

Hydroxy Compounds

II B.Sc.

Semester - III

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Outlines

1

Bromination

2

Kolbe-Schmidt reaction

3

Riemer-Tiemann reaction

4

Fries rearrangement

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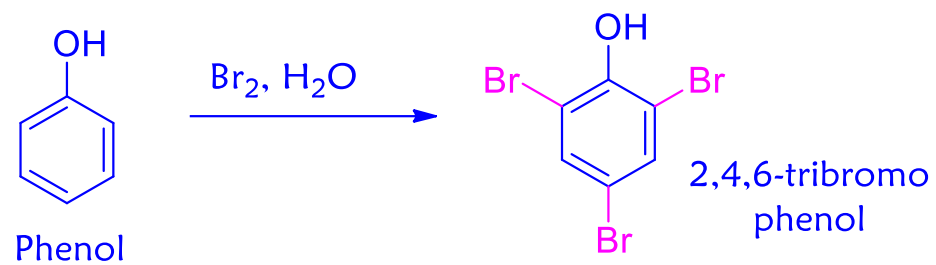
Azo-coupling

6

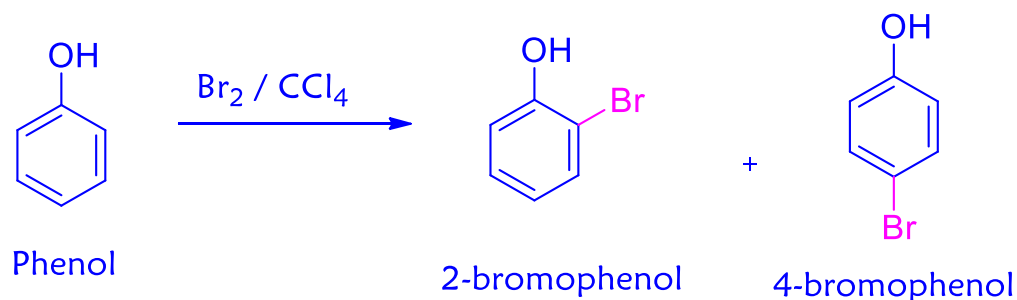
Pinacol-Pinacolone
rearrangement

Bromination

Phenol forms 2, 4, 6-tri bromo phenol as a product on reaction with Bromine water.

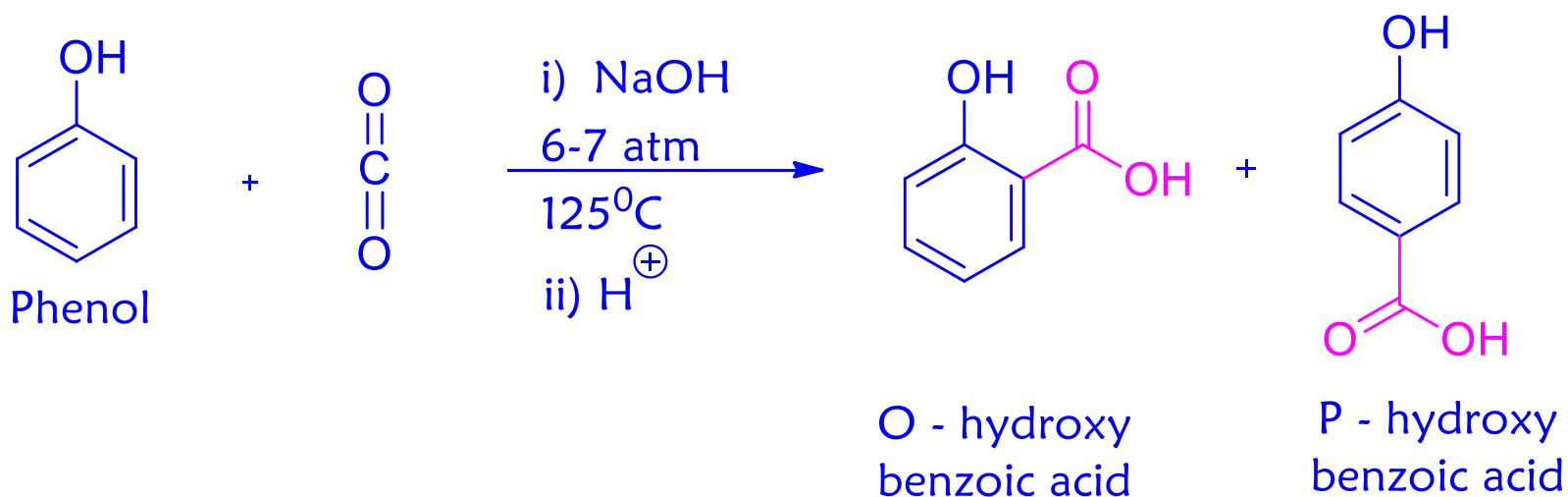


With $\text{Br}_2 / \text{CCl}_4$ or $\text{Br}_2 / \text{CS}_2$ mono bromophenol is formed



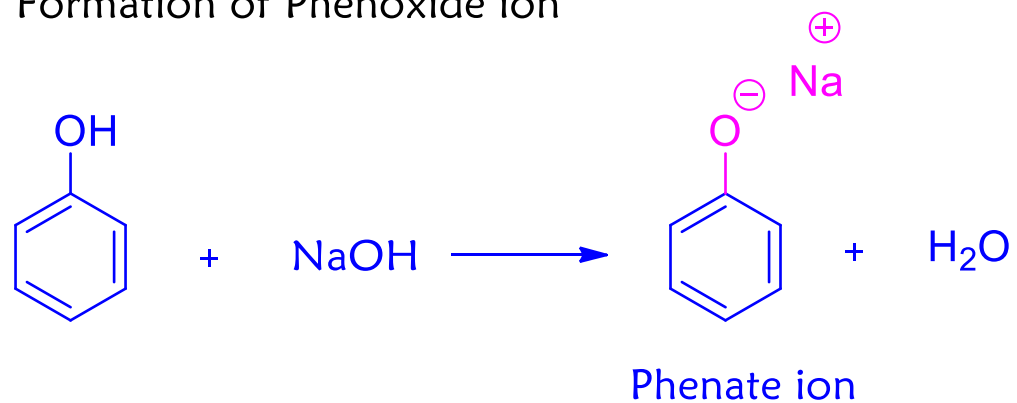
Kolbe-Schmitt Reaction

In this reaction phenol is converted to O - hydroxy benzoic acid (O - Salicylic acid) and P - hydroxy benzoic acid by reacting with carbon dioxide, base and an acid.

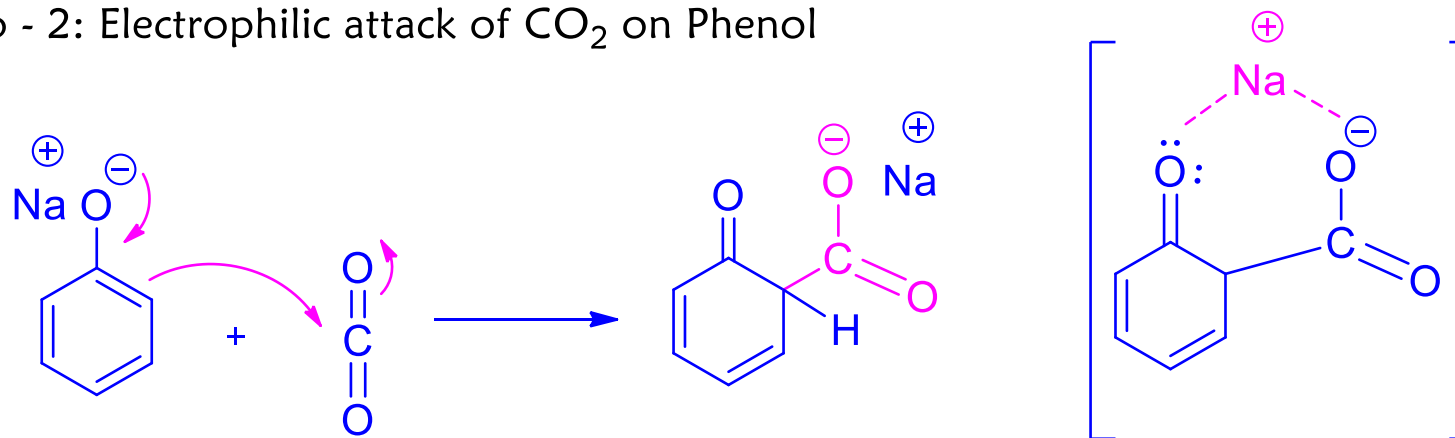


Mechanism:

