class - B.Sc. Part II (Honours)
Subject - chemistry
Paper - III C
Topic - Reimer - Tiemann reaction
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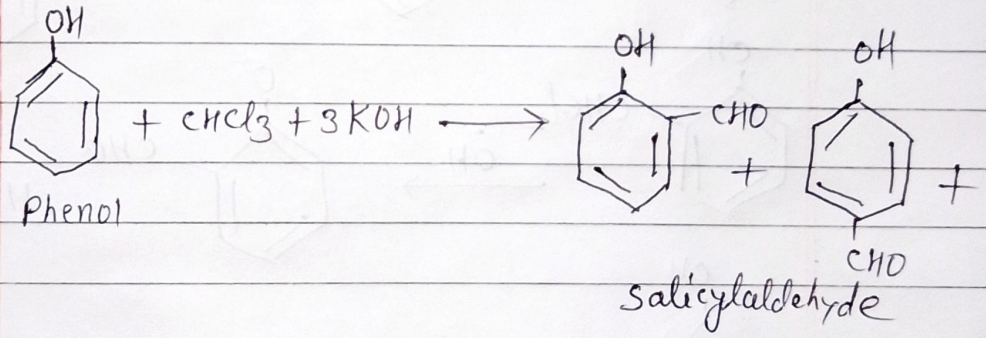
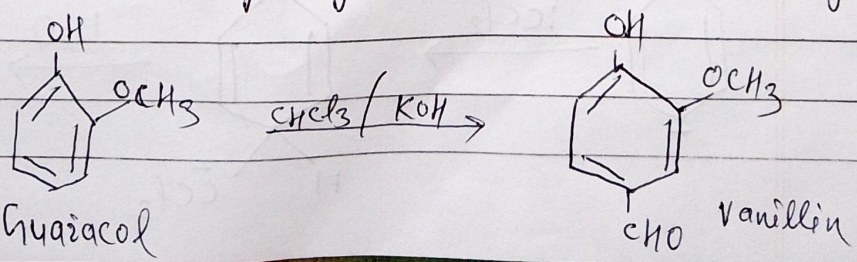
Deptt. of chemistry, H.D.J.C. Ara

Reimer - Tiemann reaction :- The conversion of Phenols into phenolic aldehyde by treatment with alkaline chloroform is known as Reimer-Tiemann reaction.



The product of Reimer - Tiemann reaction is a mixture of o- and p- aldehydes, yet the o-product predominates. If an o-position is already occupied, the aldehyde gr. goes to p-position. e.g :-

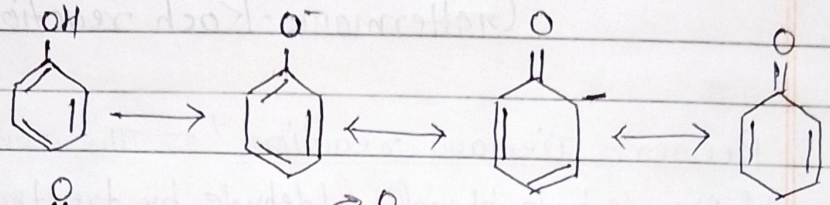


Mechanism :- The nucleophilic phenoxide ion attacks the electron deficient dichloromethylene, produced from chloroform and alkali to form Benzal chloride which on hydrolysis followed by acidification gives an aldehyde.

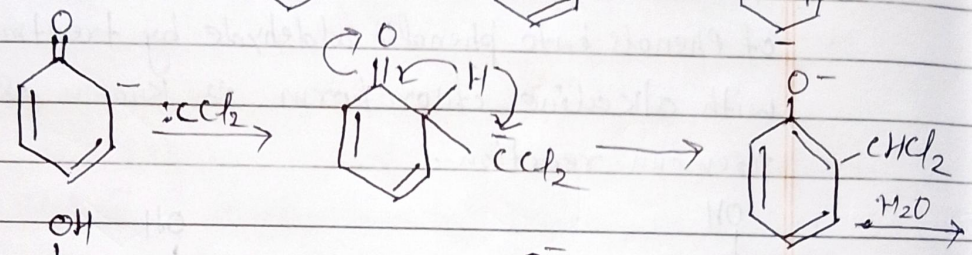
(a) Formation of dichloromethylene.

