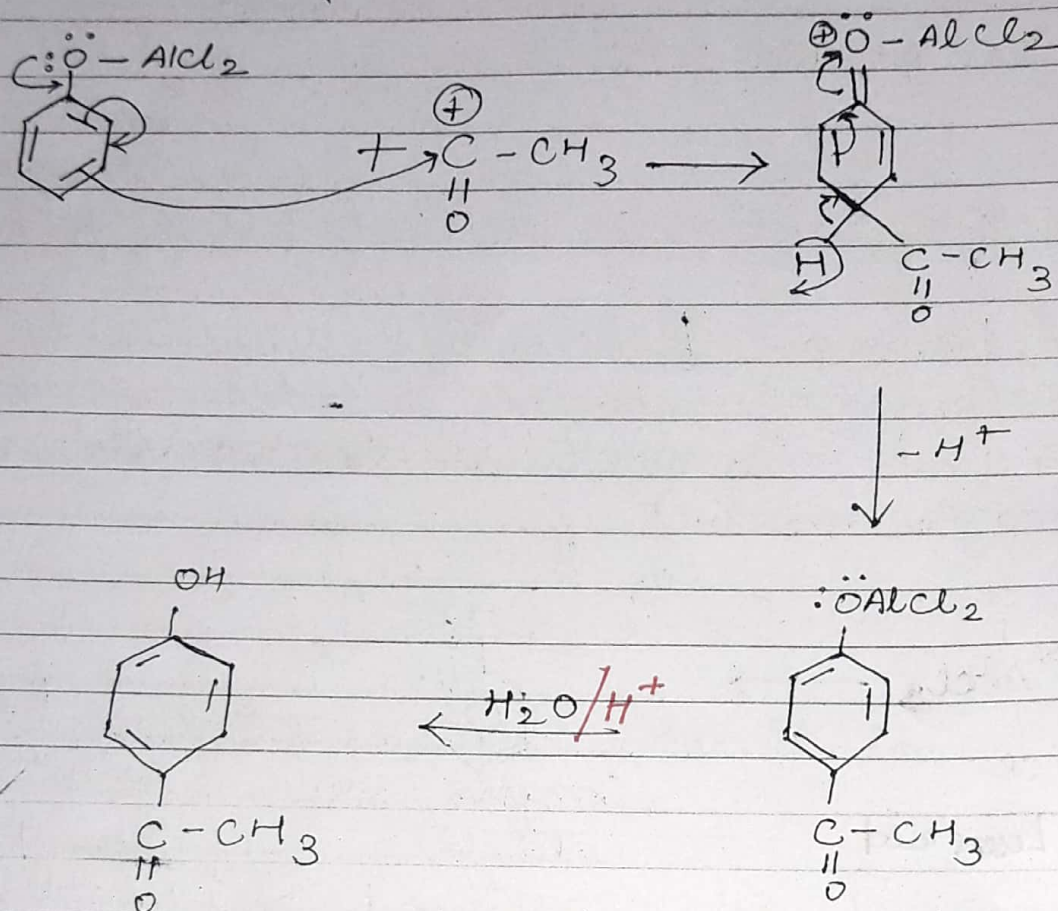


Ortho attack





# Para attack



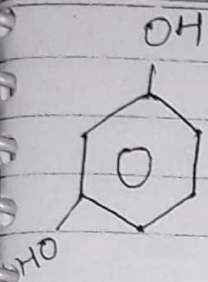
Para-hydroxy Acetophenone.

## \* Houben - Hoesch Reaction :-

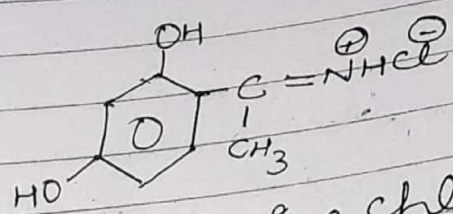
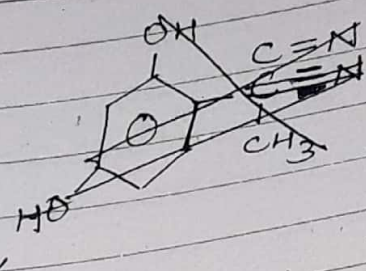
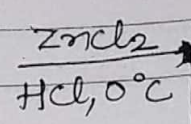
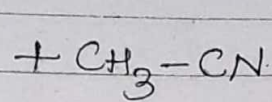
Polyhydroxy phenols (~~Resorcinol~~) undergo to acylation reaction with nitriles and  $\text{HCl}$  gas in presence of Lewis acid catalyst. This type of ~~act~~ acylation reactions are called Houben - Hoesch Reaction.