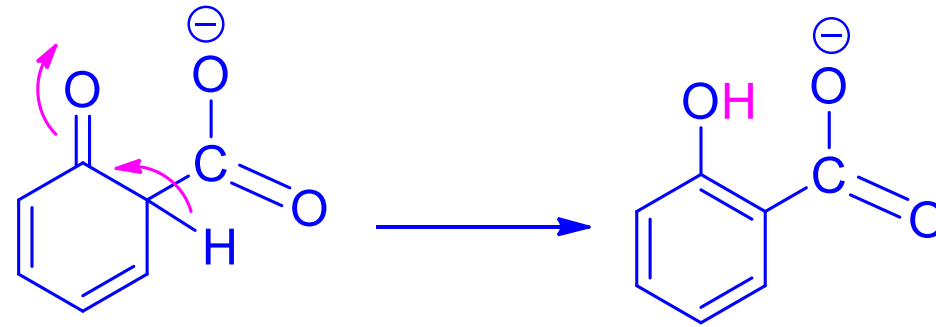
Step - 1: Formation of Phenoxide ion



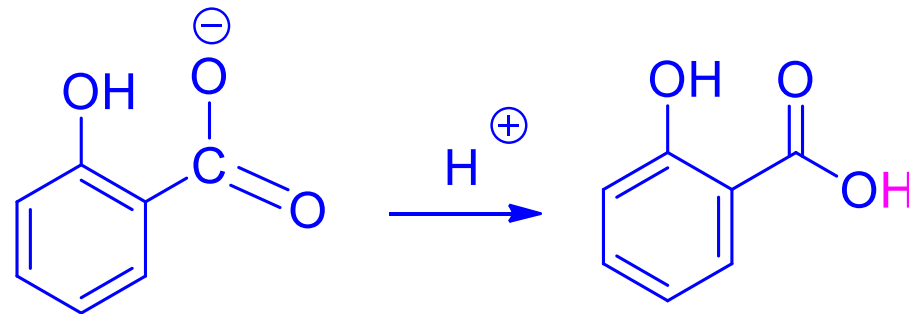
Step - 2: Electrophilic attack of CO₂ on Phenol



Step - 3: Formation of Carboxylate ion



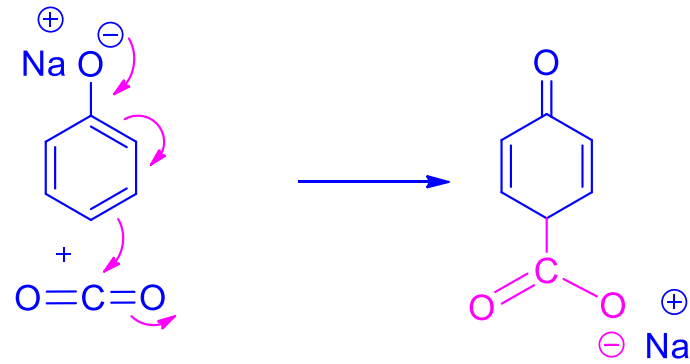
Step - 4: Formation of 2-hydroxy benzoic acid



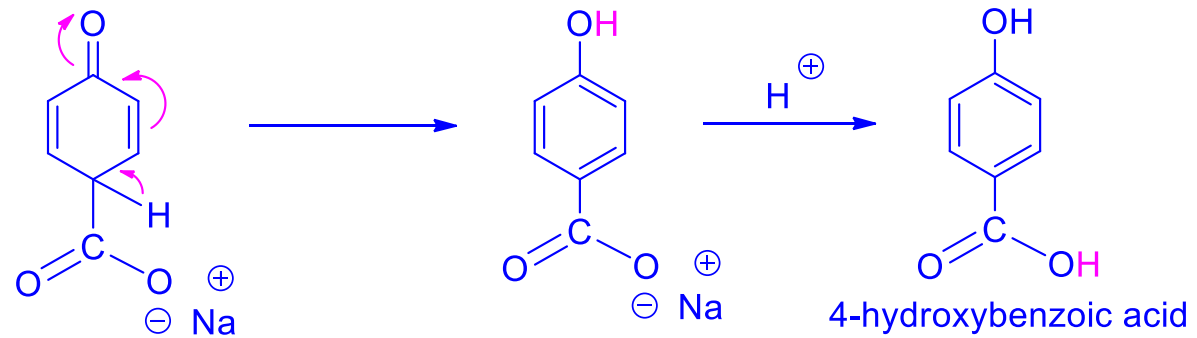
2-hydroxy benzoic acid

Formation of Para substituted product:

Step - 2: Electrophilic attack of CO₂ on Phenol

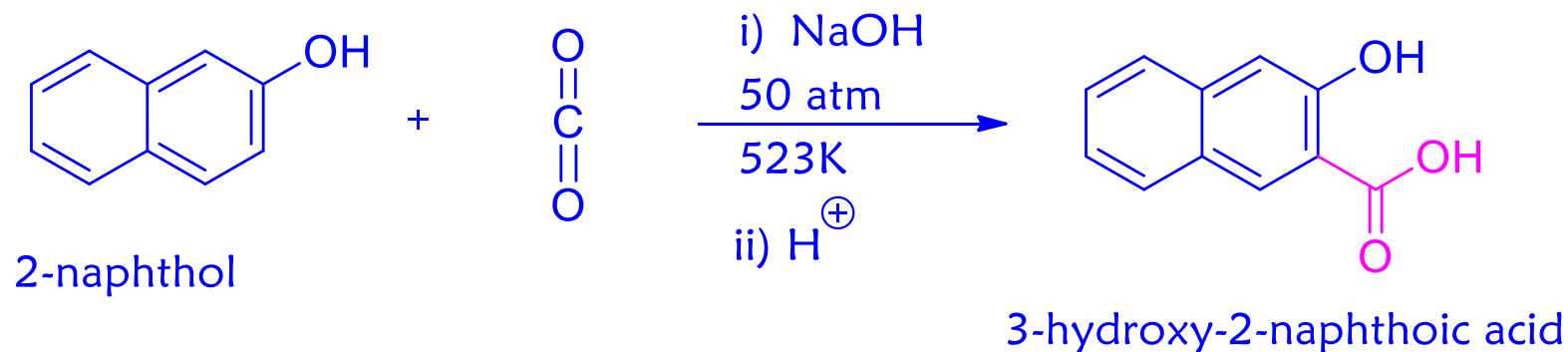


Step - 3: Formation of 4-hydroxybenzoic acid



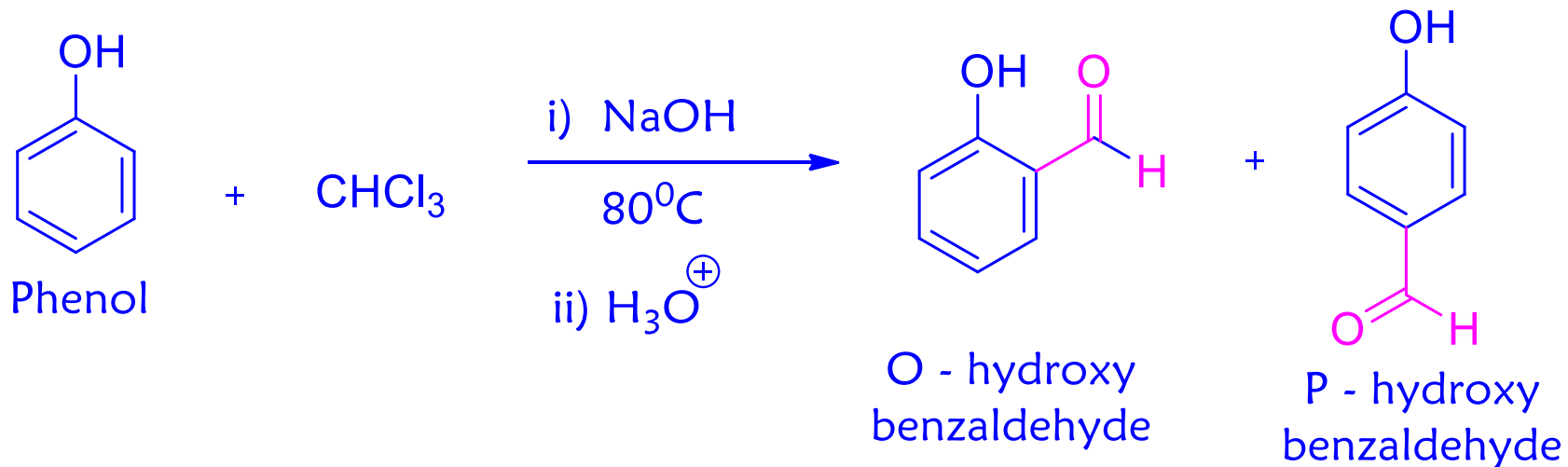
Applications of Kolbe-Schmitt Reaction:

- the formed product salicylic acid can be used as a precursor for making of Aspirin which is commonly used as pain killer.
- This reaction can also be used for the industrial synthesis of 3-hydroxy-2-naphthoic acid, which is a common precursor to azo dyes and pigments



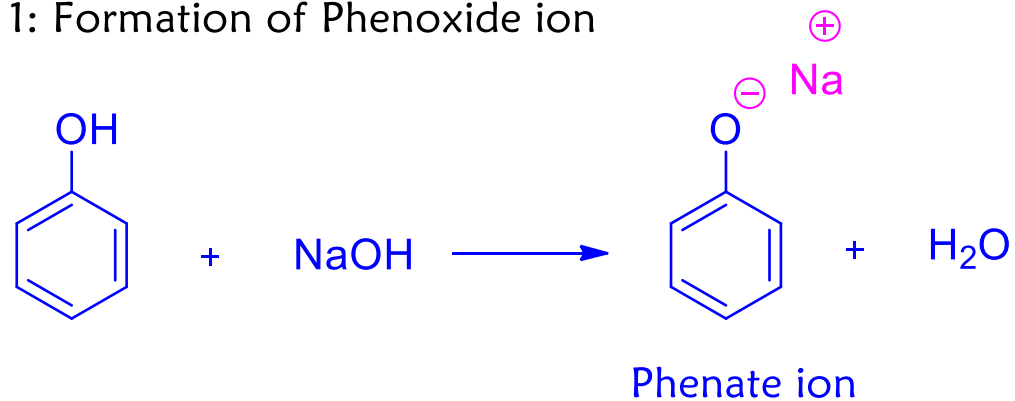
Riemer-Tiemann reaction

It is reaction used to convert phenol into O - hydroxy benzaldehyde (O - Salicylaldehyde) and P - hydroxy benzaldehyde using chloroform, base and acid.

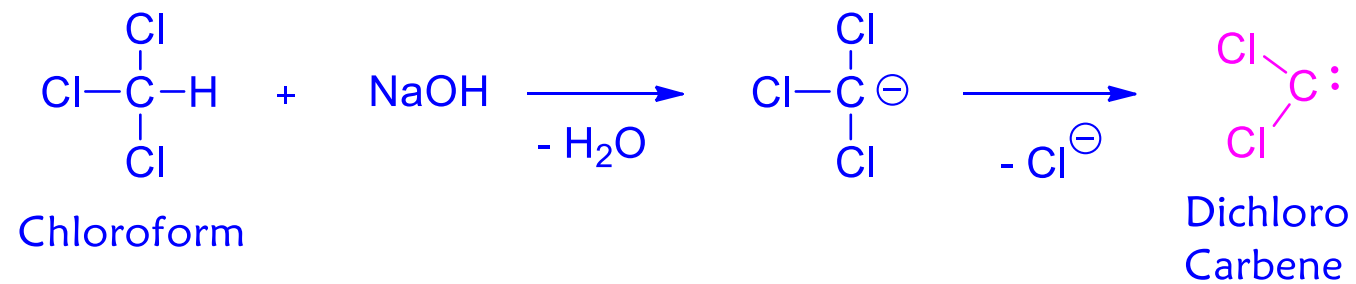


Mechanism:

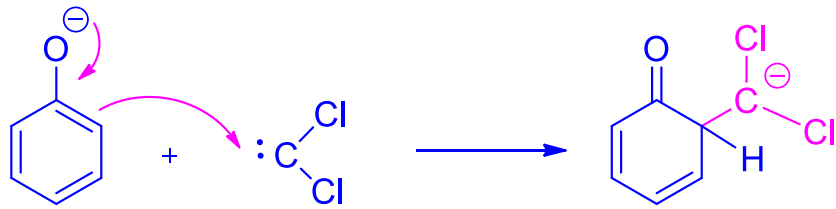
Step - 1: Formation of Phenoxide ion



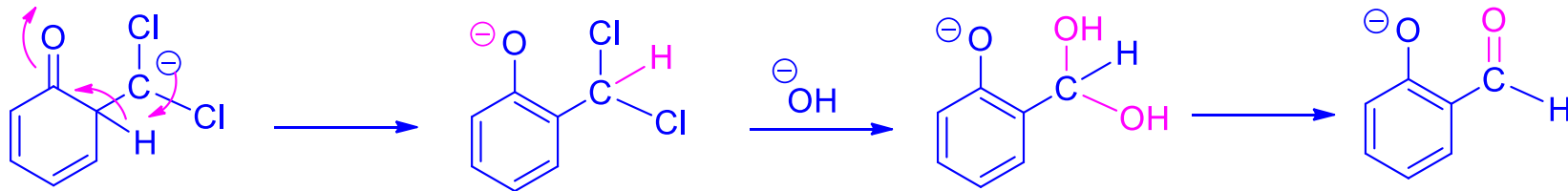
Step - 2: Generation of electrophile (Dichloro carbene Intermediate)



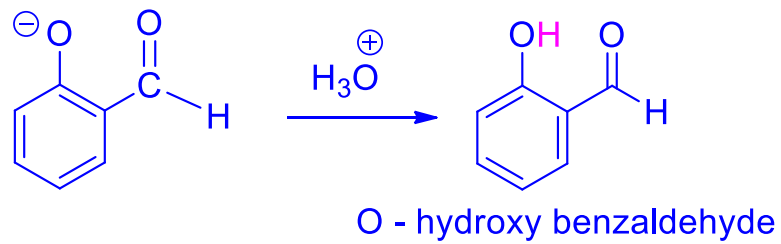
Step - 3: Electrophilic attack of carbene



Step - 4: Formation of aldehydic intermediate

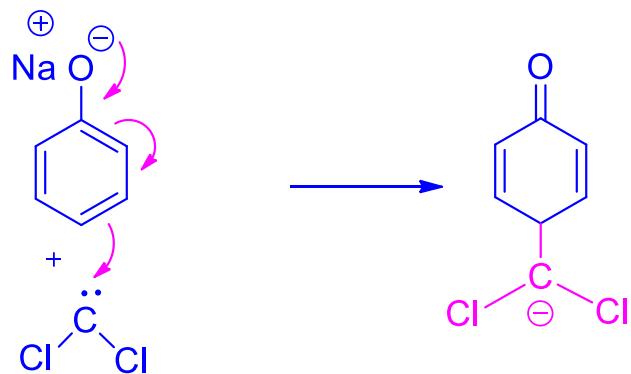


Step - 4: Formation of products

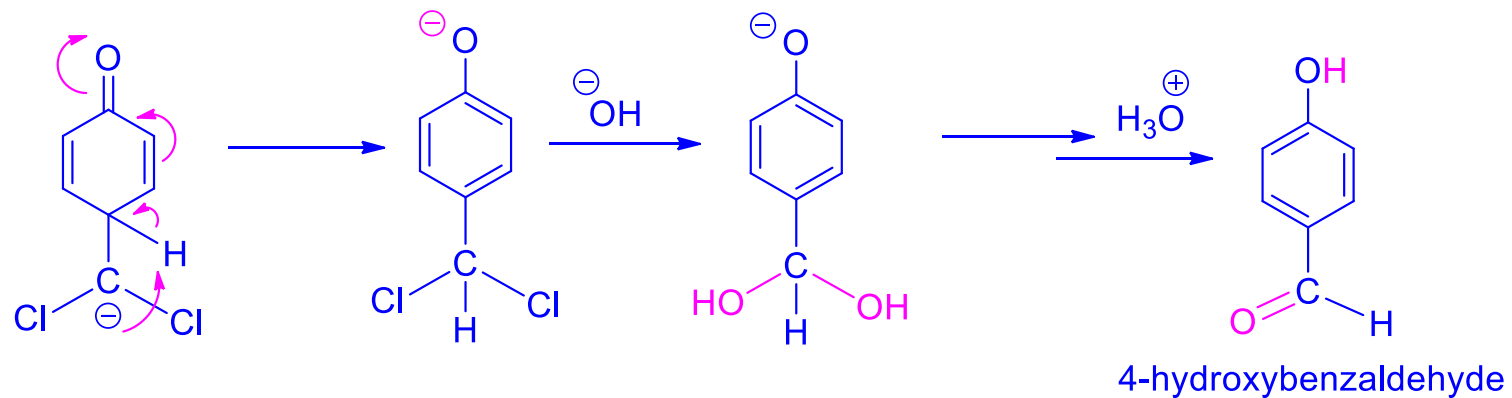


Formation of Para substituted product:

Step - 3: Electrophilic attack of CCl_2 on Phenol

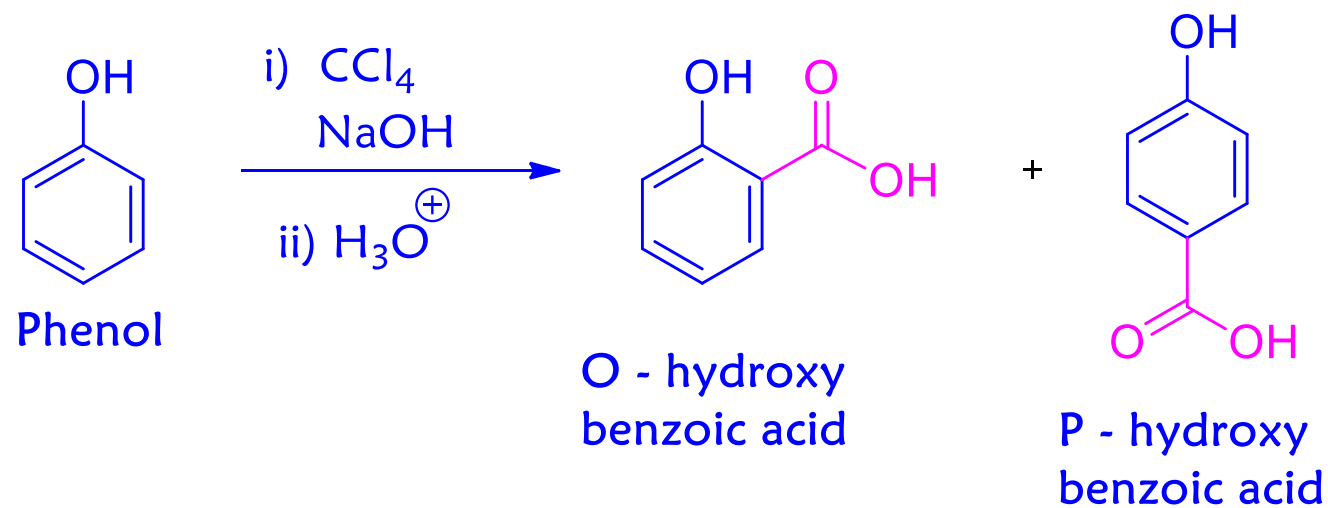


Step - 4: Formation of 4-hydroxybenzaldehyde

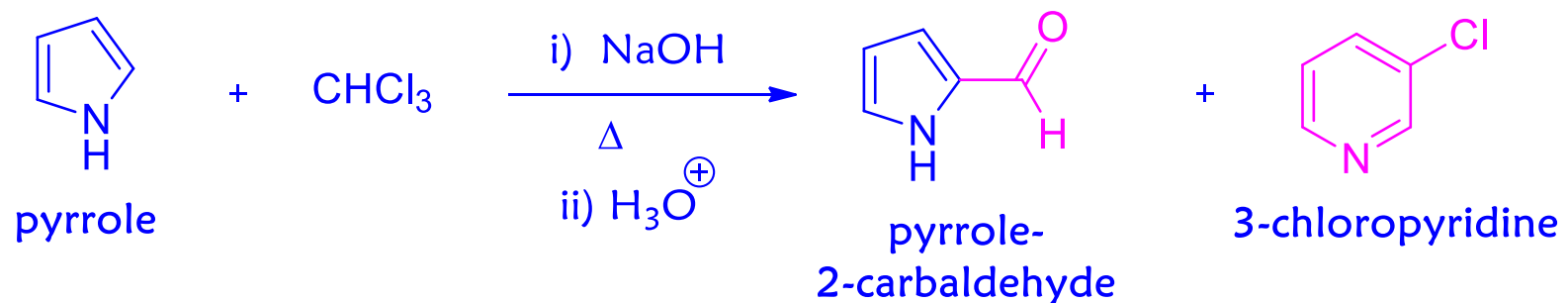
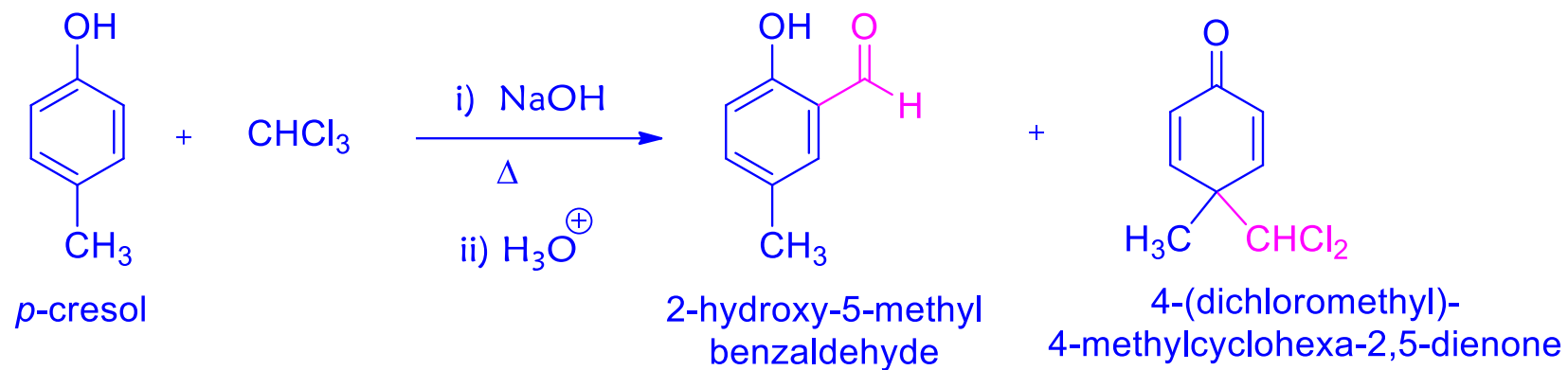


Reimer – Tiemann Reaction with CCl_4 :

- In this reaction products are o - hydroxy benzoic acid (o – Salicylic acid) and p – hydroxy benzoic acid

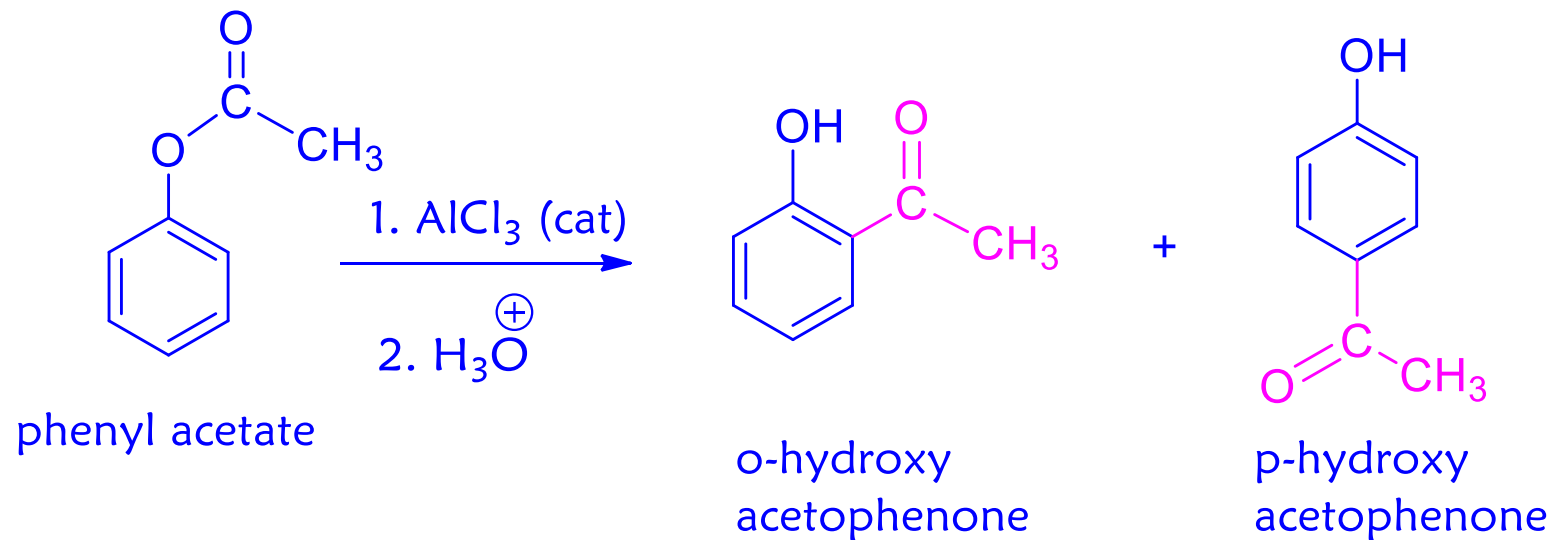


Applications:



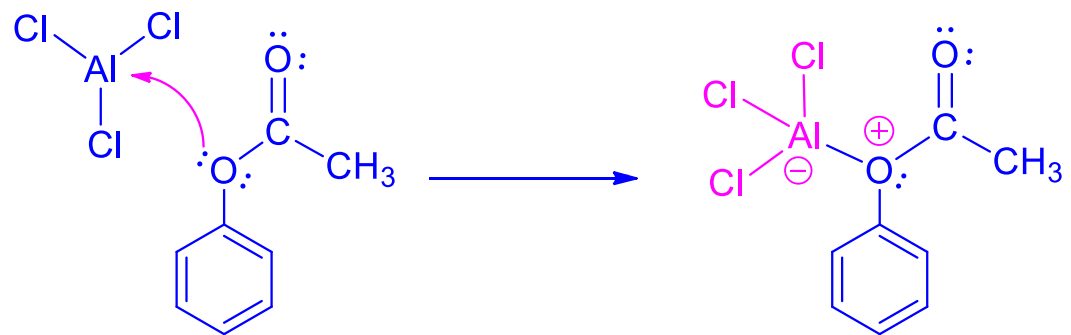
Fries rearrangement

it is an organic reaction used to convert a phenyl ester to an o- and p-hydroxy aryl ketone using a Lewis acid catalyst and Brønsted acid.

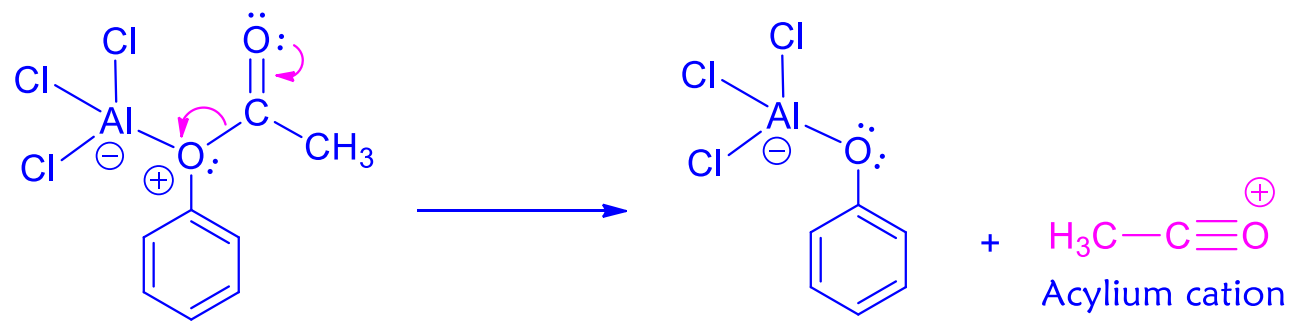


Mechanism:

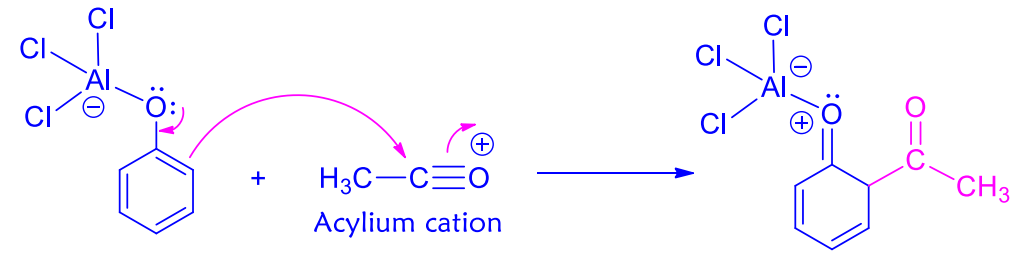
Step - 1: Coordination of the ester to Lewis acid



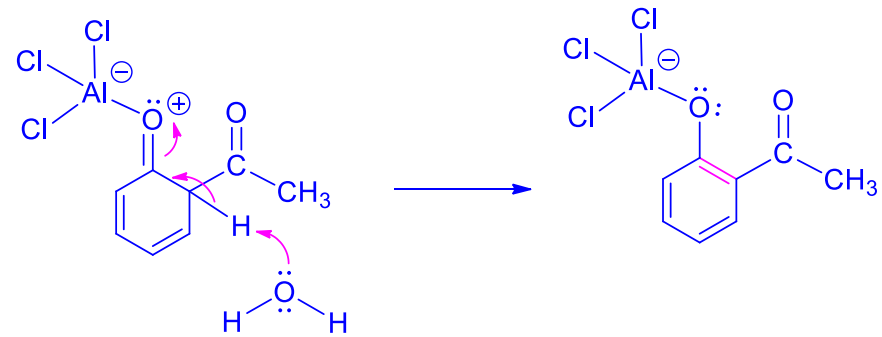
Step - 2: Generation of an electrophile (acylium cation)



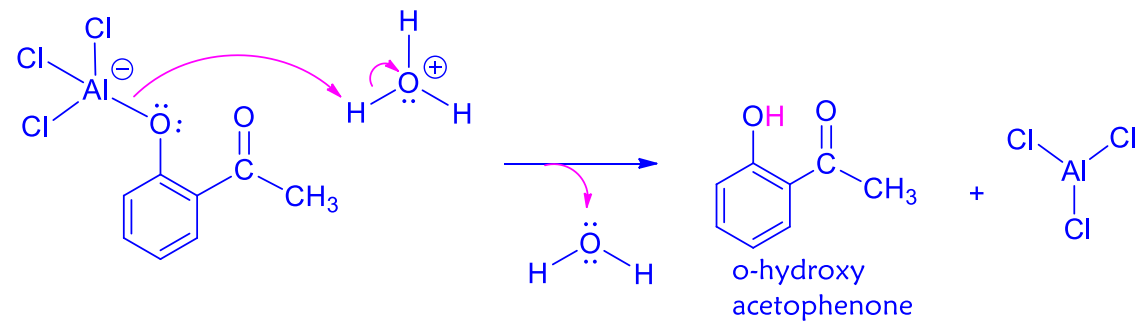
Step - 3: Aromatic electrophilic substitution



