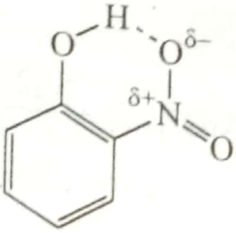
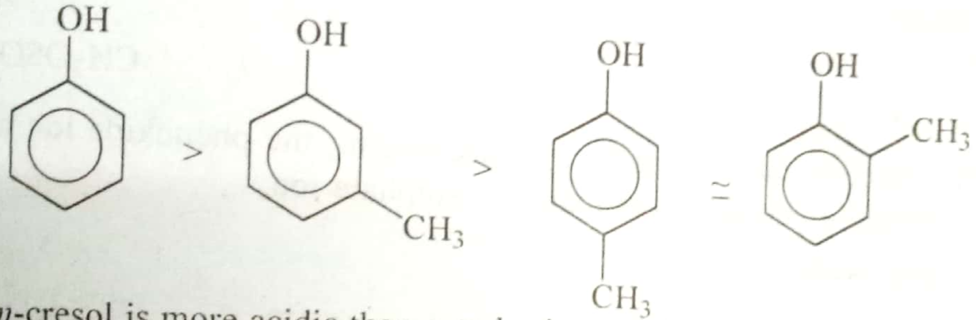
**Note** :– Picric acid is as acidic as carboxylic acid. It gives effervescence with $NaHCO_3$.

*o*-Nitrophenol is less acidic than the *p*-isomer because of intramolecular hydrogen bonding.

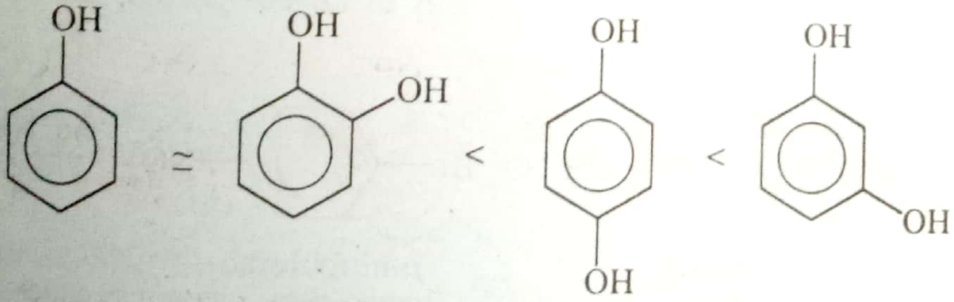


(c)



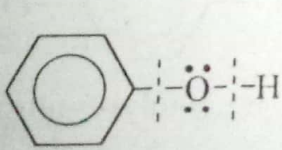
**Note** : *m*-cresol is more acidic than *o* and *p*-isomers because as soon as the negative charge comes at *o* and *p* positions, it is pushed back by +I effect of the $CH_3$ group, thus destabilising the anion.

(d)



## 3.7 REACTIONS OF PHENOL

The reactions of phenols can be studied in three parts.



3.7.1 Reactions due to cleavage of O–H bond

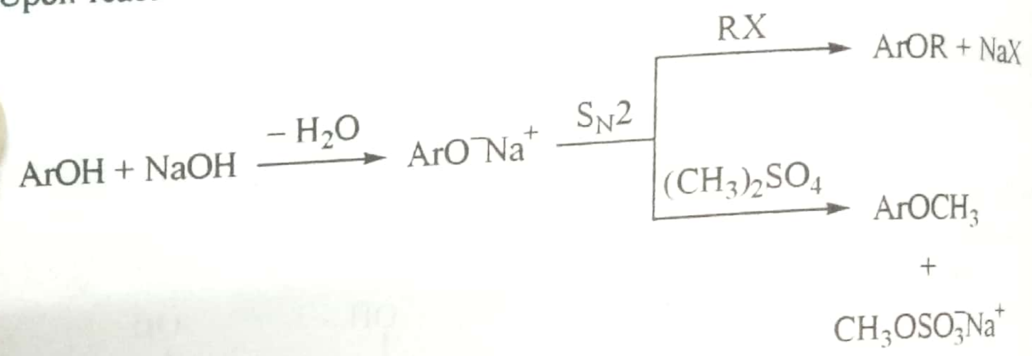
3.7.2 Reactions due to cleavage of C–OH bond

3.7.3 Reactions due to the aromatic ring

### 3.7.1 Reactions due to cleavage of O-H bond

### 1. Formation of ethers : Williamson ether synthesis

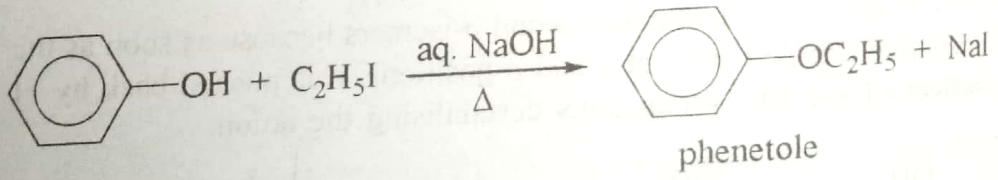
Upon reaction with alkyl halide or dimethyl sulphate, ethers are formed.

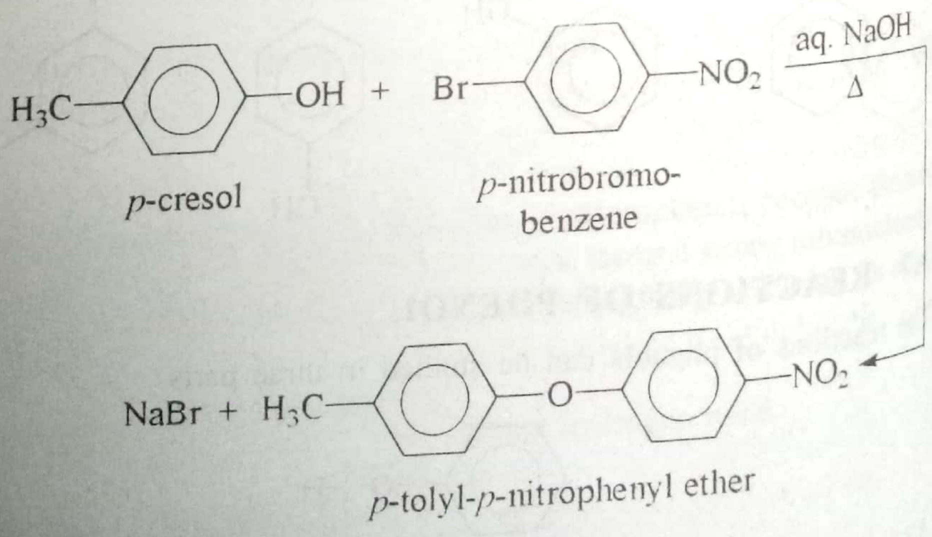


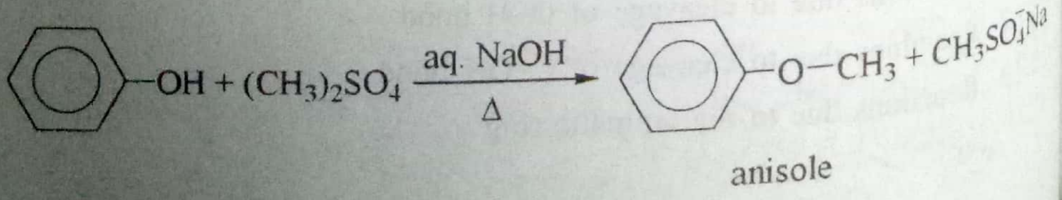
$$ArOH + NaOH \xrightarrow{-H_2O} ArO^-Na^+ \xrightarrow{S_N2} \begin{cases} \xrightarrow{RX} ArOR + NaX \\ \xrightarrow{(CH_3)_2SO_4} ArOCH_3 + CH_3OSO_3^-Na^+ \end{cases}$$

The reaction takes place by $S_N2$ mechanism, the phenoxide ion acts as a nucleophile and displaces halide or sulphate ion.

Examples are :

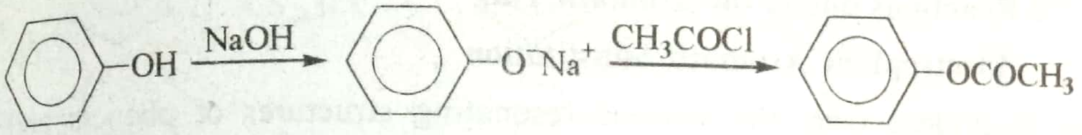




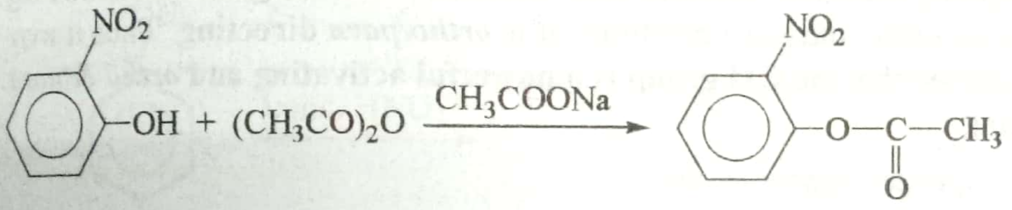


2. **Formation of esters**

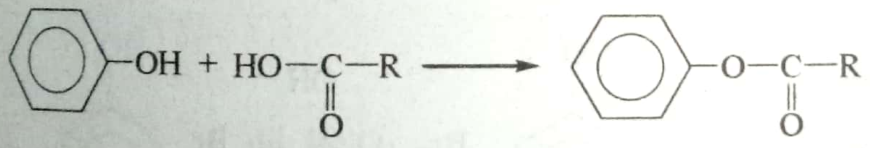
Phenols on treatment with acetic acid, acetyl chloride or acetic anhydride give corresponding esters.



phenyl acetate



o-nitrophenyl acetate



phenyl alkanoate

The esters undergo a rearrangement, known as the **Fries rearrangement**, upon heating with a Lewis acid which is discussed in detail in Section 3.8.