Its simplest form is carried out by passing dry  $\text{HCl}$  gas through an equimolar mixture of Resorcinol and ethanenitrile in presence of dry ether and anhydrous  $\text{ZnCl}_2$  catalyst at  $0^\circ\text{C}$ .

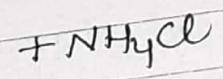
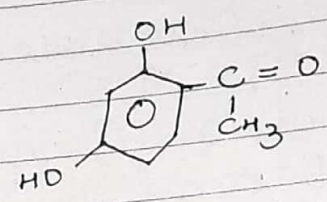
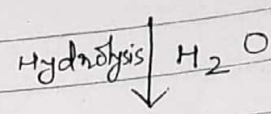




Resorcinol



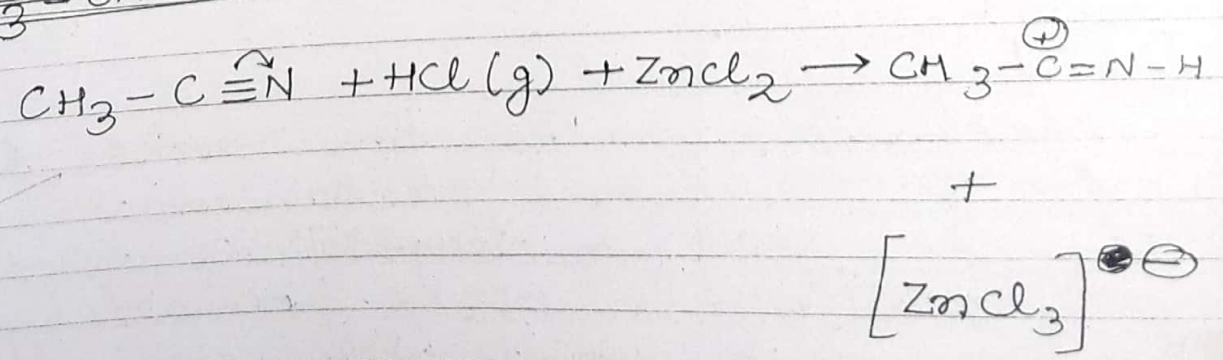
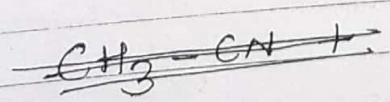
Ketimine chloride



