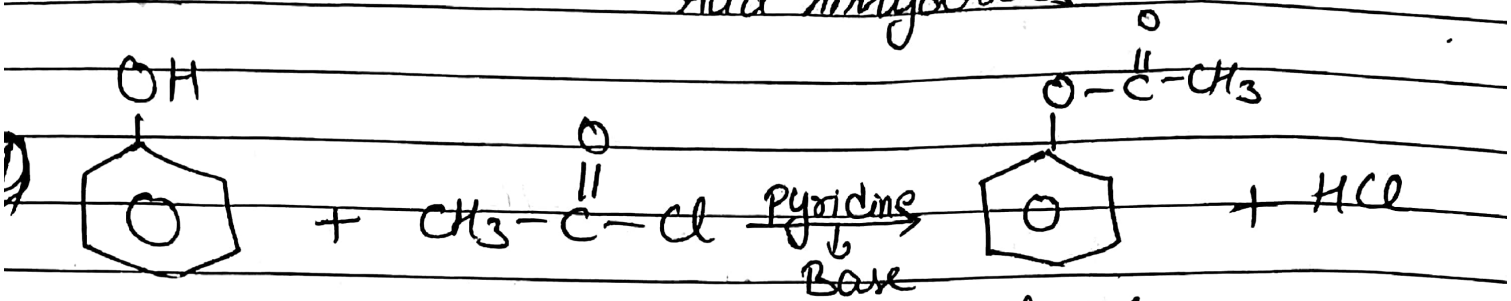
Alcohols, Phenols & Ethers – II

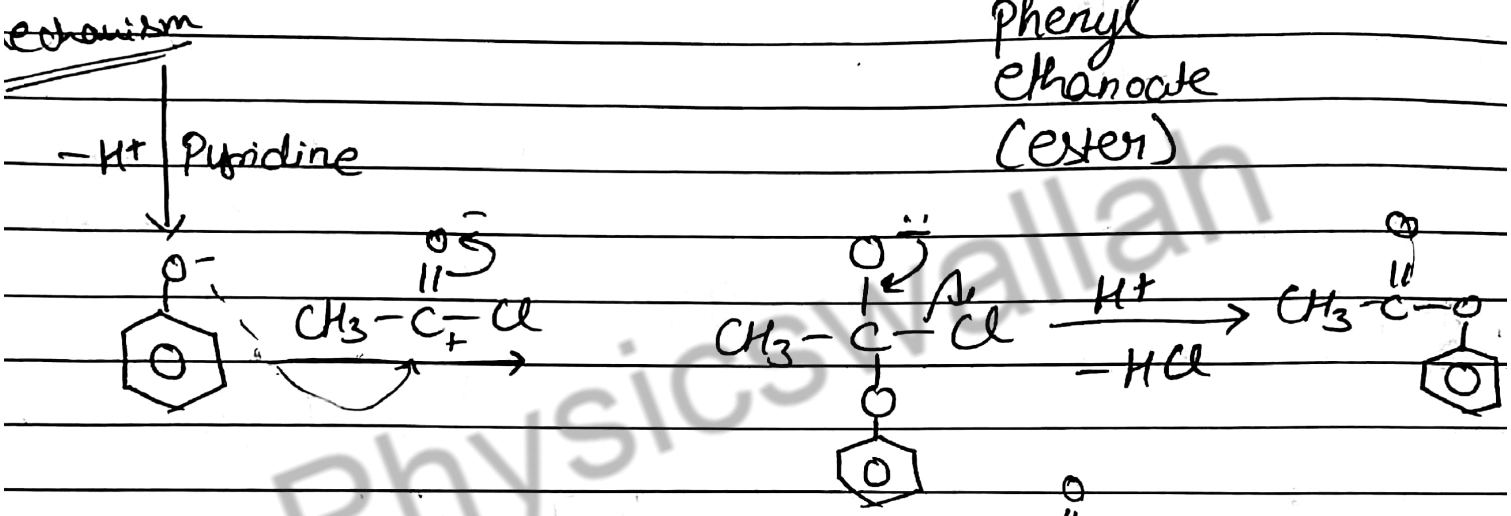
Properties of Phenols – 2

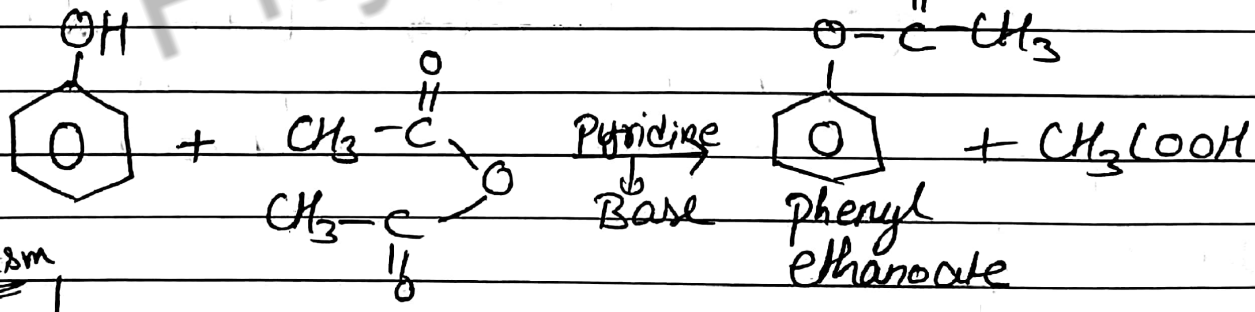
① **Esterification** : Reaction with Acid chlorides & Acid Anhydrides



Phenyl ethanoate (ester)

