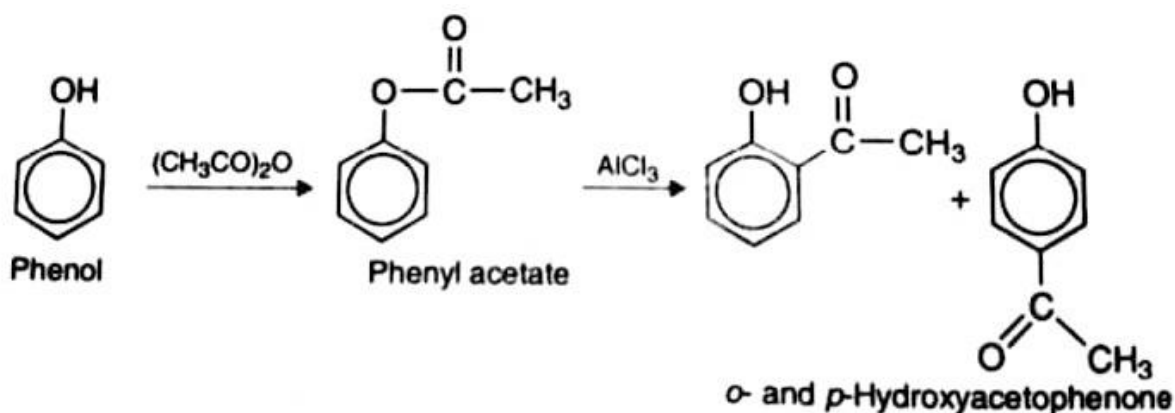
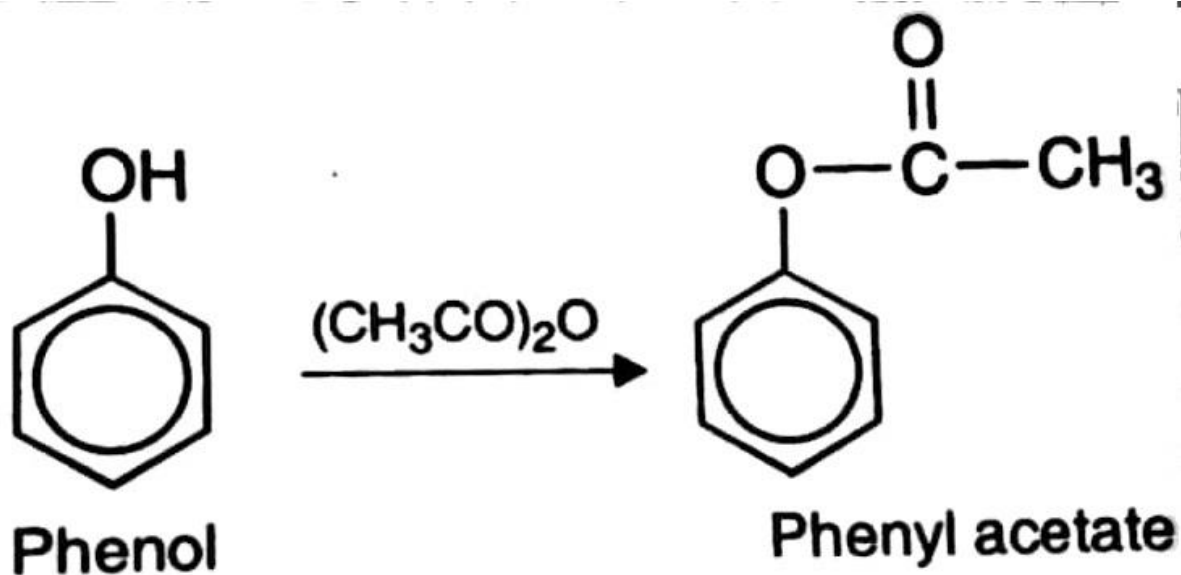


**(13) Fries Rearrangement.** The phenol is first treated with acetic anhydride in the presence of aqueous sodium hydroxide to give phenyl acetate. The ester is then heated with aluminium chloride catalyst when the acyl group migrates from the phenolic oxygen to an ortho or para position of the ring. The product is a mixture of o- and p-hydroxyacetophenone.