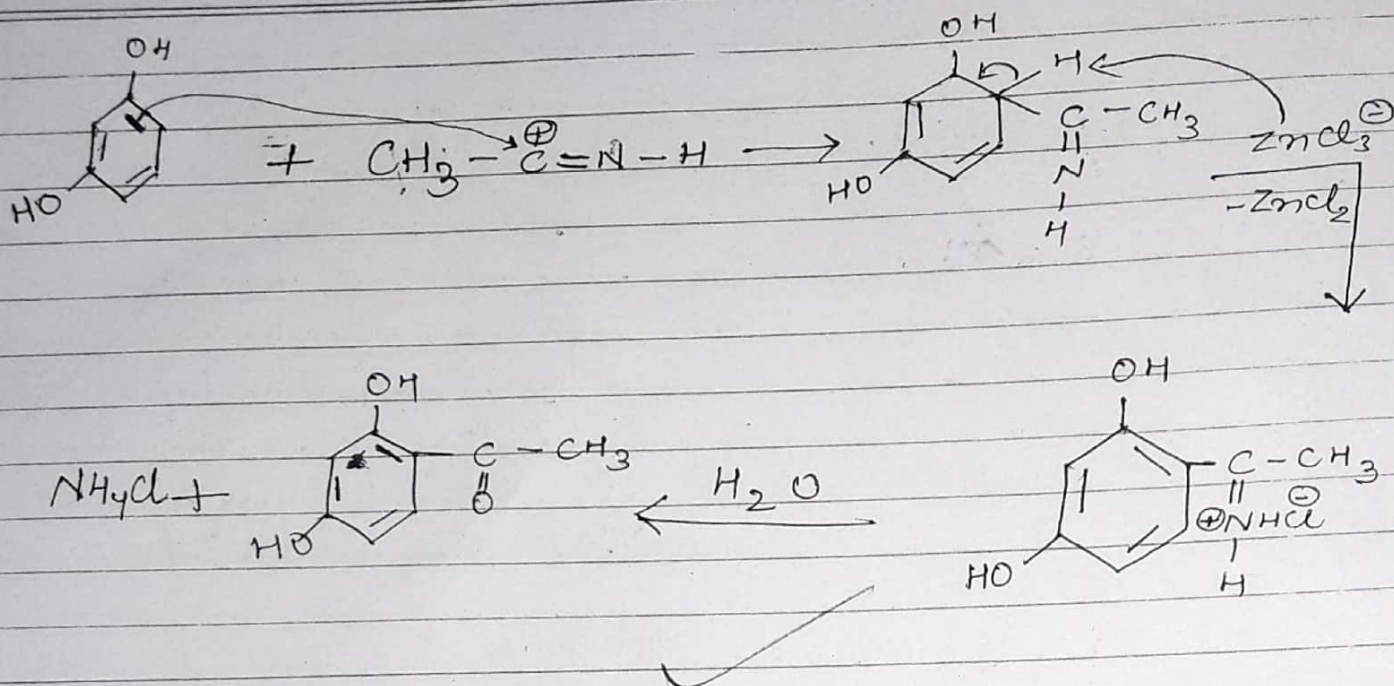
2,4-Dihydroxyacetophenone

↳ Mechanism:-

In this reaction attacking species is the imine hydrochloride. The resulting imine salt on hydrolysis gives the product.

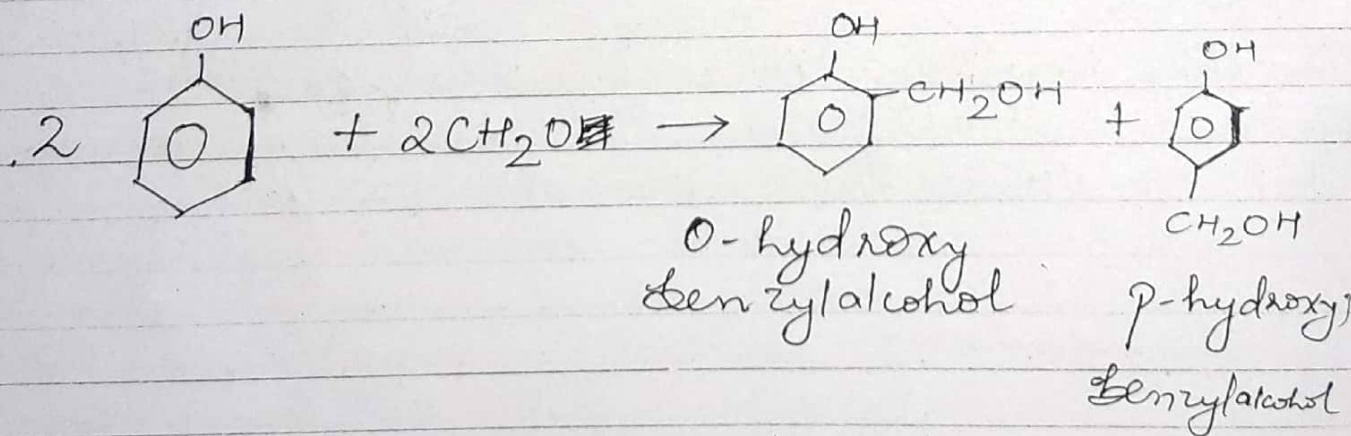






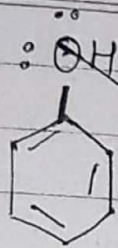
### \* Lederer-Mannasse Reaction :-

It is conversion of phenol into <sup>a mixture of</sup> o-hydroxybenzylalcohol and p-hydroxybenzylalcohol on heating with formaldehyde.

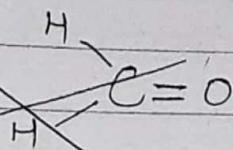


Mechanism :- Reaction involves the mechanism of nucleophilic condensation reaction in which formaldehyde behaves as nucleophile. Following steps are involved in the reaction.

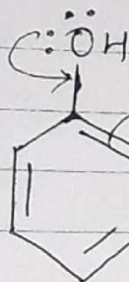




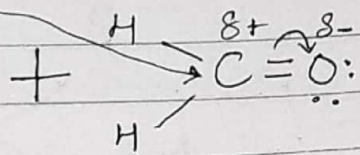
Phenol



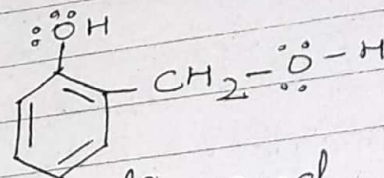
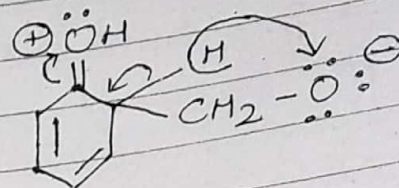
Formaldehyde