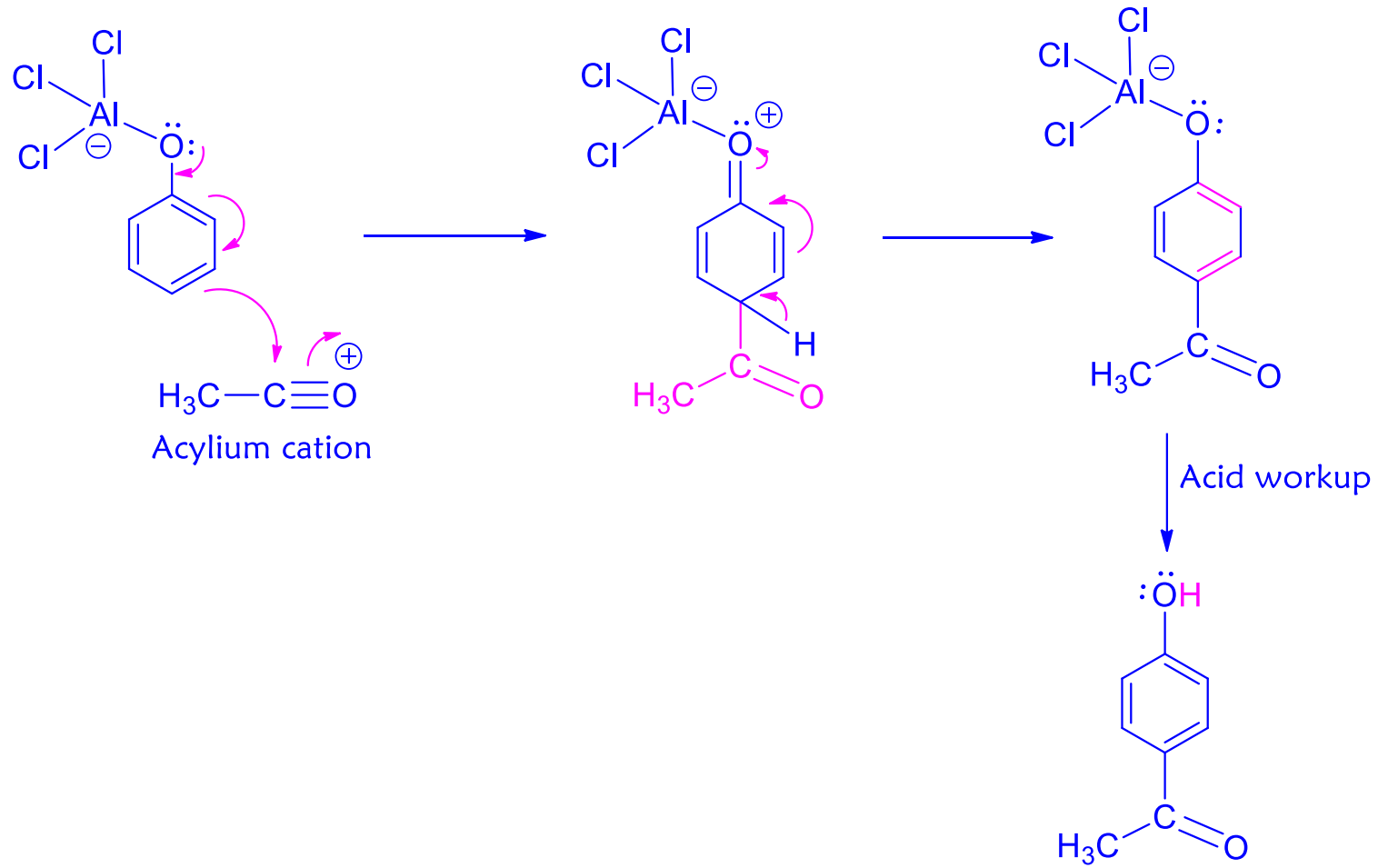
Step - 4: Deprotonation



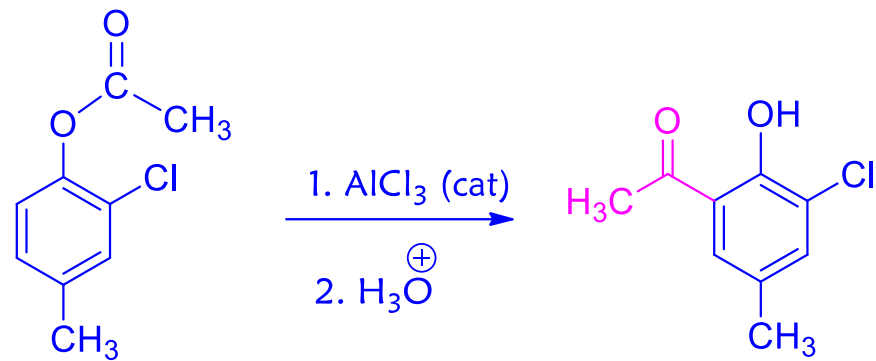
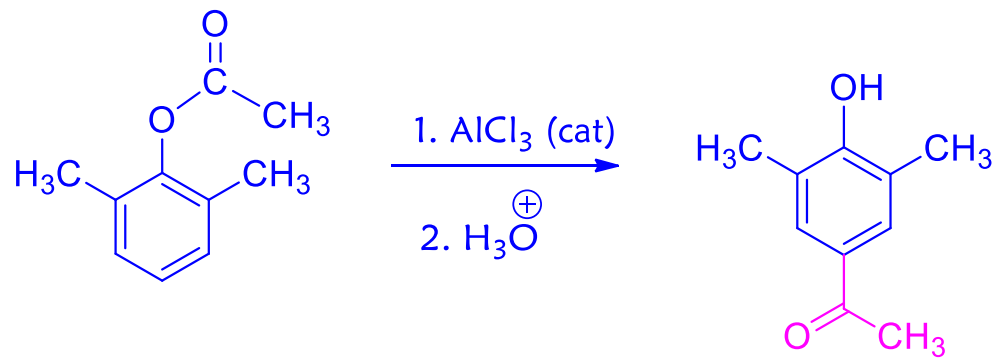
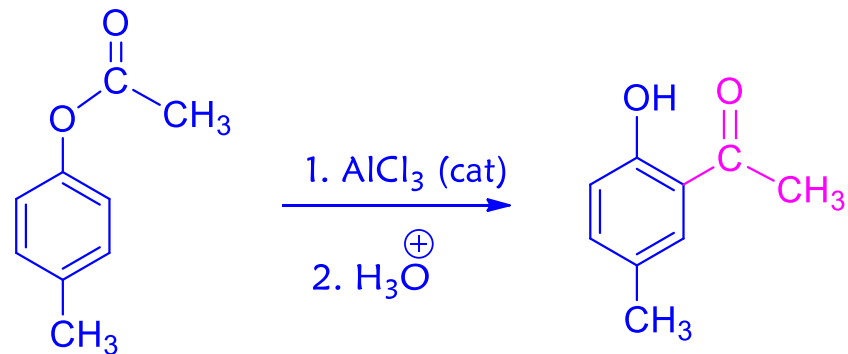
Step - 4: Formation of Final Product



Formation of Para substituted product:

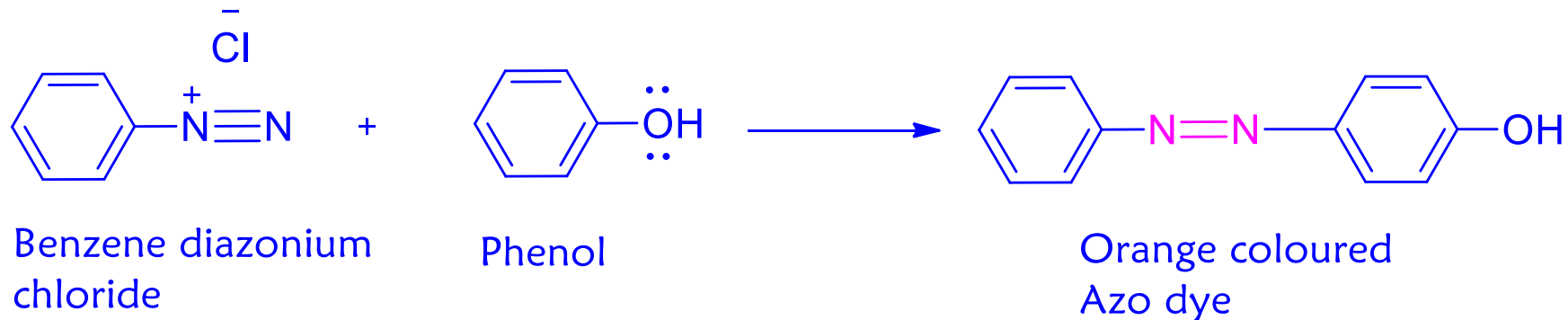


Applications:

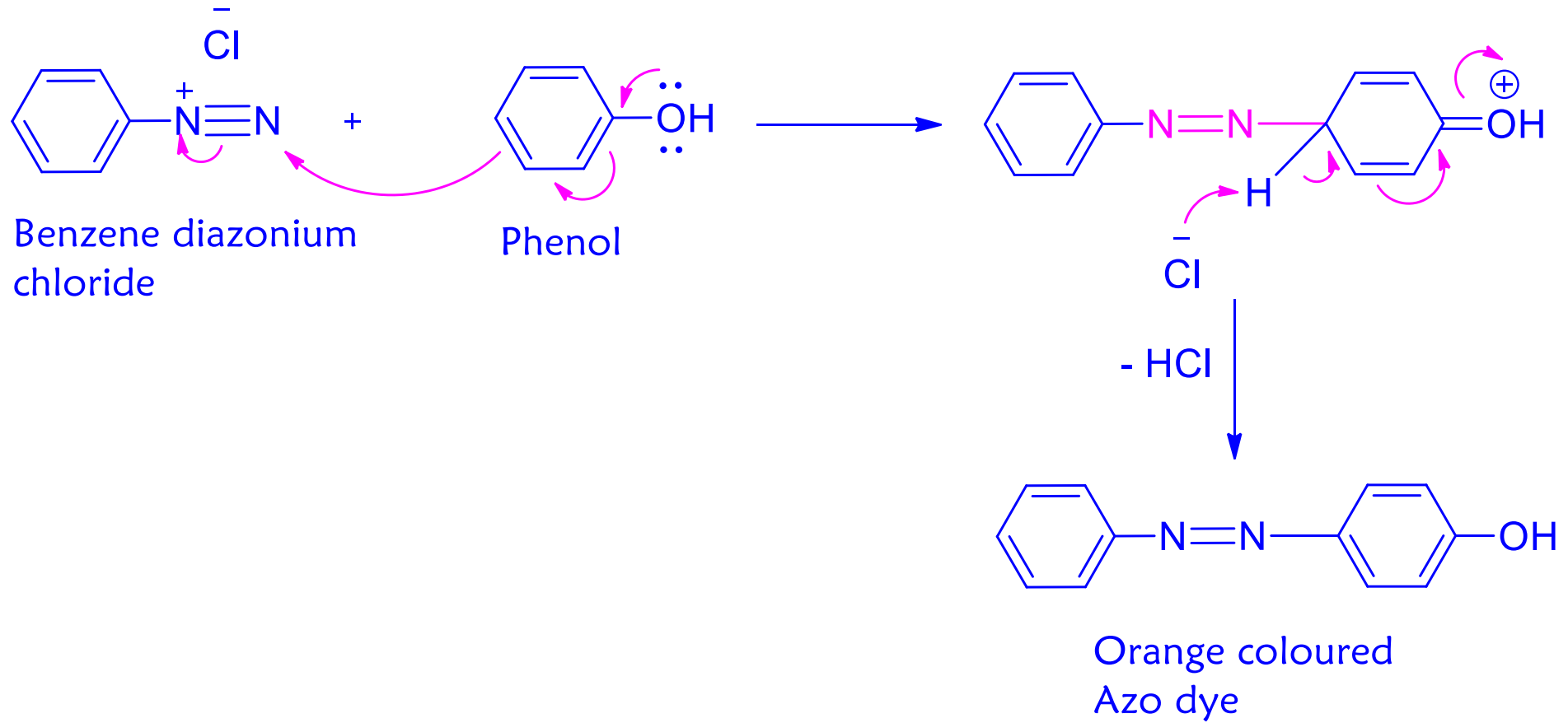


Azo-coupling reaction

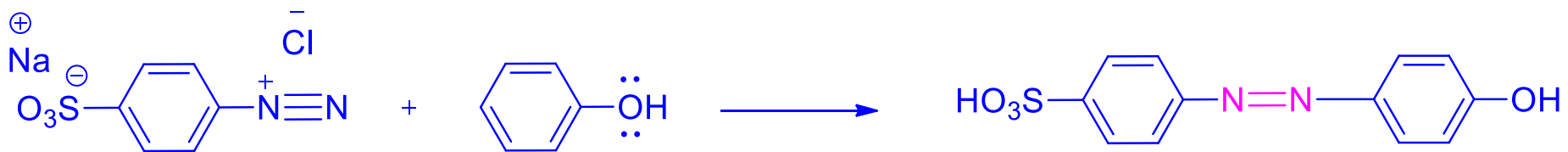
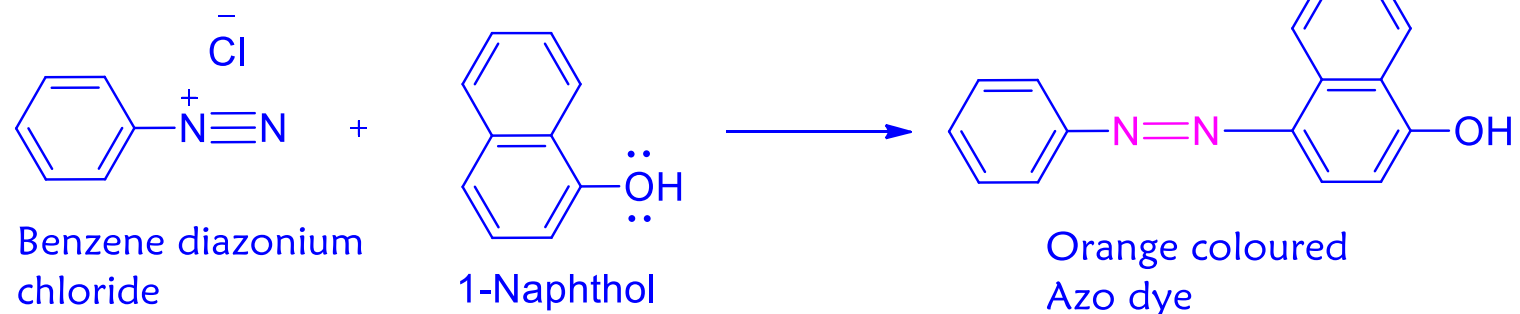
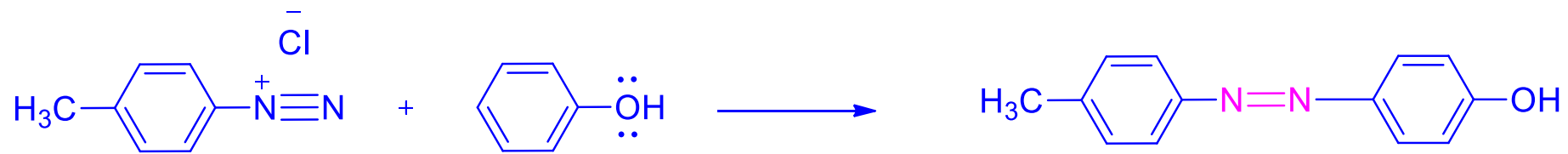
- It is an electrophilic aromatic substitution reaction of a diazonium cation with another aromatic ring to form a diazo compound.
- phenol forms orange colored Azo- dye when treated with benzene diazonium chloride.



Mechanism:

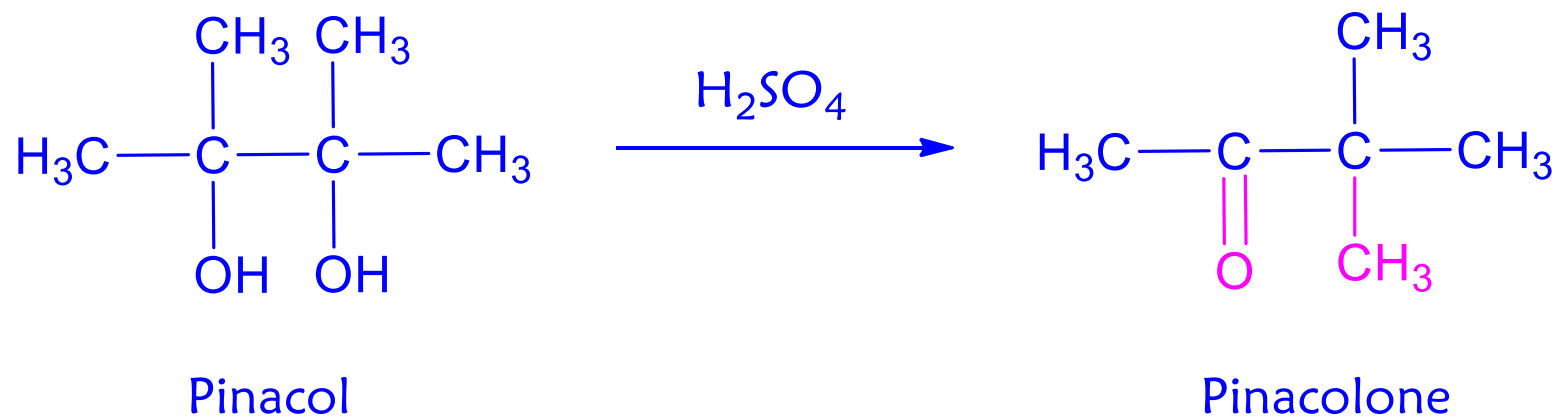


Applications:



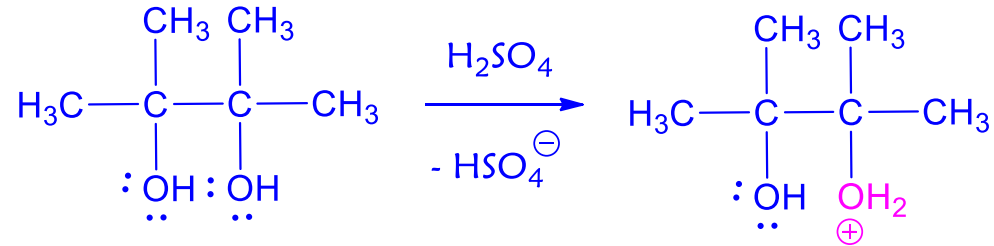
Pinacol-Pinacolone rearrangement

It is an organic reaction in which 1,2 – glycols are converted to carbonyl compounds in the presence of acid catalyst (like H_2SO_4 , H_3PO_4 , P_2O_5 etc.).