### 3.7.2 Reactions due to cleavage of C-OH bond

3. **Reduction :** Treatment with zinc dust affords benzene or an arene.

$$ArOH + Zn \longrightarrow Ar\text{–}H + ZnO$$

4. **Reaction with ammonia :** Treatment with ammonia produces aniline.

$$C_6H_5OH + NH_3 \xrightarrow[\text{or} \\ \text{heat alone at } 200^\circ C]{ZnCl_2 / \text{heat}} C_6H_5NH_2 + H_2O$$

5. **Reaction with $PCl_5$ :** Treatment with $PCl_5$ mainly gives triaryl phosphate.

$$ArOH + PCl_5 \longrightarrow ArCl + POCl_3 + HCl$$

$$3Ar\text{-}OH + POCl_3 \longrightarrow Ar_3PO_4 \text{ or } (ArO)_3P{=}O + HCl$$

triaryl phosphate

6. **Laboratory test or Diagnostic test :** Most phenols give characteristic colour (violet, red, purple, blue or green) with neutral or weakly acidic $FeCl_3$ solution. This reaction is usually used as laboratary test for phenols.

### 3.7.3 Reactions due to the aromatic ring

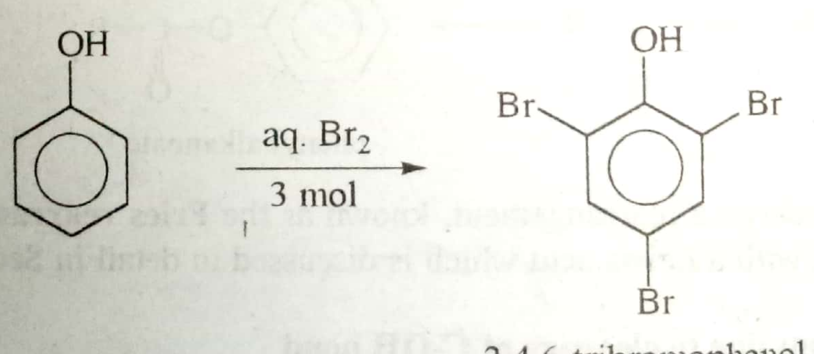
7. **Electrophilic Aromatic Substitution**

As is evident from the various resonating structures of phenols and phenoxide ions (Schemes 3.2 & 3.3) the –OH group increases electron density on the benzene ring and hence it **activates the ring** powerfully in electrophilic aromatic substitutions. Since the –ve charge on benzene ring resides on *ortho* and *para* positions, it is ***ortho/para*** **directing**. Thus it may be concluded that the **OH group is a powerful activating and *ortho* & *para* directing**.

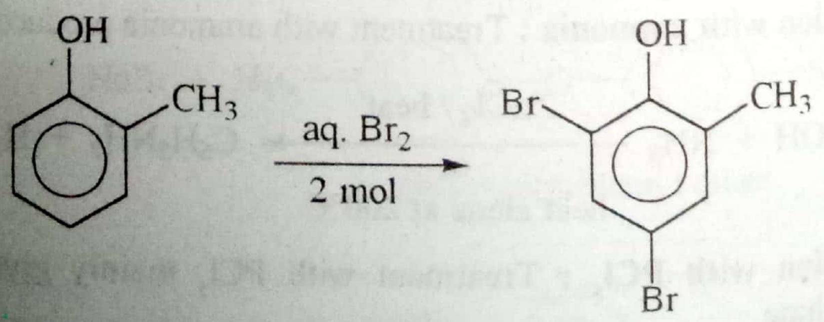
Some important reactions are –

(i) **Halogenation**

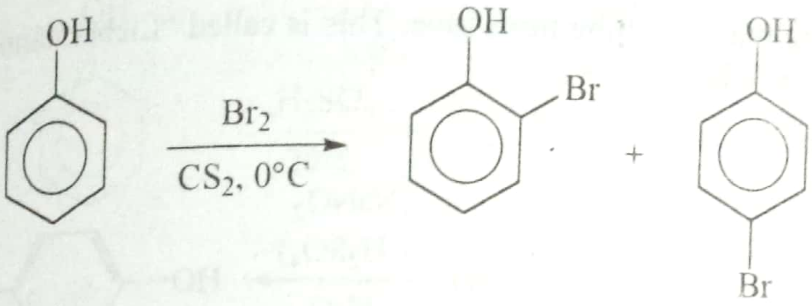
Treatment of phenols with aqueous solution of bromine, results in substitution of every hydrogen *ortho* & *para* to OH group.



2,4,6-tribromophenol

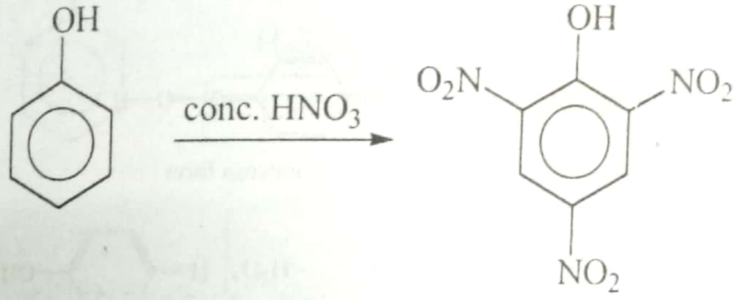


If the halogenation is carried out in a solution of less polarity, such as $CHCl_3$, $CCl_4$ or $CS_2$, mono-halogenation product is obtained.

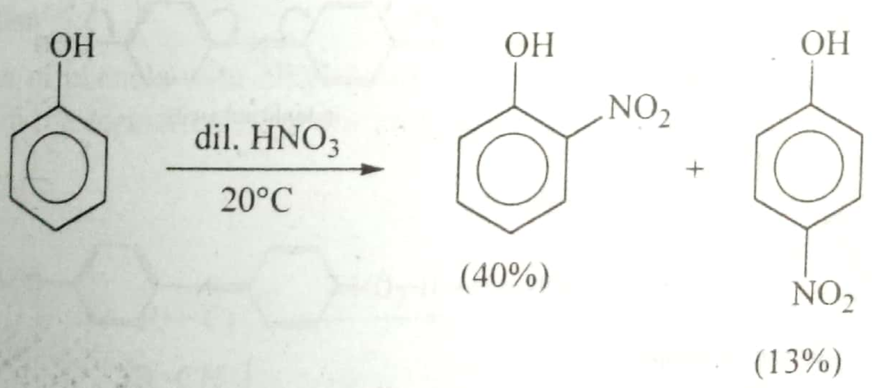


(ii) **Nitration**

Phenol upon treatment with conc. HNO$_3$ gives picric acid.

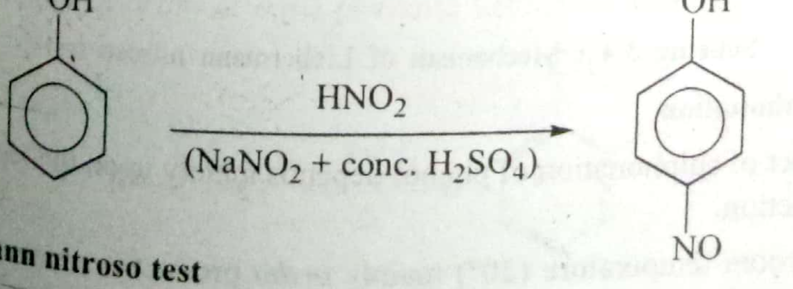


However, with dilute HNO$_3$, mono-nitration product is formed.



(iii) **Nitrosation**

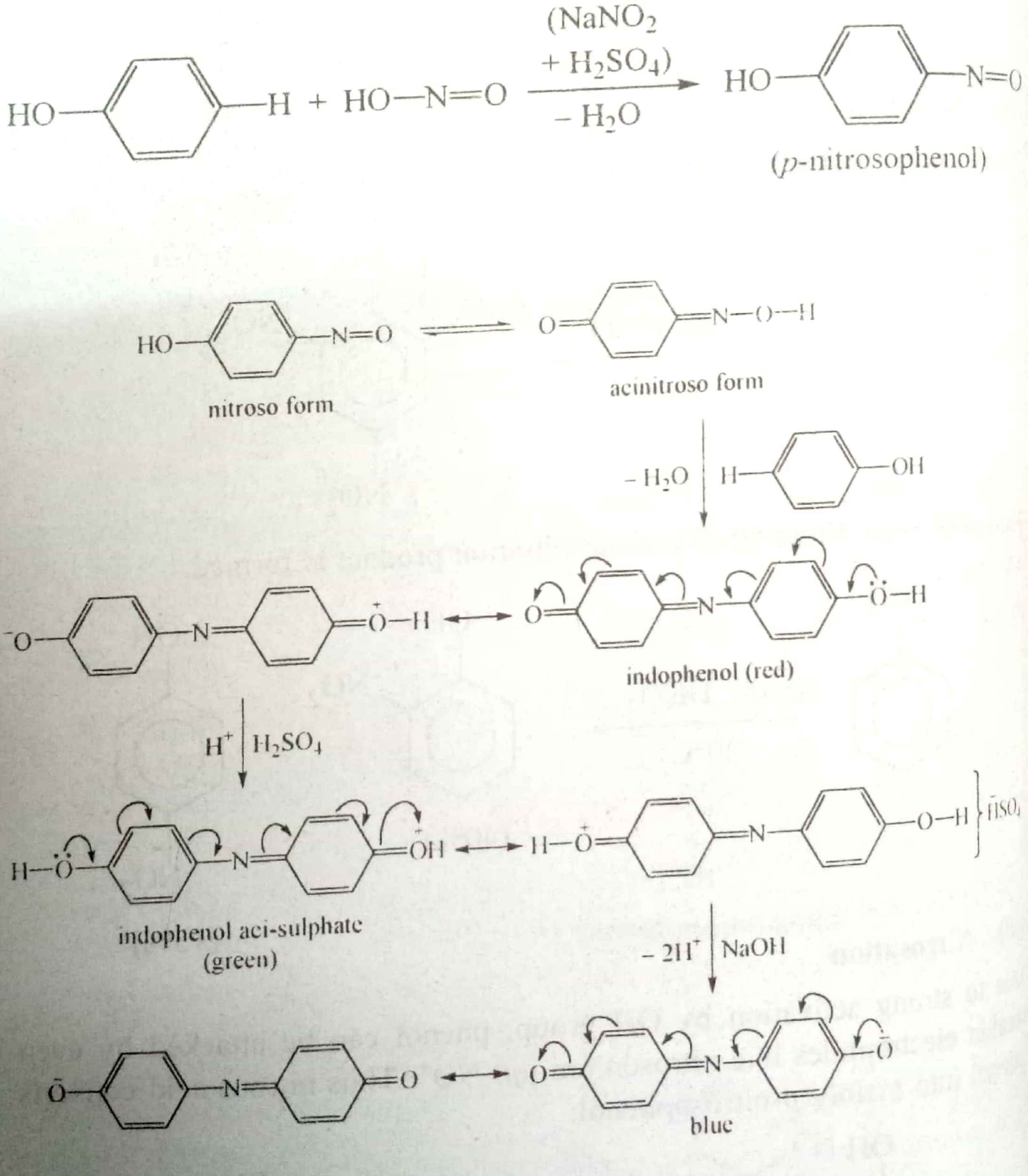
Due to strong activation by OH group, phenol can be attacked by even weaker electrophiles like nitrosonium ion NO$^+$. Thus nitrous acid converts phenol into mainly *p*-nitrosophenol.



