

SUBJECT - CHEMISTRY

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CLASS - B.Sc (Hons) PART - II

PAPER - IV GROUP - B

TOPIC - Reimer-Tiemann reaction:

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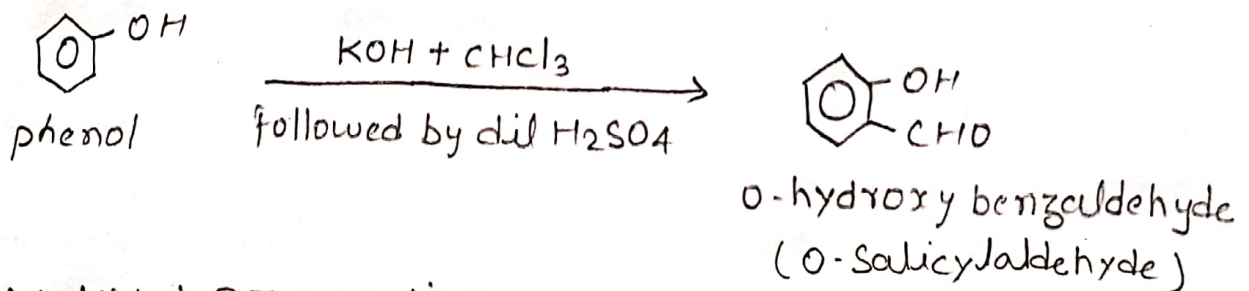
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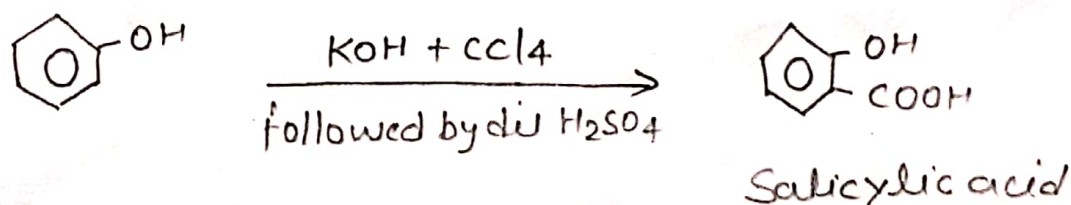
Reimer-Tiemann reaction:

When an alkaline solution of the mixture containing phenol and chloroform is refluxed at  $60^\circ$  and then acidified with  $H_2SO_4$ , a mixture of o- & p-hydroxybenzaldehyde is formed. They are separated by steam distillation, o-isomer distills over and p-isomer is left behind as o-position of phenol is blocked, the -CHO group tends to go to p-position.

The reaction is called 'Reimer-Tiemann reaction' By an extension of R-T reaction, using  $CCl_4$  in presence of alkali, phenolic acid are prepared -

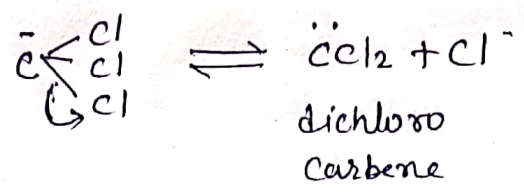
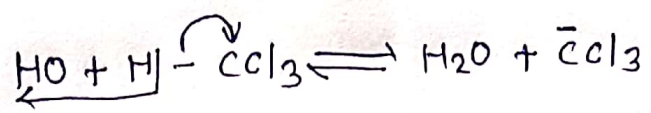


Modified RT reaction



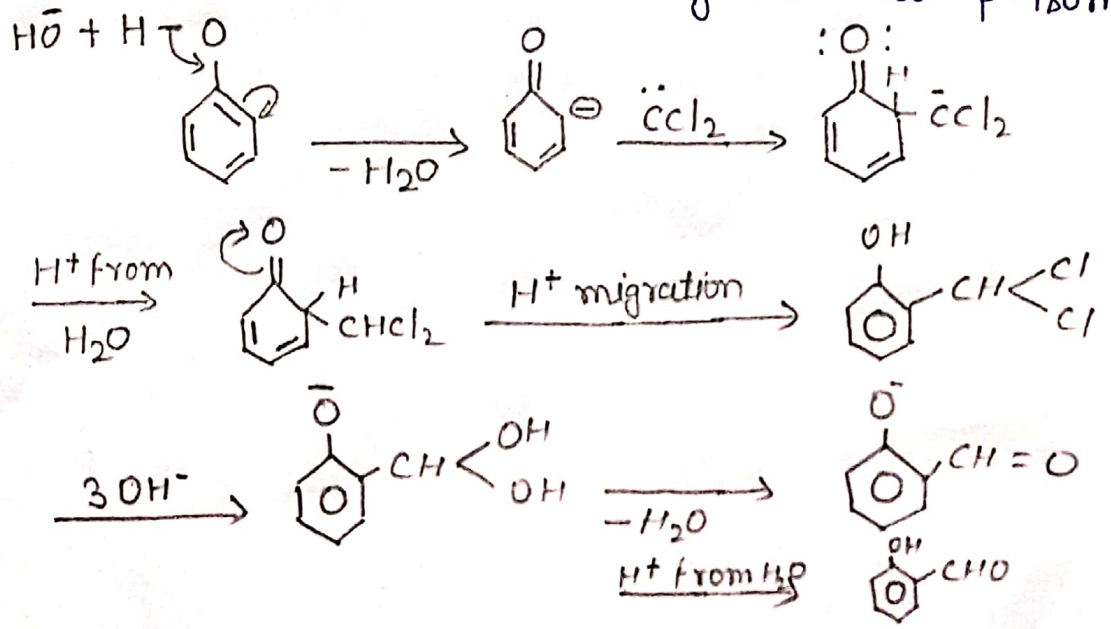
This reaction is an example of electrophilic aromatic substitution reaction. Therefore in the first step, the strong electrophile dichloro carbene is generated by the action of strong alkali on chloroform. The H-atom of  $H-CCl_3$  being acidic due to -I-effect of Cl-atom is