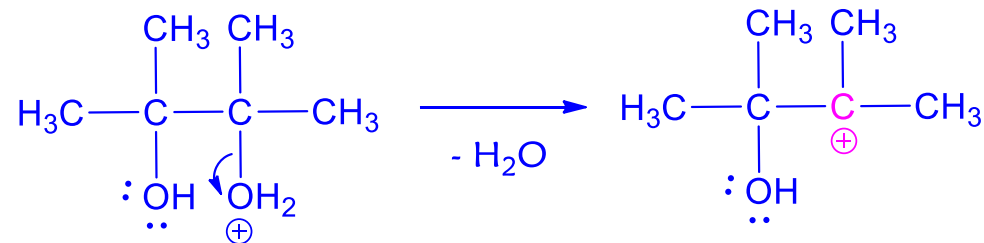


Mechanism:

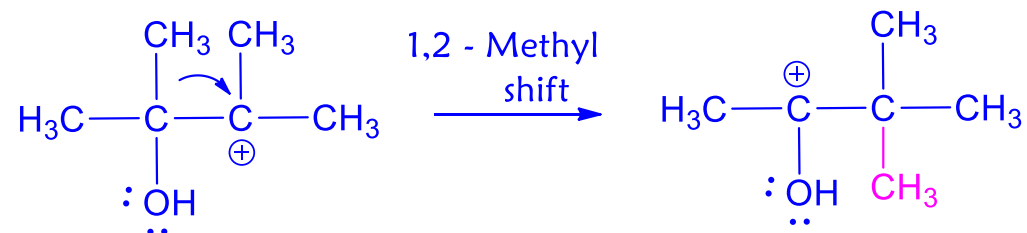
Step-1: Protonation of Diol



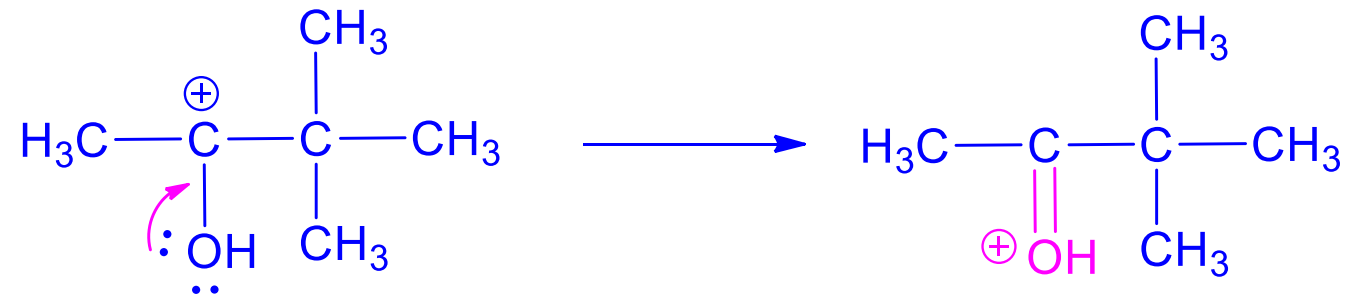
Step-2: Formation of carbocation intermediate



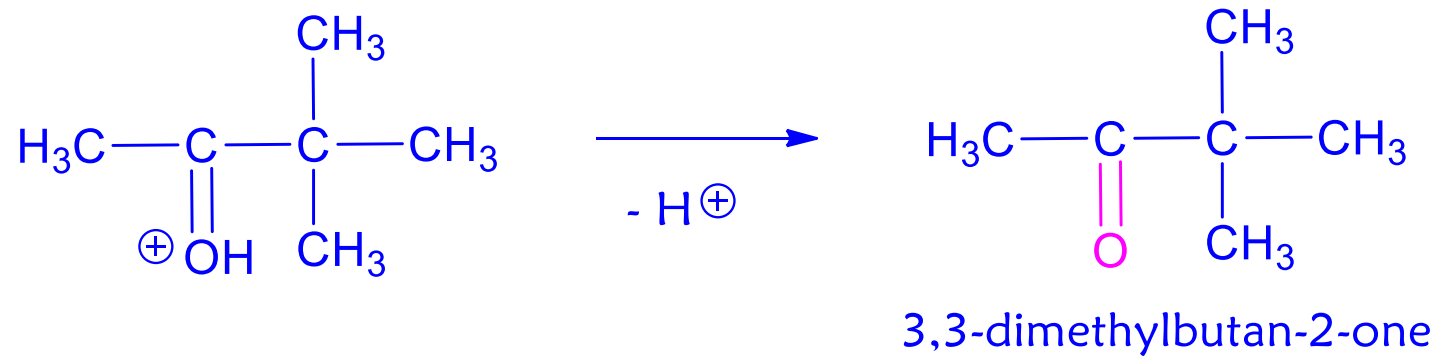
Step-3: 1,2 - Methyl migration



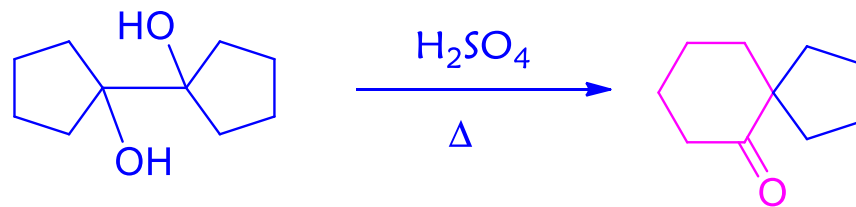
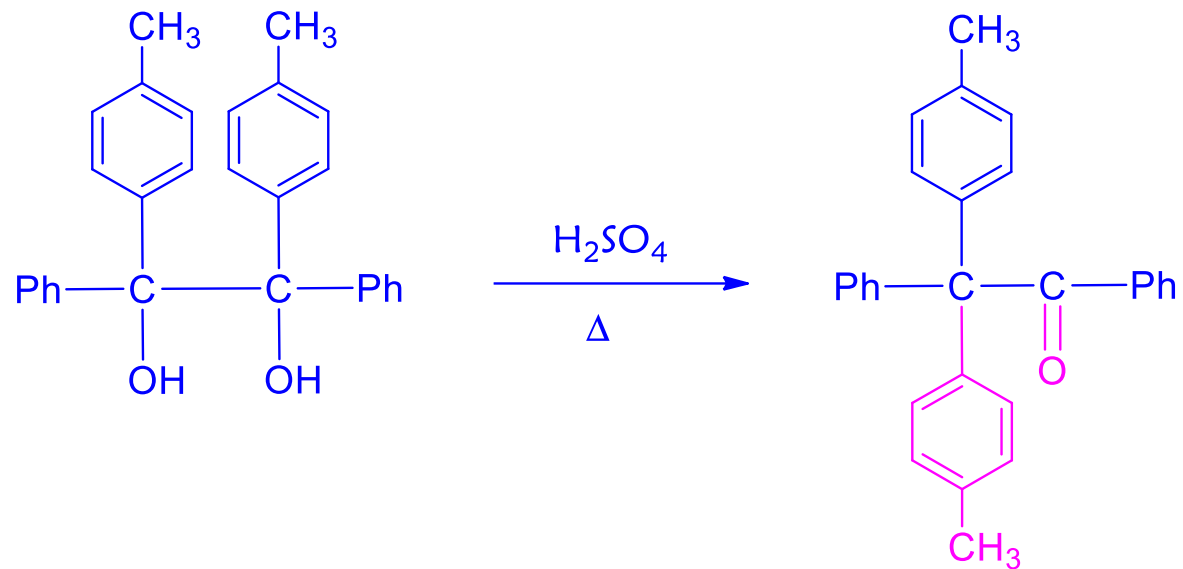
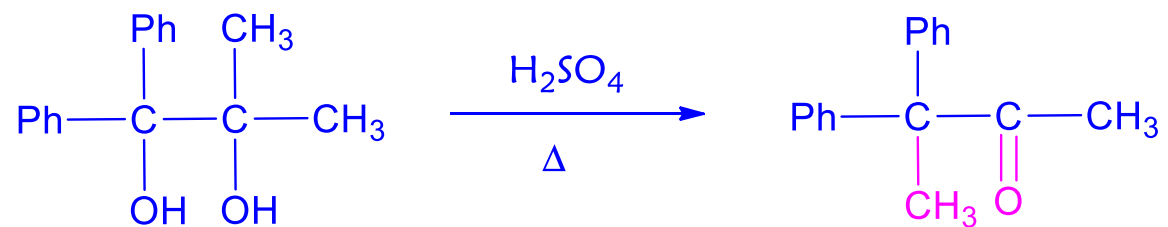
Step-4: Formation of Oxonium ion



Step-5: Formation of Pinacolone



Applications:





THANK YOU