**Liebermann nitroso test**

When mixture of phenol and NaNO$_2$ is treated with 1-2 drops of con. H$_2$SO$_4$, deep green colour is obtained which upon dilution with water becomes red and on being made alkaline turns blue. This is called "Liebermann nitroso test" (Scheme 3.4).

**Mechanism :**

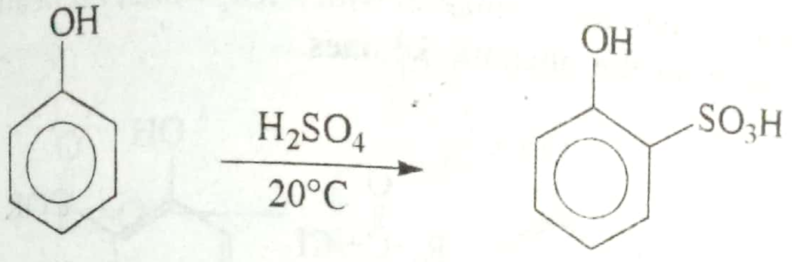


**Scheme 3.4 :** Mechanism of Liebermann nitroso test

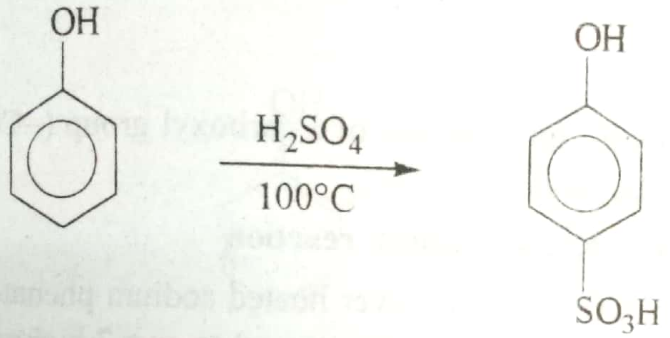
### (iv) Sulphonation

The product of sulphonation of phenol depends mainly upon the temperature of the reaction.

- At room temperature (20°) mainly *ortho* product is obtained.
- At 100° mainly *para* isomer is formed.



*o*-phenolsulphonic acid

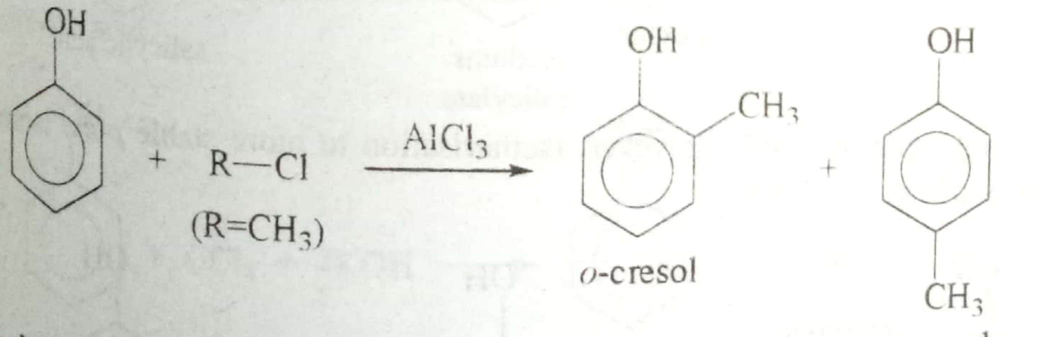


*p*-phenolsulphonic acid

(v) **Friedel-Crafts alkylation and acylation**

**Alkylation**

Reaction of phenols with alkyl halide in the presence of anhydrous $AlCl_3$ results in the formation of *ortho* and *para* alkylated phenols.

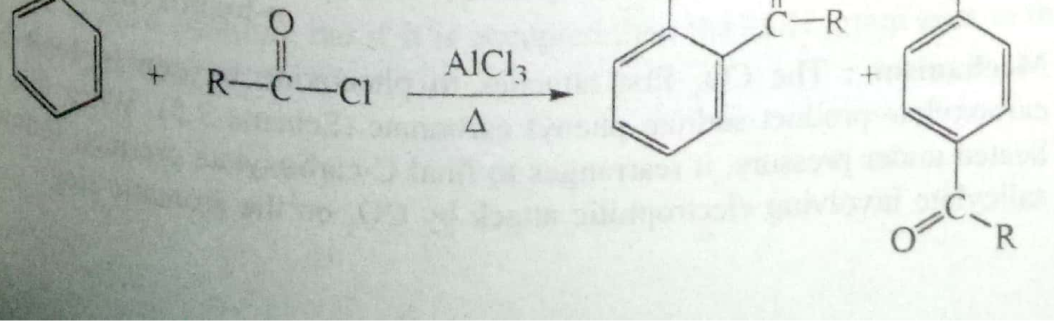


*o*-cresol

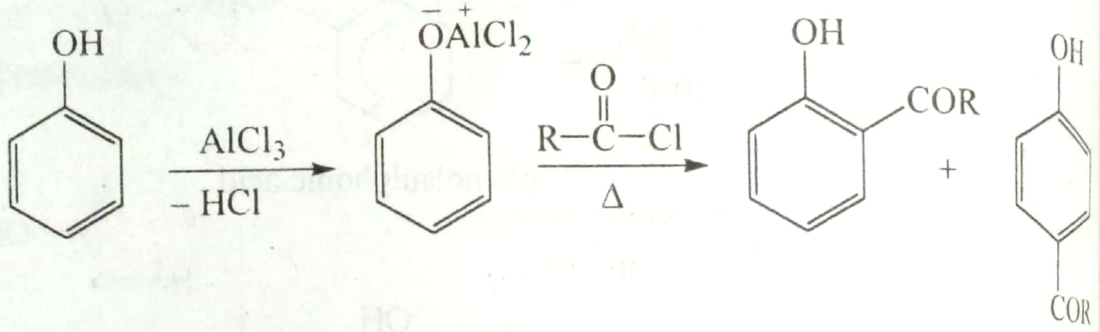
*p*-cresol

**Acylation**

Similarly when phenol is treated with an acyl halide in the presence of Lewis acid, a mixture of *ortho* & *para* phenolic ketones is formed.



The mechanism involves salt formation with $AlCl_3$ which on heating with an acyl chloride leads to the phenolic ketones.

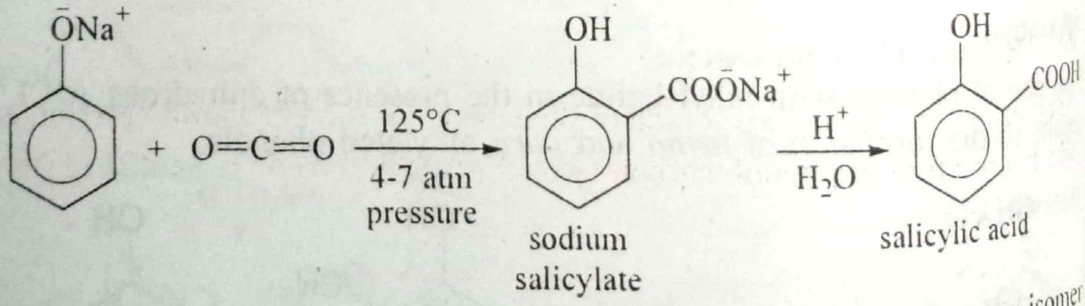


## (vi) Carboxylation

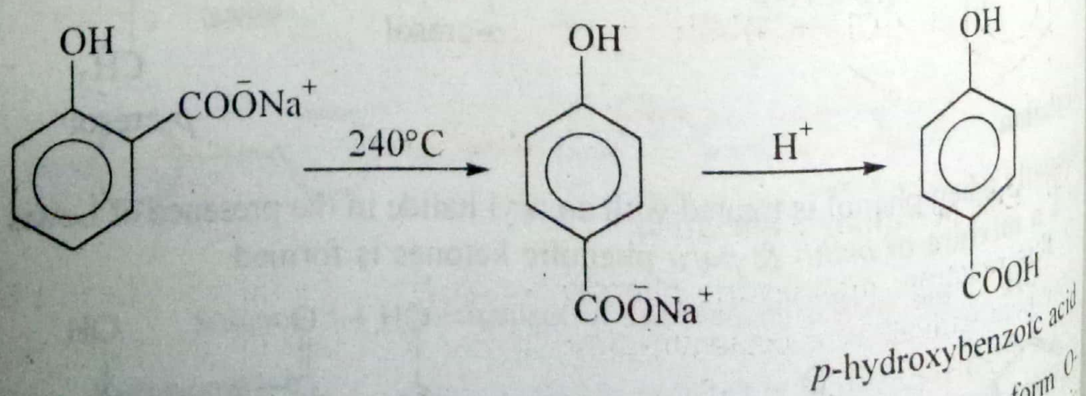
There are two methods for introduction of a carboxyl group (–COOH) in a phenol to give phenolic acids.