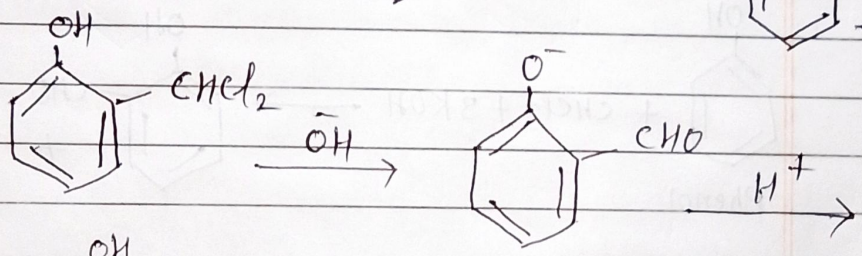
$$CHCl_3 + \bar{O}H \rightleftharpoons H_2O + :\bar{C}Cl_3 \longrightarrow :CCl_2 + Cl^-$$

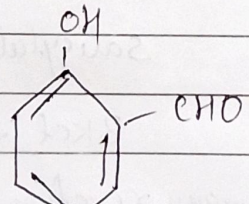
(b)



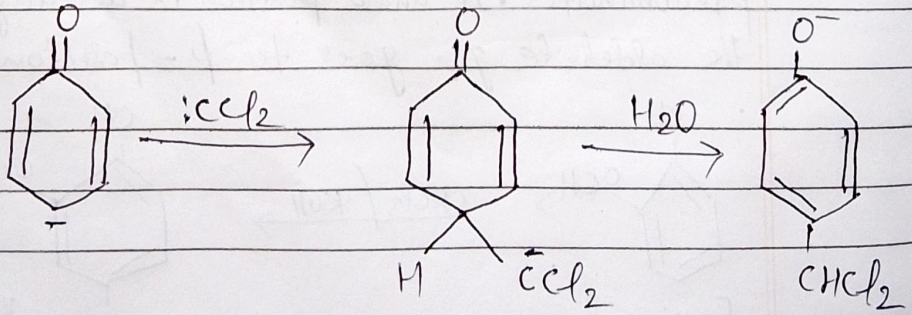
(c)

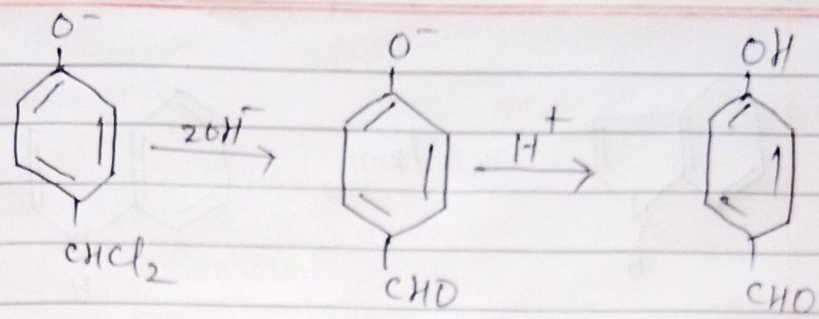






o - hydroxybenzaldehyde





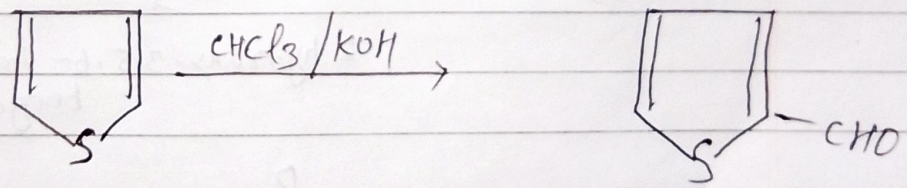
P-hydroxybenzaldehyde

The presence of -I groups like $-NO_2$, CN, COOH, SO_3H (i.e. m-orienting) inhibits the reaction.