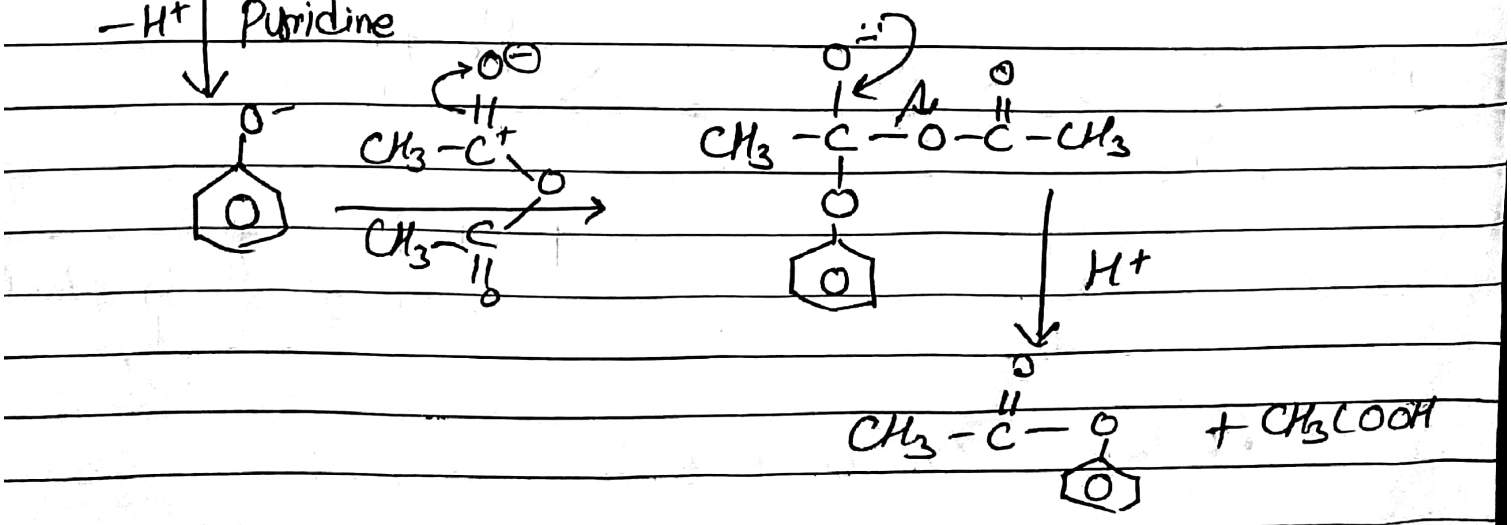
Mechanism



② 

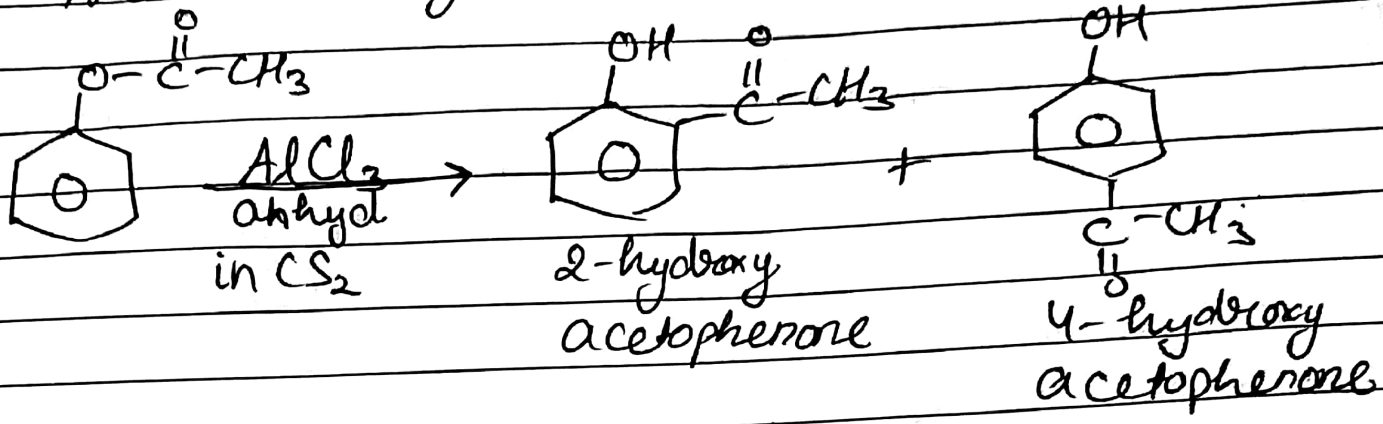