### (a) Kolbe reaction or Kolbe-Schmidt reaction

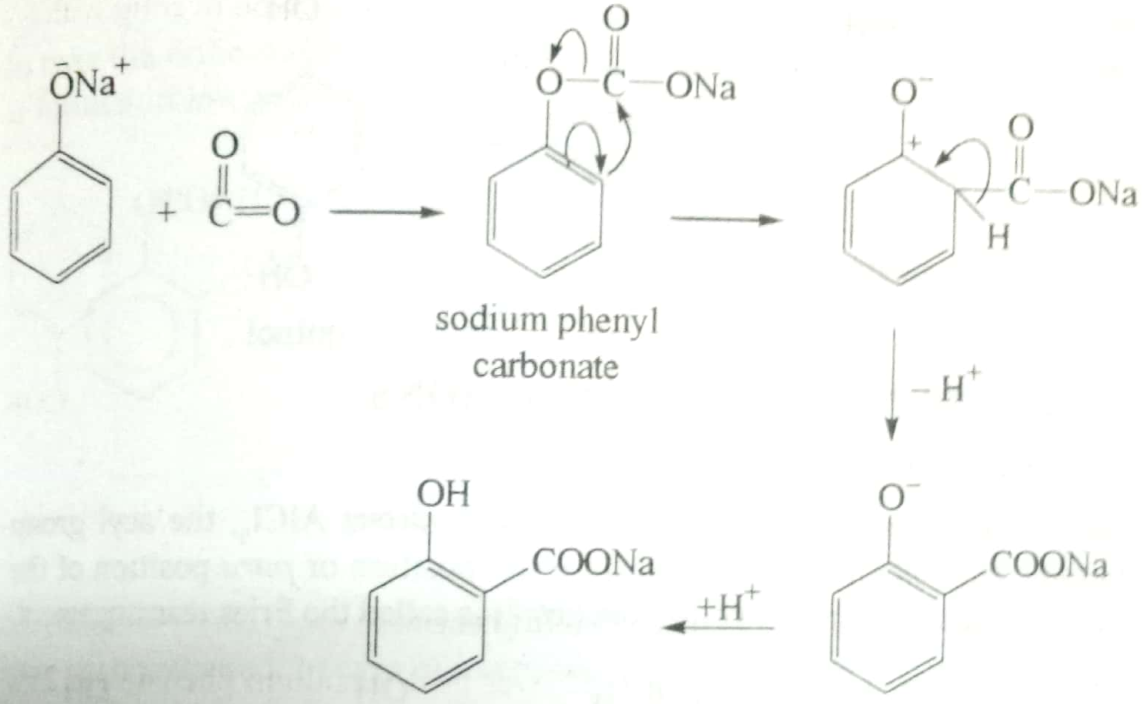
In the Kolbe reaction, $CO_2$ is passed over heated sodium phenate at 125°C under reduced pressure (4-7 atmospheric pressure) to give 2-hydroxybenzoate (sodium salicylate) which upon acidic hydrolysis gives salicylic acid.



At high temp of 240°, however, isomerisation to more stable *para* isomer takes place.



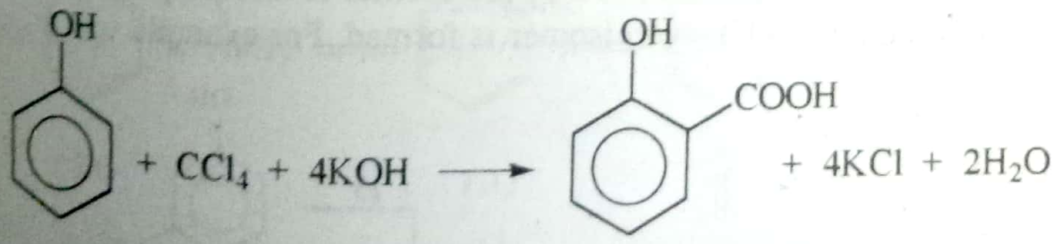
**Mechanism :** The $CO_2$ first attaches to phenoxide oxygen to form O-carboxylate product sodium phenyl carbonate (Scheme 3.5). When this is heated under pressure, it rearranges to final C-carboxylate product, sodium salicylate involving electrophilic attack by $CO_2$ on the aromatic ring.



**Scheme 3.5 :** Mechanism of carboxylation of phenol

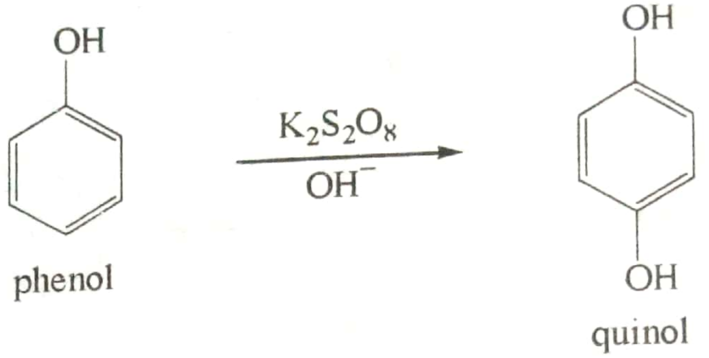
### (b) Reimer-Tiemann reaction

Another method for carboxylation of phenols is Reimer-Tiemann reaction in which a mixture of phenol, carbon tetrachloride and KOH is heated to give salicylic acid.



### (vii) Elbs persulphate oxidation

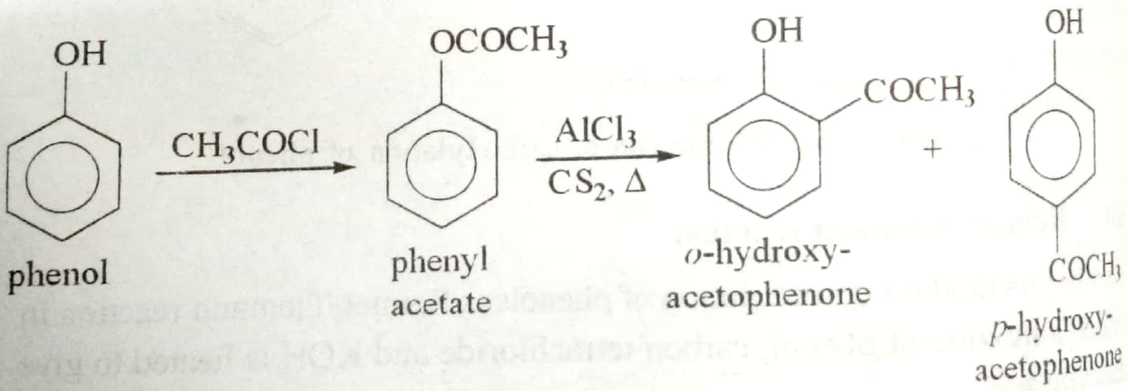
In this reaction, monohydric phenols are oxidised to dihydric phenols by treatment with alkaline potassium persulphate. Hydroxylation, generally takes place in *para* position, but if it is occupied then the –OH group goes to the *ortho-* position.



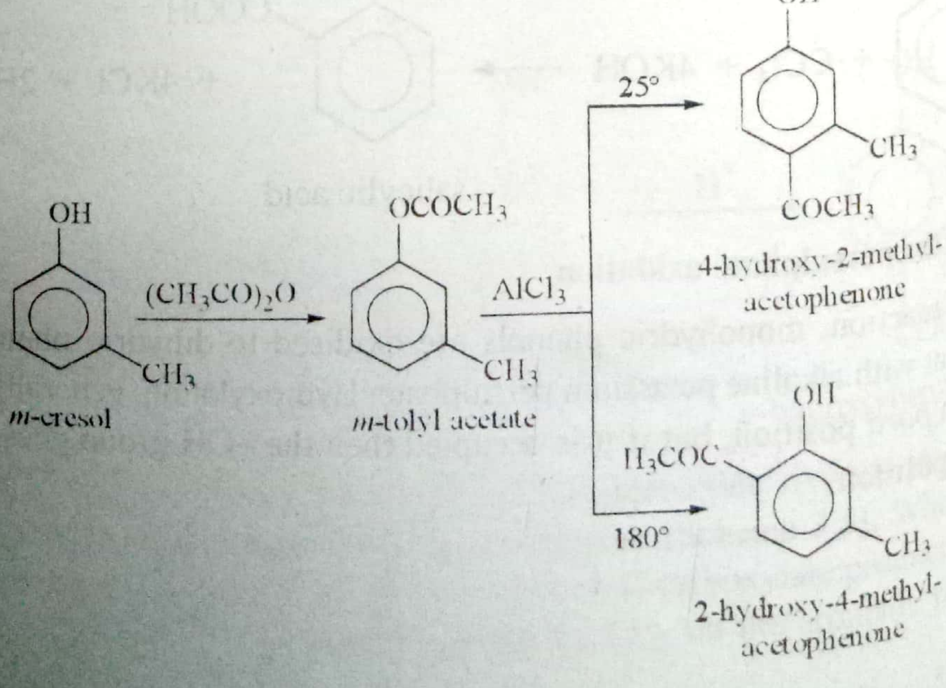
## 3.8 IMPORTANT NAME REACTIONS

### 1. Fries Rearrangement

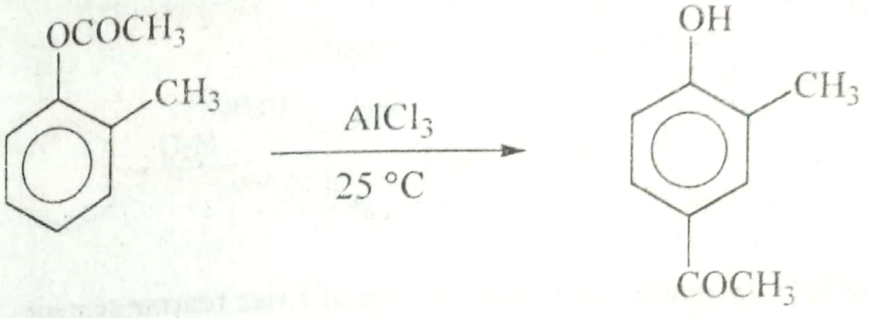
When esters of phenols are heated with anhydrous $AlCl_3$, the acyl group migrates from phenolic oxygen to an *ortho* position or *para* position of the ring yielding a mixture of hydroxyketones. It is called the Fries rearrangement.