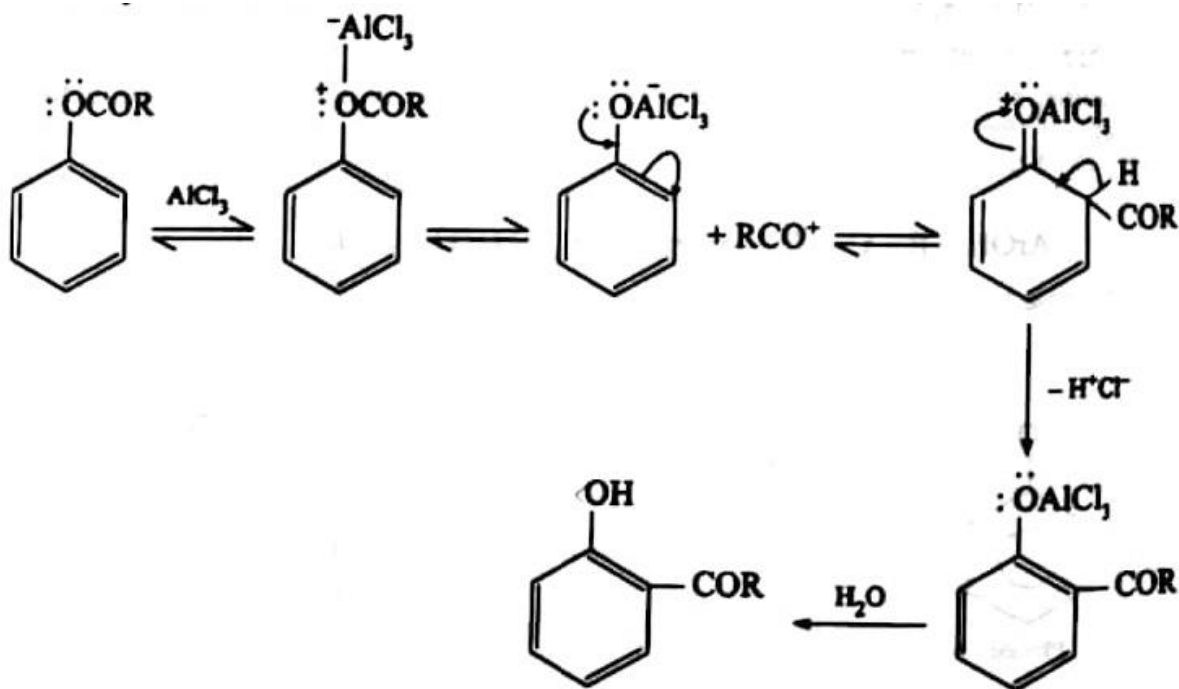


The Fries rearrangement is also given by other phenols and introduces -COR group in the ortho

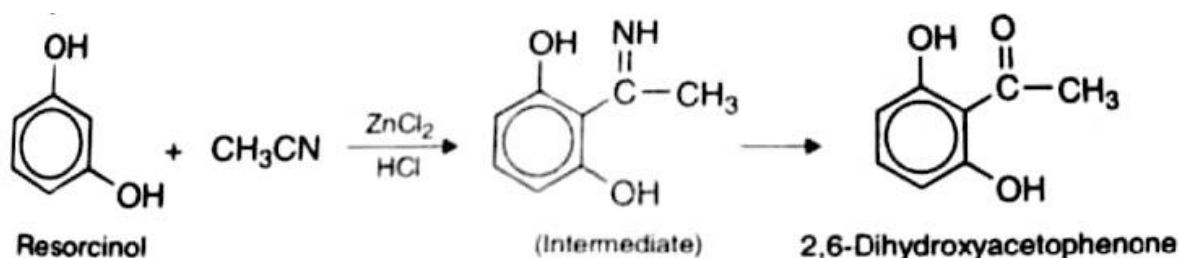
At low temperature, para product predominates while at high temperature ortho isomer is the main product.