Applications :—

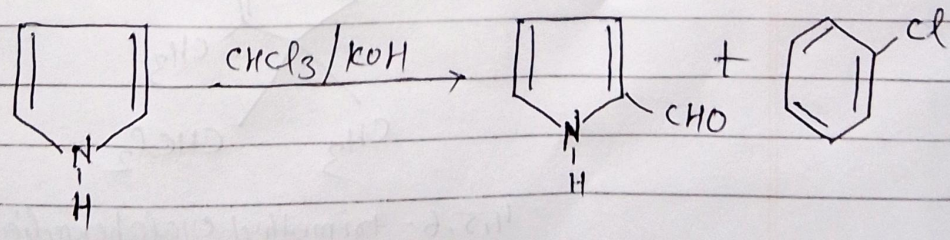
(i) The reaction can be applied on some hetero-cyclic compounds also. e.g :—

a.



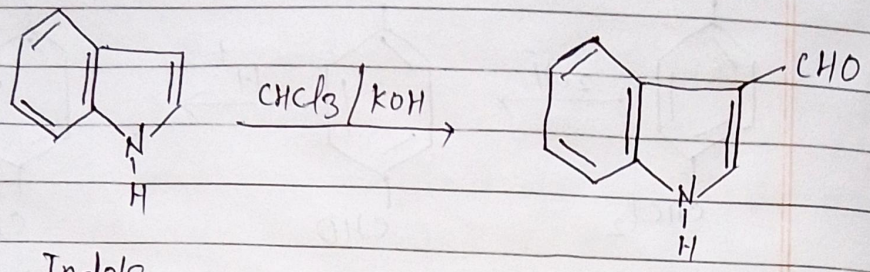
Thiophene

b.



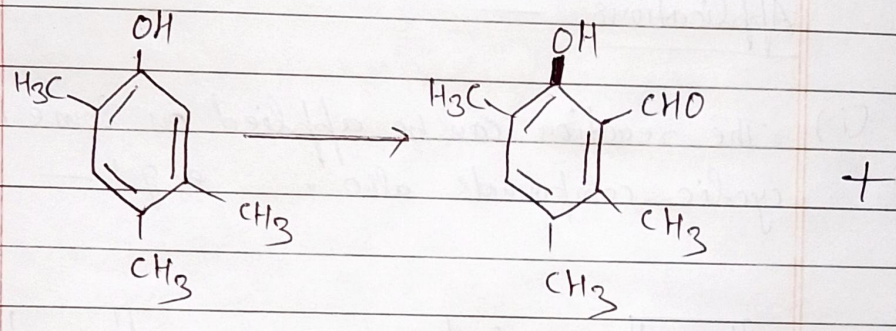
Pyrrole

c.

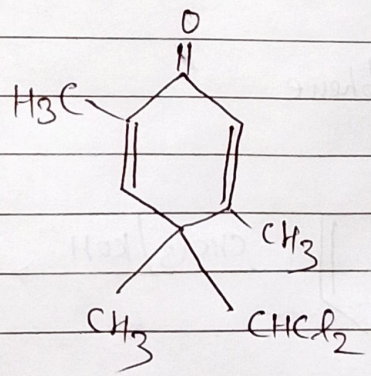


Indole

(ii) Phenols with blocked p-position gives cyclohexadienones, since they can't tautomerize to regenerate the phenolic system.



2-hydroxy-3,5,6-trimethyl-benzaldehyde



4,5,6-trimethyl cyclohexadiene-1-one