Generally at low temperature (<60°) *para* isomer is formed predominantly, but at high temp (>160°) *ortho* isomer is formed. For example –



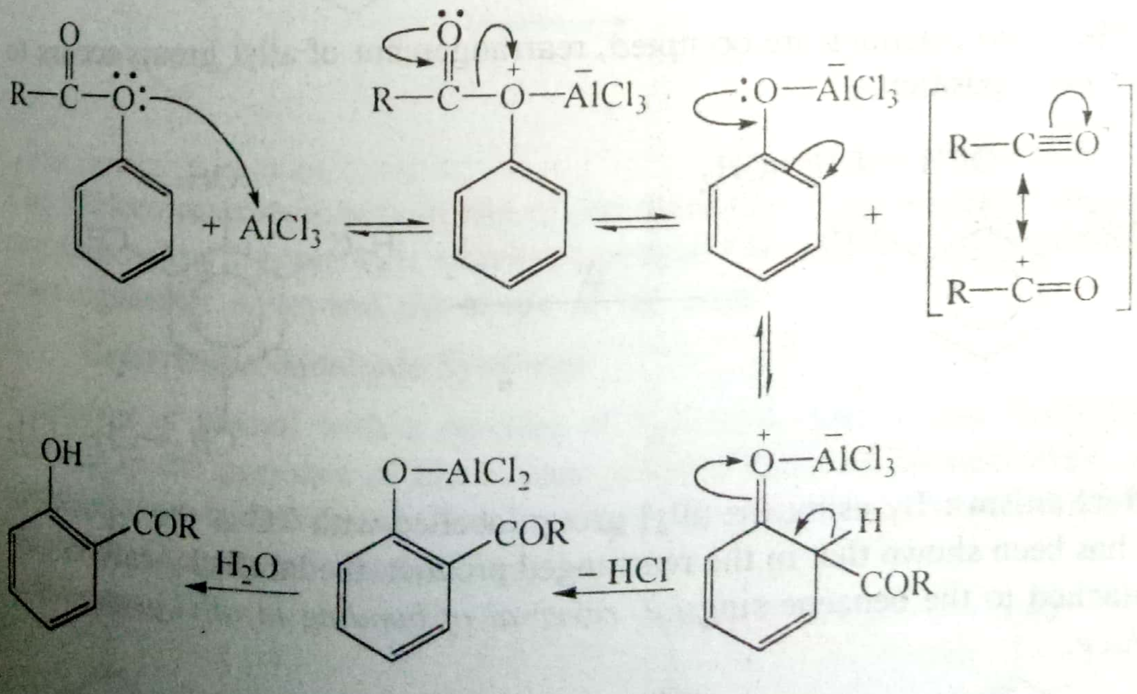
In case the ortho position is occupied by other substituent, a single product is formed in low yield.



3-methyl-4-hydroxyacetophenone

**Mechanism :** Two types of mechanisms – intermolecular and intramolecular, have been proposed. In case of intermolecular mechanism (Scheme 3.6), the intermediate is an acylium ion ($R-C\equiv O^+$) which attacks the ring as in case of Friedel-Crafts acylation.

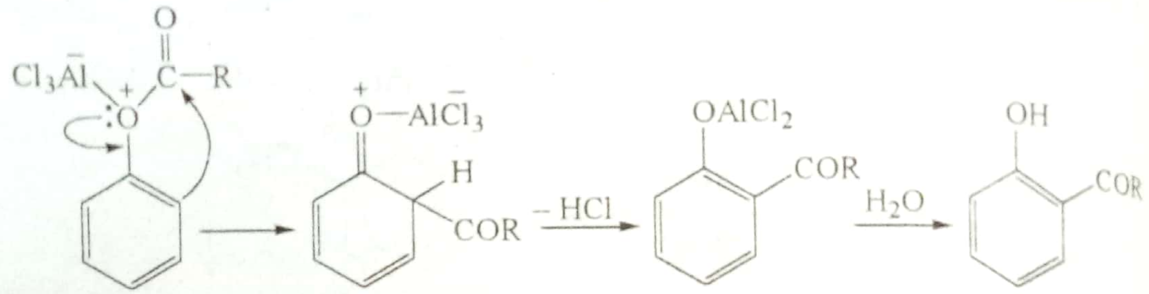
**Intermolecular Mechanism**



**Scheme 3.6 :** Intermolecular mechanism of Fries rearrangement

However, this rearrangement can also occur by the intramolecular mechanism as depicted in Scheme 3.7.

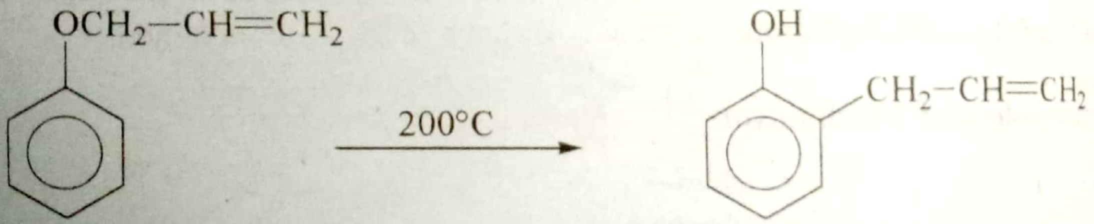
### Intramolecular Mechanism



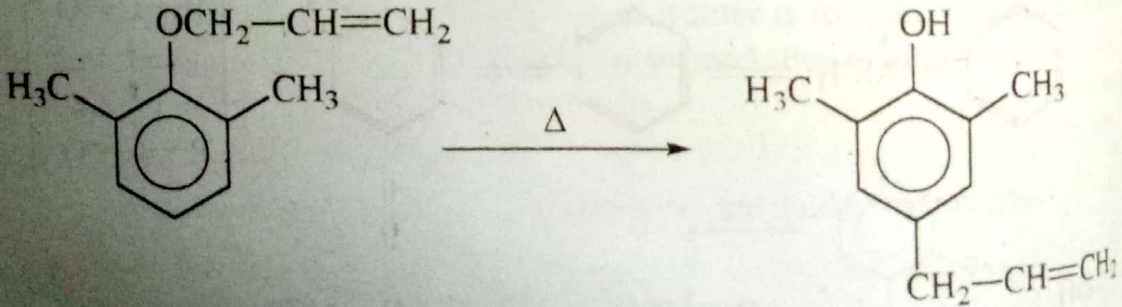
**Scheme 3.7 :** Intramolecular mechanism of Fries rearrangement

## 2. Claisen Rearrangement

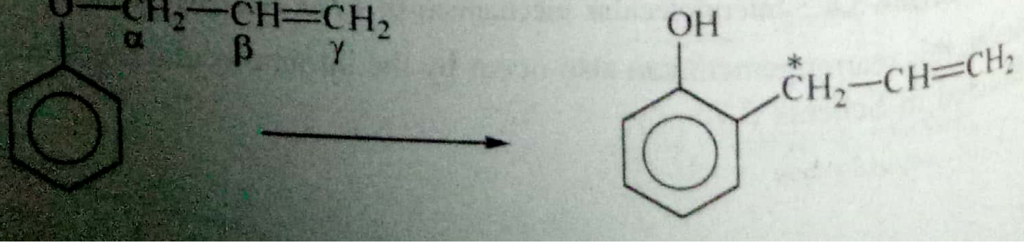
Rearrangement of allyl aryl ethers to allyl phenols simply by heating the substrate alone at 200°C is known as Claisen rearrangement. It may be noted that NO catalyst is required.



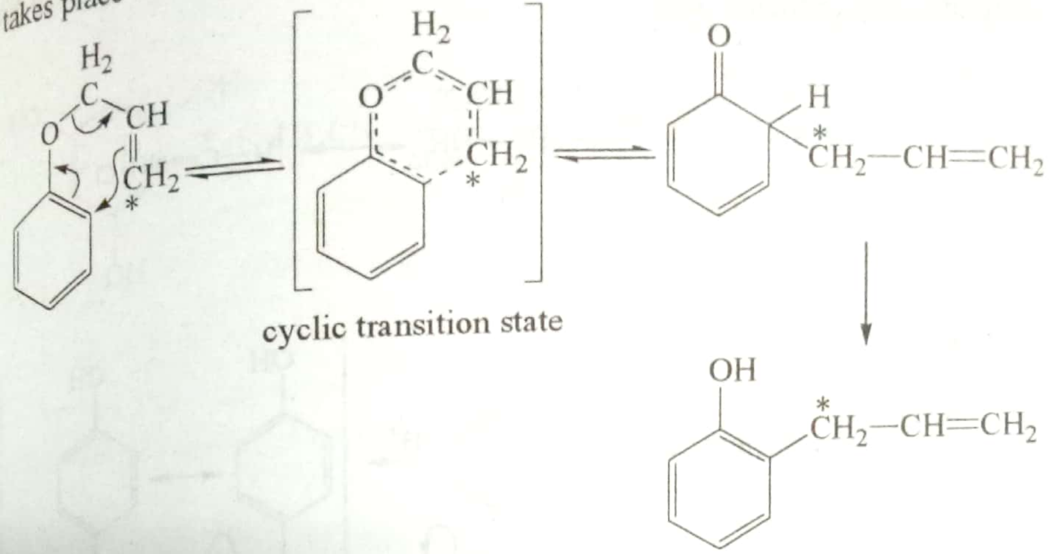
If the *ortho* positions are occupied, rearrangement of allyl group occurs to the *para* position.