Mechanism. Fries rearrangement probably involves the formation of an acylium ion (RCO<sup>+</sup>) which then attacks the aromatic ring as in Friedel-Crafts acylation. The complete mechanism may be summed up as follows :



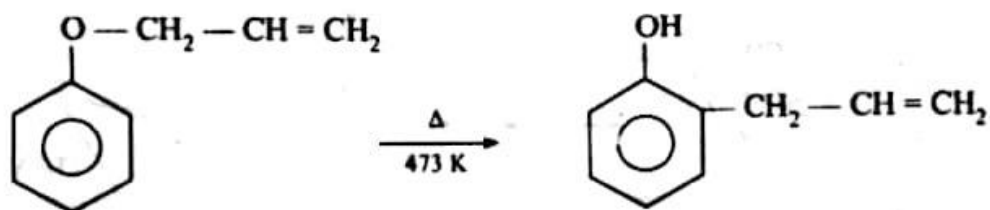
**Houben-Hoesch Reaction.** This reaction involves the treatment of a dihydric or a trihydric phenol with an alkyl cyanide in the presence of zinc chloride and hydrogen chloride. The product on hydrolysis yields a phenolic ketone.



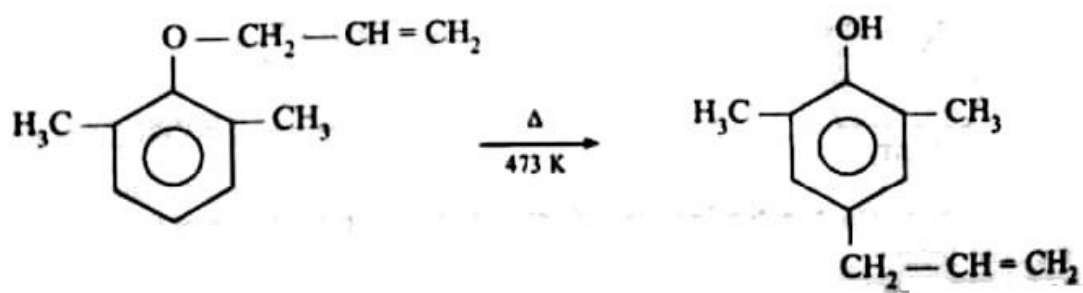
The Houben-Hoesch reaction provides a method for indirect ring acylation of polyhydric phenols. Phenol does not give this reaction.

## Claisen Rearrangement

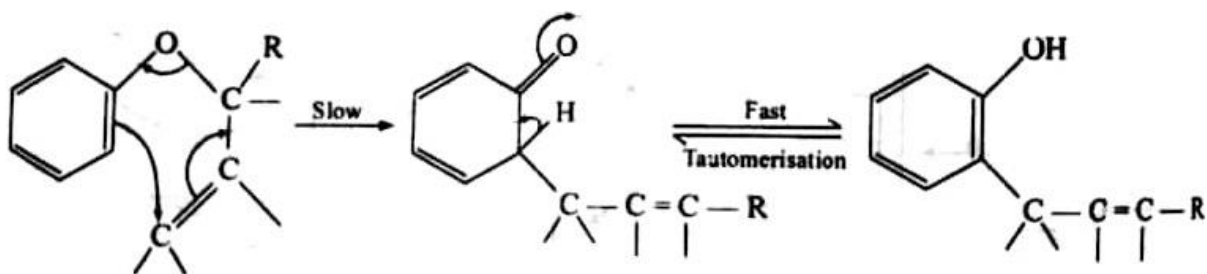
When a simple or substituted alkyl aryl ether is heated at 473 K, an isomerisation takes place in which the allyl group migrates from the ether oxygen atom to a carbon atom of the aromatic ring. The allyl group goes to the ortho position preferentially.