removed by OH<sup>-</sup> ion forming dichloro carbene



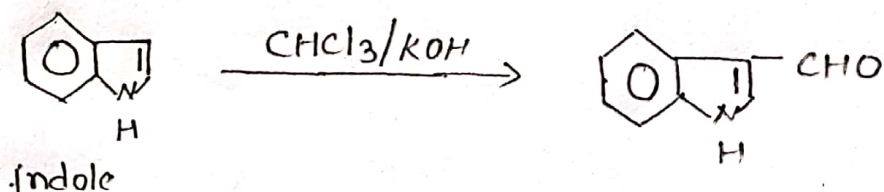
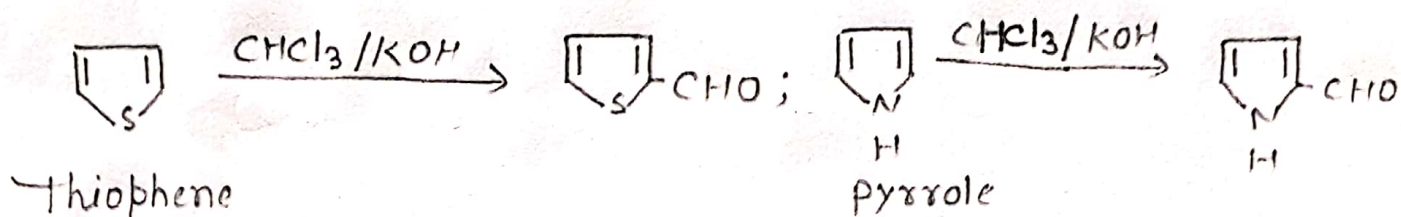
Though dichloro carbene appears to be nucleophile but actually it is an electrophile as it has only sextet of electron around C-atom s.e it is a typical electron deficient species.

This electrophile now attacks on the activated sites s.e O- & p-positions of the phenolate ion formed by the action of alkali on phenol forming intermediate which takes up proton from H<sub>2</sub>O in order to maintain aromatic sextet, migration of H<sup>+</sup> takes place from adjacent C-H to O atom Then both Cl- atoms are substituted by OH<sup>-</sup> ions followed by dehydration finally it gets protonated from H<sub>2</sub>O to yield to o-isomer as the main product because o-isomer is more stabilised by intramolecular H-bonding than its p-isomer:

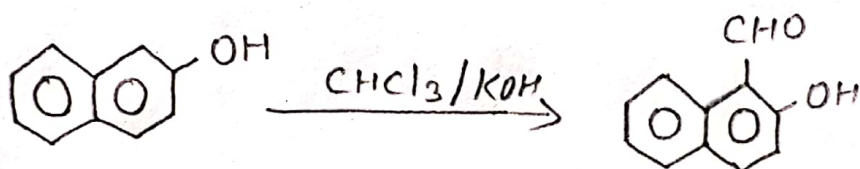


## Applications:

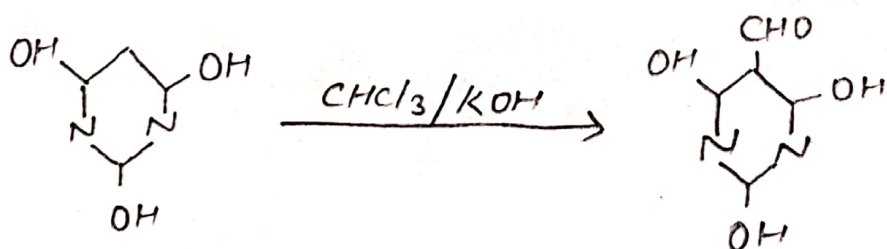
(1) In the preparation of heterocyclic derivatives -



(2) 2-Naphthol gives 2-hydroxy-1-naphthaldehyde -



(3) In the preparation of pyrimidine aldehydes



2:4:6-trihydroxy  
pyrimidine

2:4:6-trihydroxy pyrimidine  
3-Carboxyaldehyde