**Mechanism :** By using the allyl group labelled with $^{14}C$ at the γ-position, it has been shown that in the rearranged product, the labelled γ-carbon gets attached to the benzene ring *i.e. reversal of bonding in allyl group takes place.*

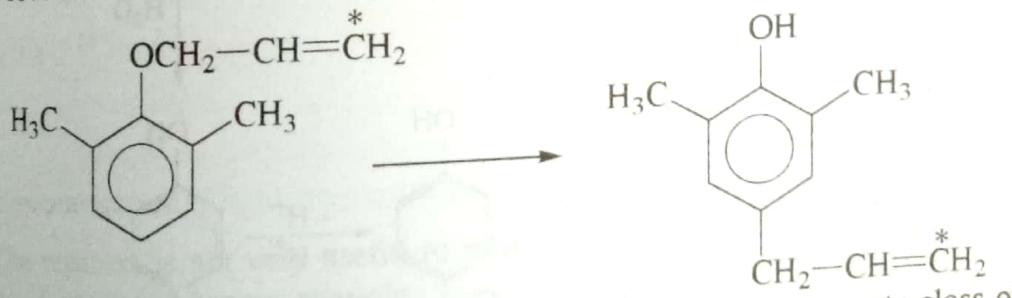


These observations suggested that the rearrangement is intramolecular and takes place *via* a six-membered cyclic transition state (Scheme 3.8).



**Scheme 3.8 :** Intramolecular mechanism for Claisen Rearrangement

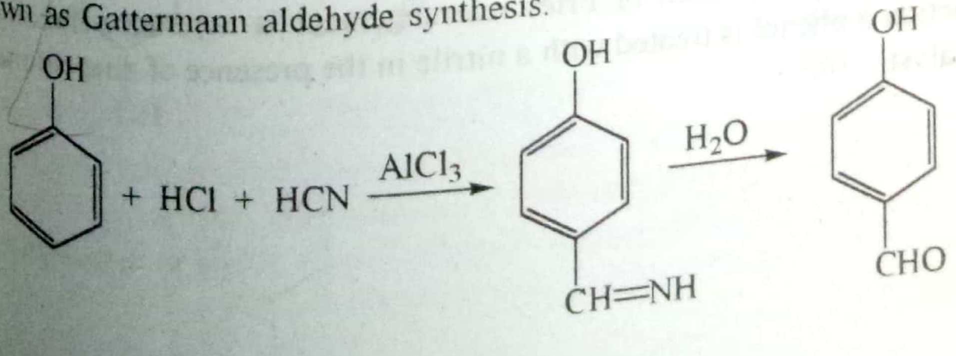
In case of *p*-rearrangement, the mechanism involves two stages each causing a reversal so that the final product, without reversal, is obtained.



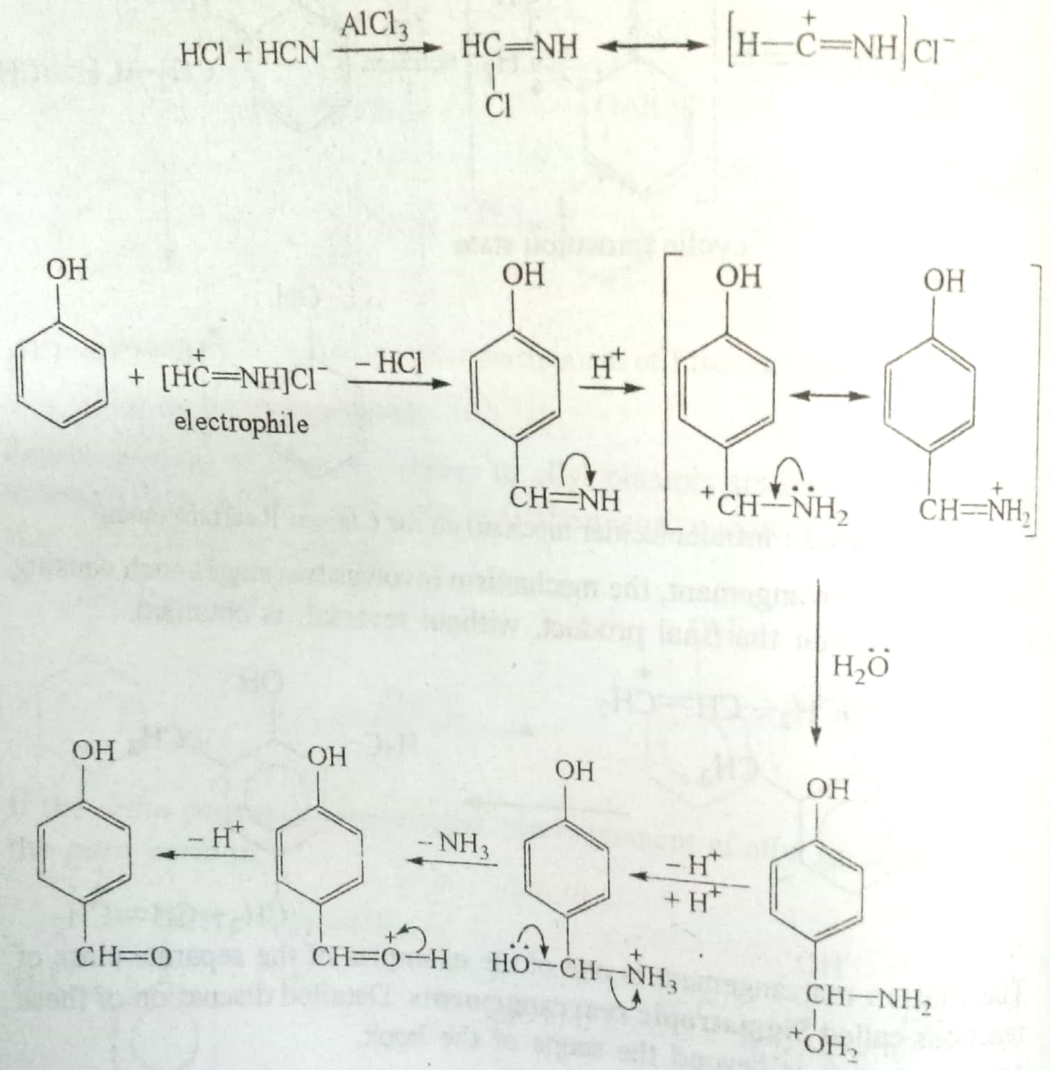
The Claisen rearrangement is one of the examples of the separate class of reactions called **Sigmatropic rearrangements**. Detailed discussion of these rearrangements is beyond the scope of the book.

### 3. Gattermann Aldehyde Synthesis

Treatment of phenol with a mixture of hydrogen cyanide and hydrogen chloride in the presence of aluminium chloride followed by hydrolysis of intermediate *p*-hydroxybenzaldimine, afford *p*-hydroxybenzaldehyde. This is known as Gattermann aldehyde synthesis.



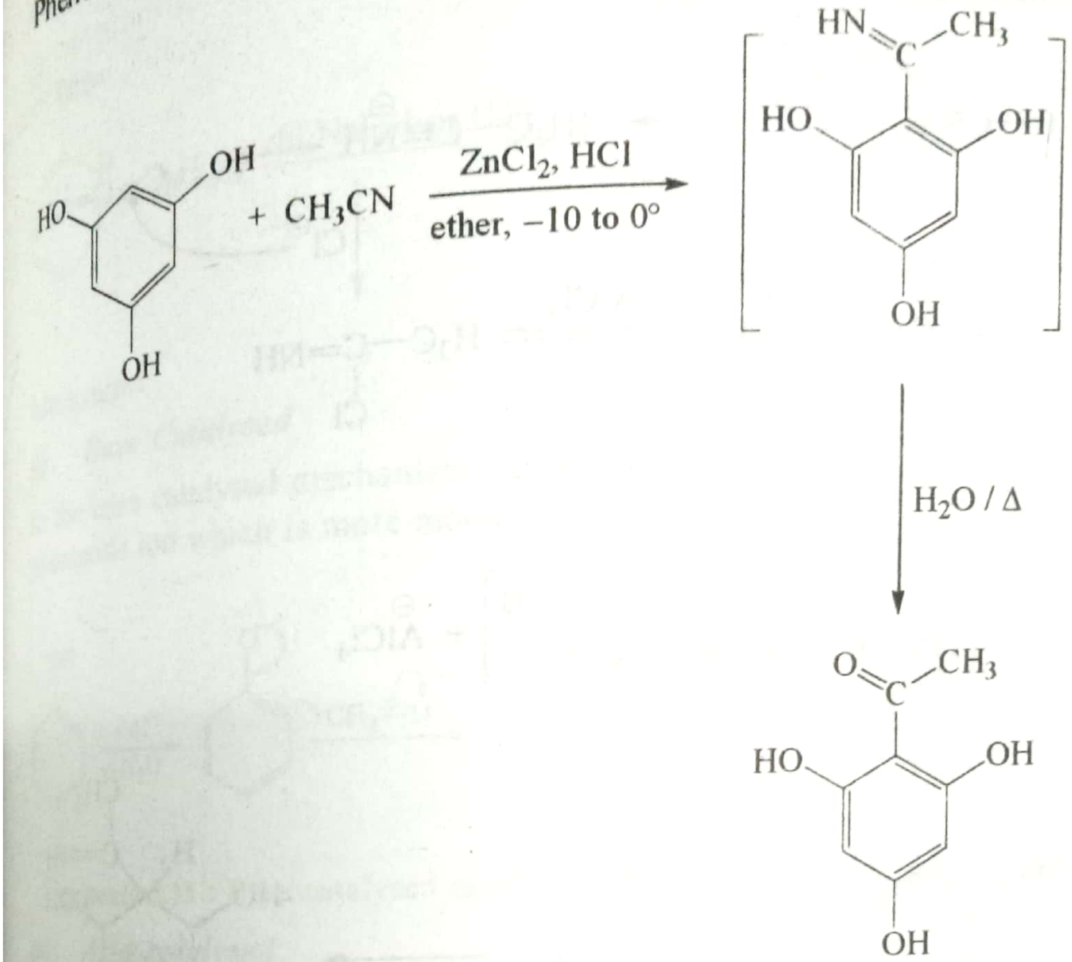
**Mechanism** : The mechanism of the reaction involves formation of imidoformyl chloride as intermediate which acts as formylating agent for aromatic ring (Scheme 3.9).