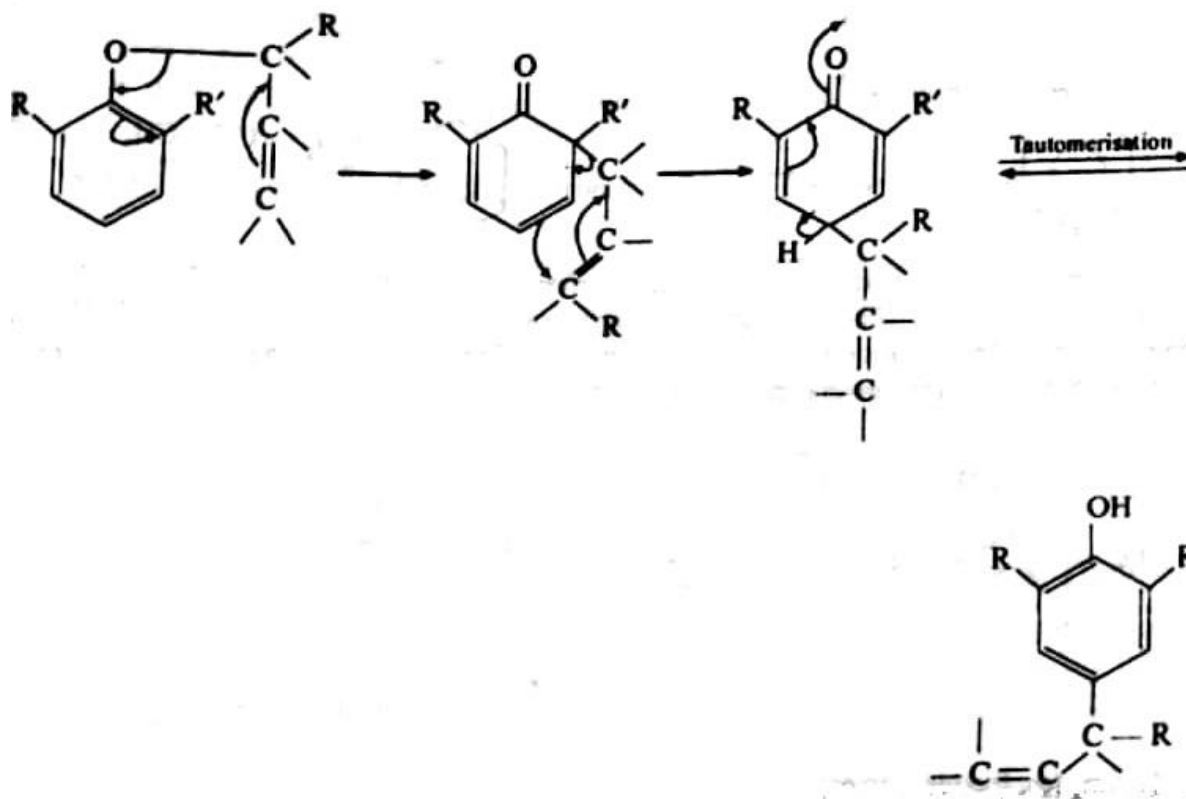
If both the ortho positions are occupied, migration takes place to the para position.



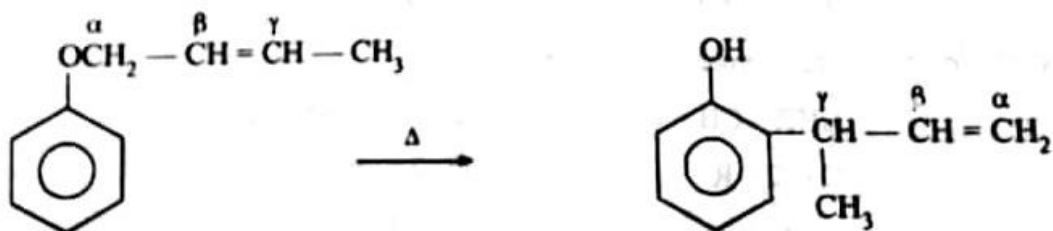
Migration to meta position is not observed. In the ortho migration, the allyl group always undergoes an allylic shift. In the para migration, there is never an allylic shift and the allyl group is found exactly as it was in the original ether. Mechanism for the ortho rearrangement is given below:



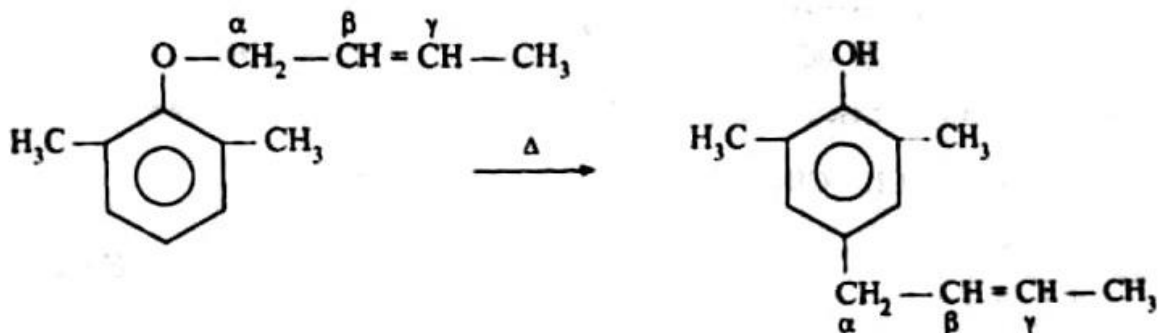
The mechanism of Claisen rearrangement when both the ortho positions are blocked is given