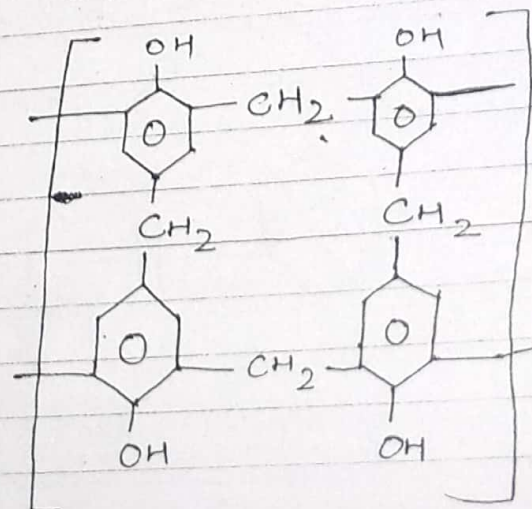
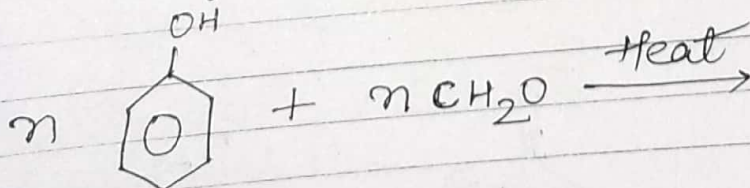
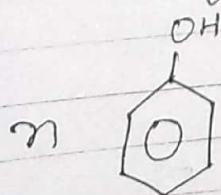
Phenol



Formaldehyde



When excess formaldehyde is used di- and tri-substituted products are obtained which undergo to intermolecular condensation reaction and converted into high molecular weight crosslinked polymer called Bakelite.

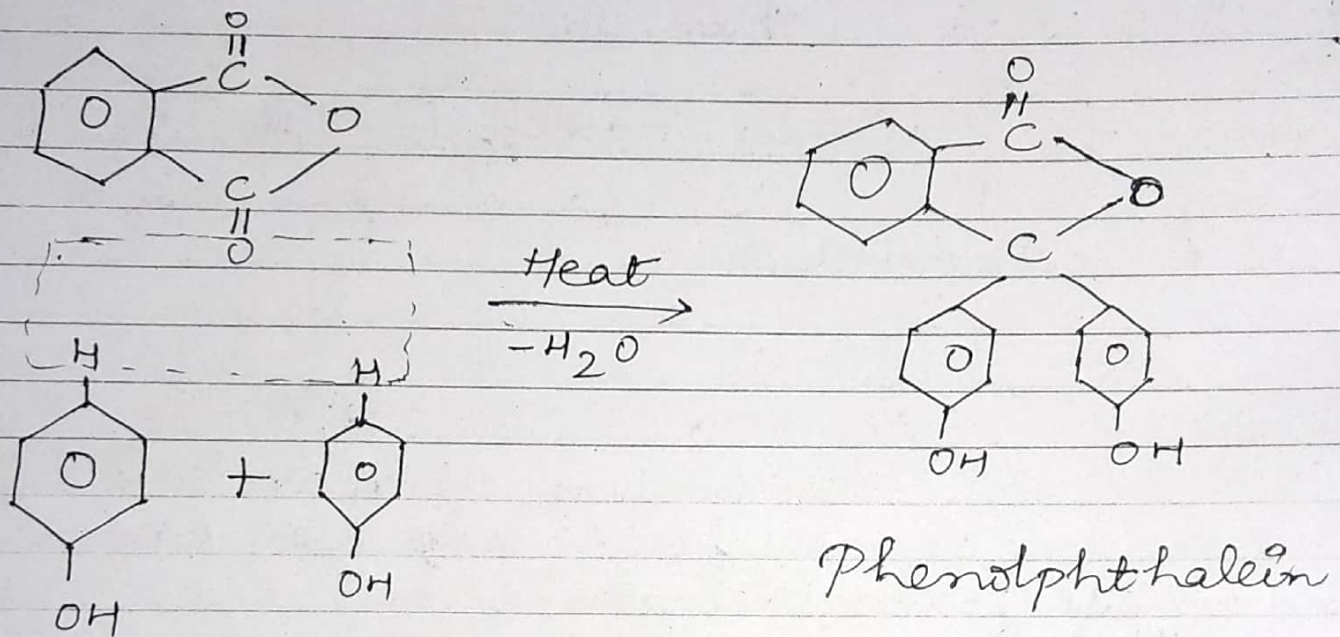


Bakelite polymer



# \* Reaction of Phenol with phthalic anhydride:-

On condensation of Phenol with phthalic anhydride phenolphthalein is obtained which is used as acid-base indicator.



## ⇒ Resonating str. of nitrophenol