**Scheme 3.9** : Mechanism of Gattermann Aldehyde Synthesis

### 4. Houben-Hoesch Reaction

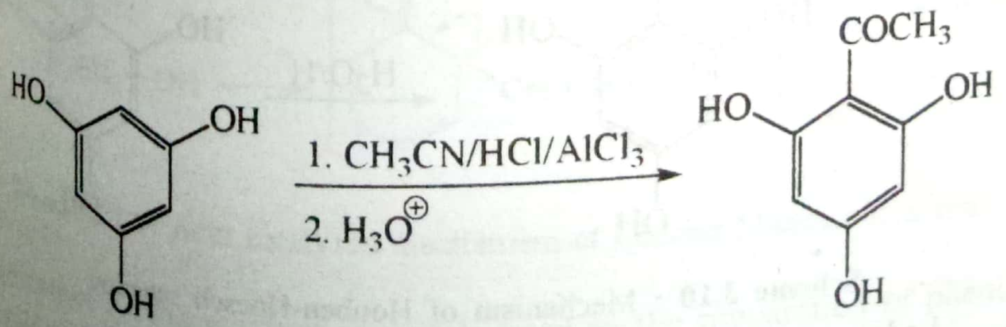
This is an alternative method to prepare hydroxy-acetophenones where Friedel-Crafts acylation or Fries rearrangement is not successful. In this reaction a phenol is treated with a nitrile in the presence of zinc chloride as catalyst.



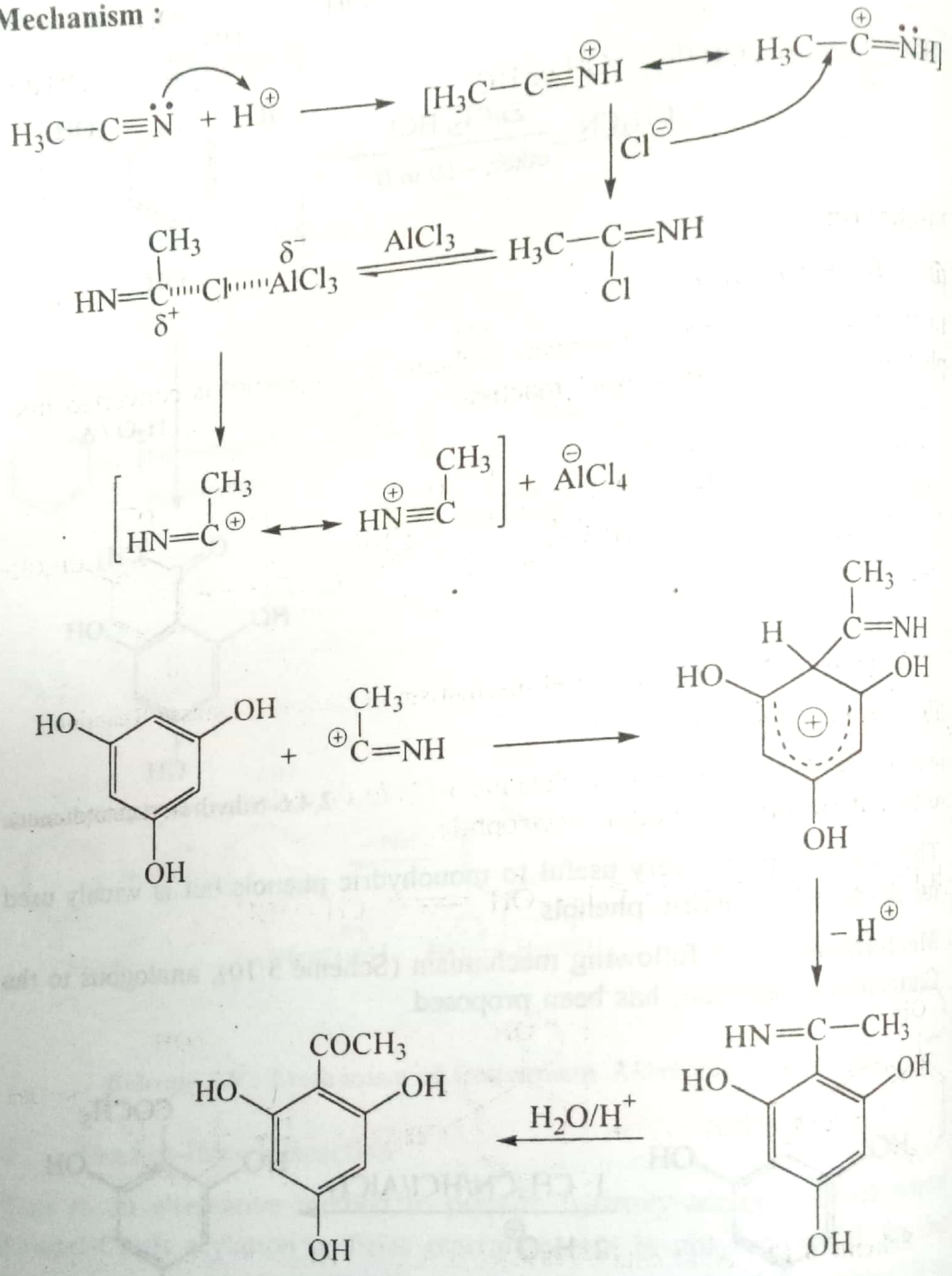
2,4,6-trihydroxyacetophenone

The reaction is not very useful to monohydric phenols but is widely used for di- and polyhydric phenols.

**Mechanism :** The following mechanism (Scheme 3.10), analogous to the Gattermann reaction, has been proposed.



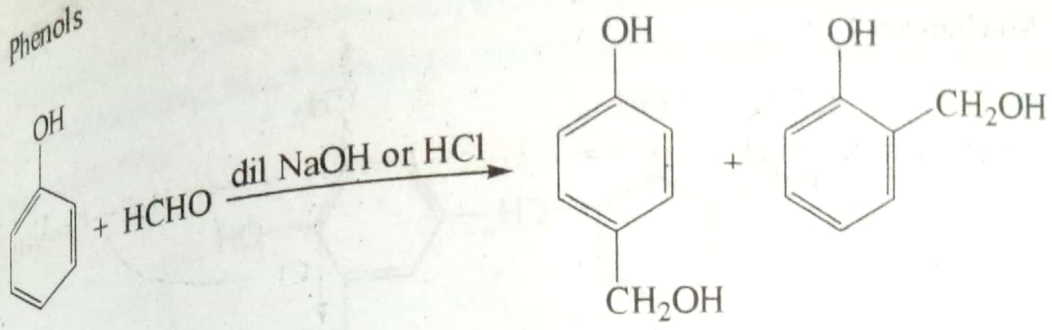
**Mechanism :**



Scheme 3.10 : Mechanism of Houben-Hoesch reaction

## 5. Lederer-Manasse Reaction

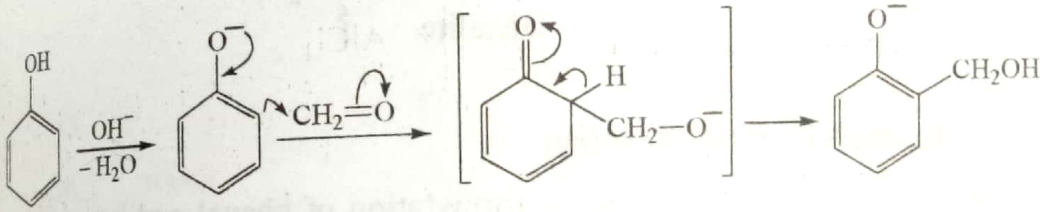
Condensation of phenol with formaldehyde in the presence of dil. acid or alkali to give *p*-hydroxybenzyl alcohol as main product along with small amount of *o*-hydroxybenzyl alcohol is known as Lederer-Manasse reaction.



**Mechanism**

(i) ***Base Catalysed***

In the base catalysed mechanism (Scheme 3.11) phenol is converted into phenoxide ion which is more reactive.