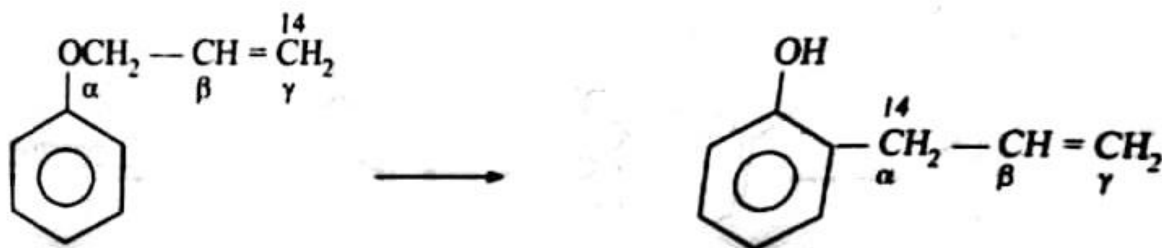
As Claisen condensation involves a cyclic mechanism, it is not influenced by the substituents on the ring. Ortho isomerisation is accompanied by inversion of the position of substituent with respect to that of the starting material.



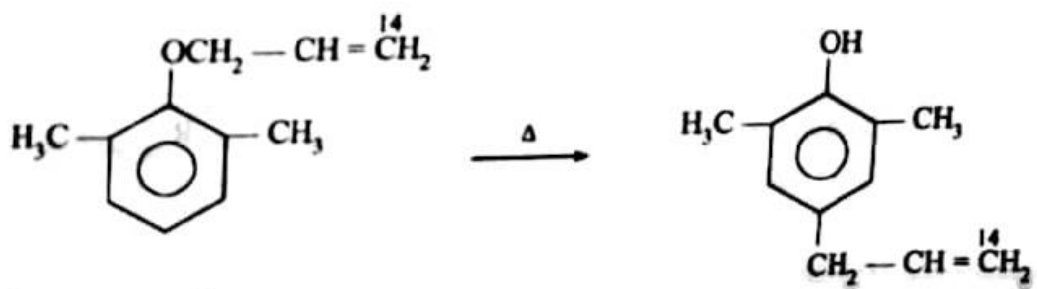
But no such inversion takes place when para isomerisation is involved.



To prove that ortho isomerisation takes place with inversion of position, Schmidi carried out the rearrangement of phenyl allyl ether labelled with  $^{14}\text{C}$  in the  $\gamma$ -position and obtained o-allyl phenol having  $^{14}\text{C}$  in the  $\alpha$ -position.



The experiment with para isomerisation was performed with 2, 6 dimethyl allyl ether labeled with  $^{14}\text{C}$  in the  $\gamma$ -position. This compound rearranges to 4-allyl-2, 6-dimethyl phenol with  $^{14}\text{C}$  still in the position of the allyl group which occurs due to double migration of the allyl group, in each migration, there occurs the inversion of the allyl group.

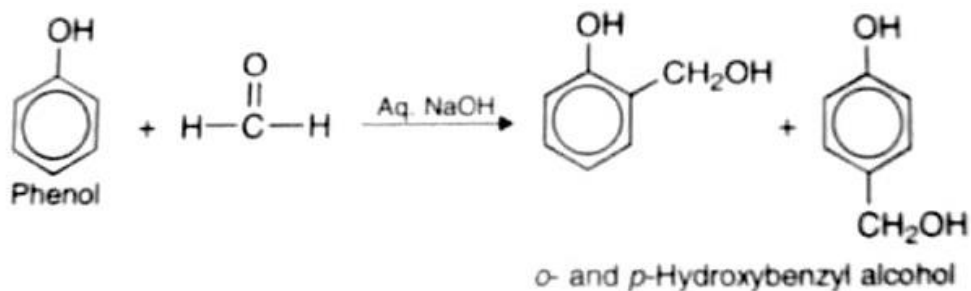


## Lederer Manasse

### Reaction

When phenol is treated with an alkaline solution of

formaldehyde, a mixture of o- and p-hydroxybenzyl alcohol is formed.



If the reaction is carried at high temperature and in excess of formaldehyde, hard thermosetting plastic Bakelite is formed.