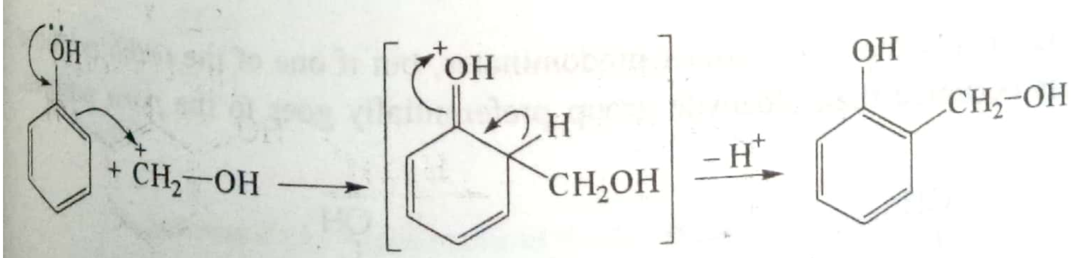


**Scheme 3.11 :** Base catalysed mechanism of Lederer-Manasse Reaction

(ii) ***Acid catalysed***

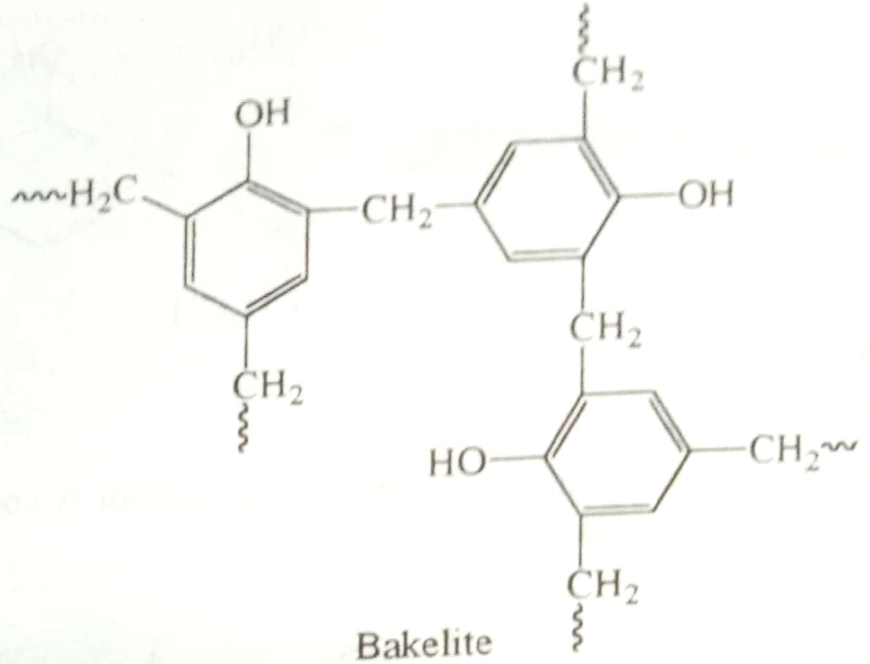
In acid catalysed mechanism (Scheme 3.12) formaldehyde is first protonated so that it becomes a better electrophile.

$$H_2C{=}O + H^+ \rightleftharpoons CH_2{=}\overset{+}{O}H \rightleftharpoons \overset{+}{C}H_2{-}OH$$



**Scheme 3.12 :** Acid catalysed mechanism of Lederer-Manasse Reaction

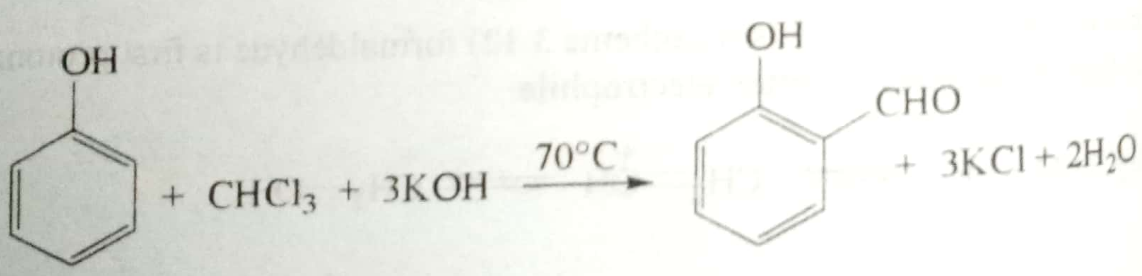
**Application :** This reaction is widely used in the preparation of phenol-formaldehyde resins called **Bakelites**. For example, phenol upon condensation with excess formalin (40% aqueous solution of formaldehyde) in the presence of dil NaOH gives '*Cross linked*' polymer Bakelite.



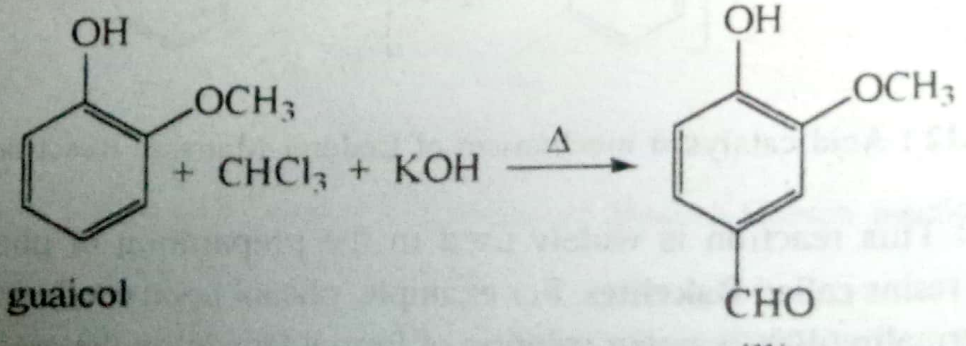
Bakelite

6. **Reimer-Tiemann Reaction**

This is an alternative method for formylation of phenol and is carried out by heating a mixture of phenol, chloroform and alkali (KOH) at 70°C to produce *o*-hydroxybenzaldehyde *i.e.* salicylaldehyde.



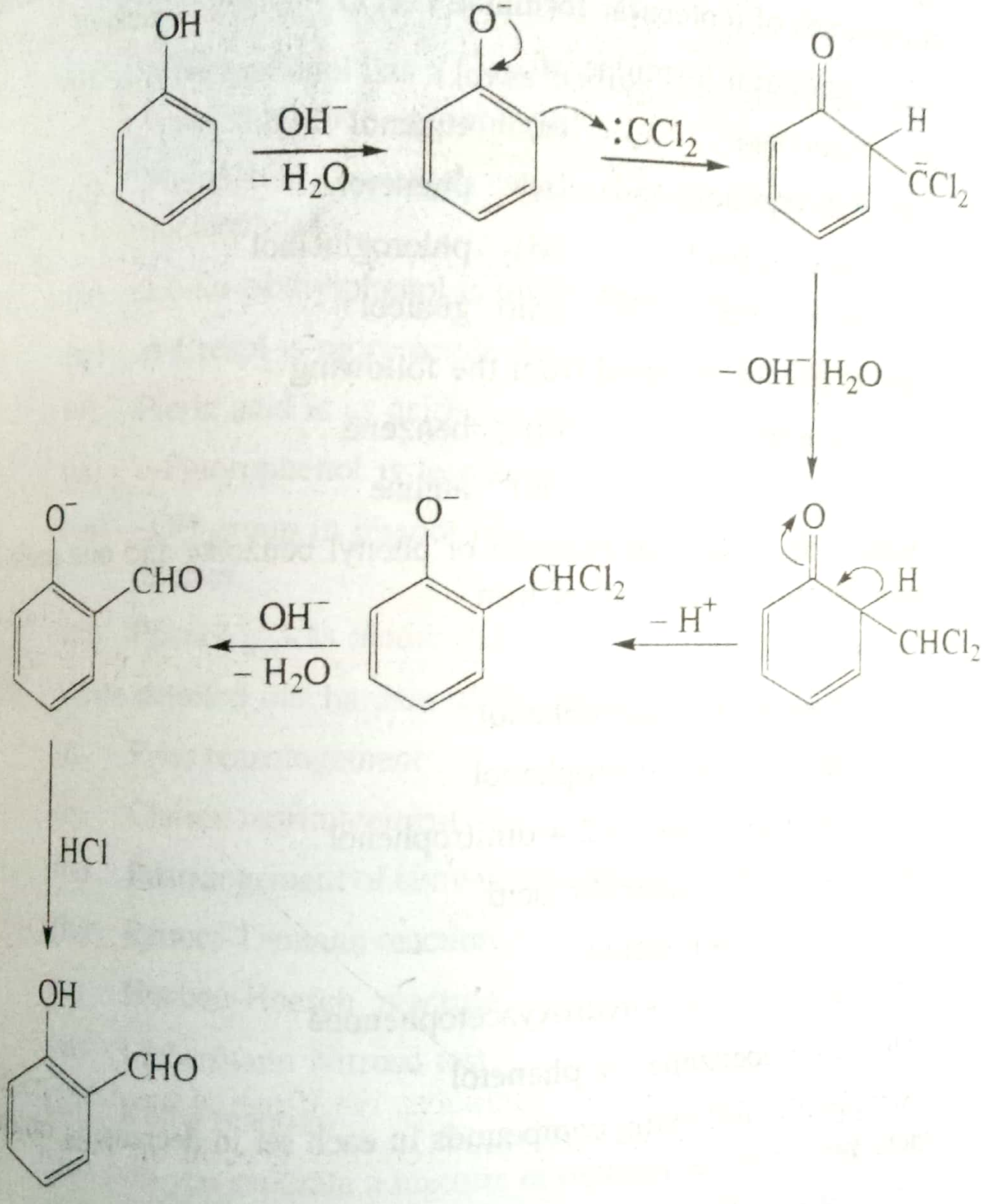
Generally the *ortho* isomer predominates, but if one of the *ortho* positions is occupied then aldehyde group preferentially goes to the *para* position.



guaicol

vanillin

**Mechanism :** The mechanism involves (Scheme 3.13) intermediate formation of dichlorocarbene which acts as an electrophile to attack the highly reacted phenoxide ring.



**Scheme 3.13 :** Mechanism of Reimer-Tiemann Reaction