Phenyl ethanoate

Mechanism

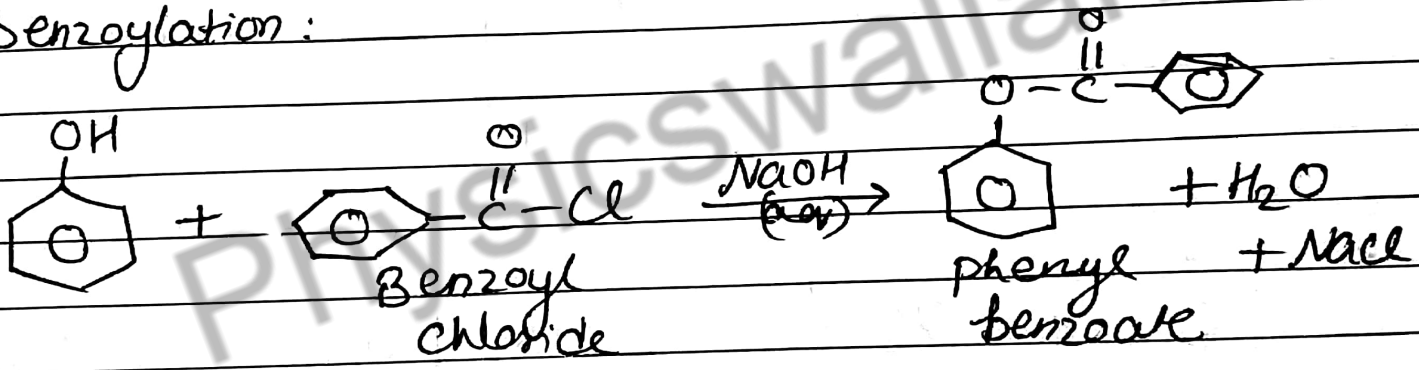


Fries Rearrangement :

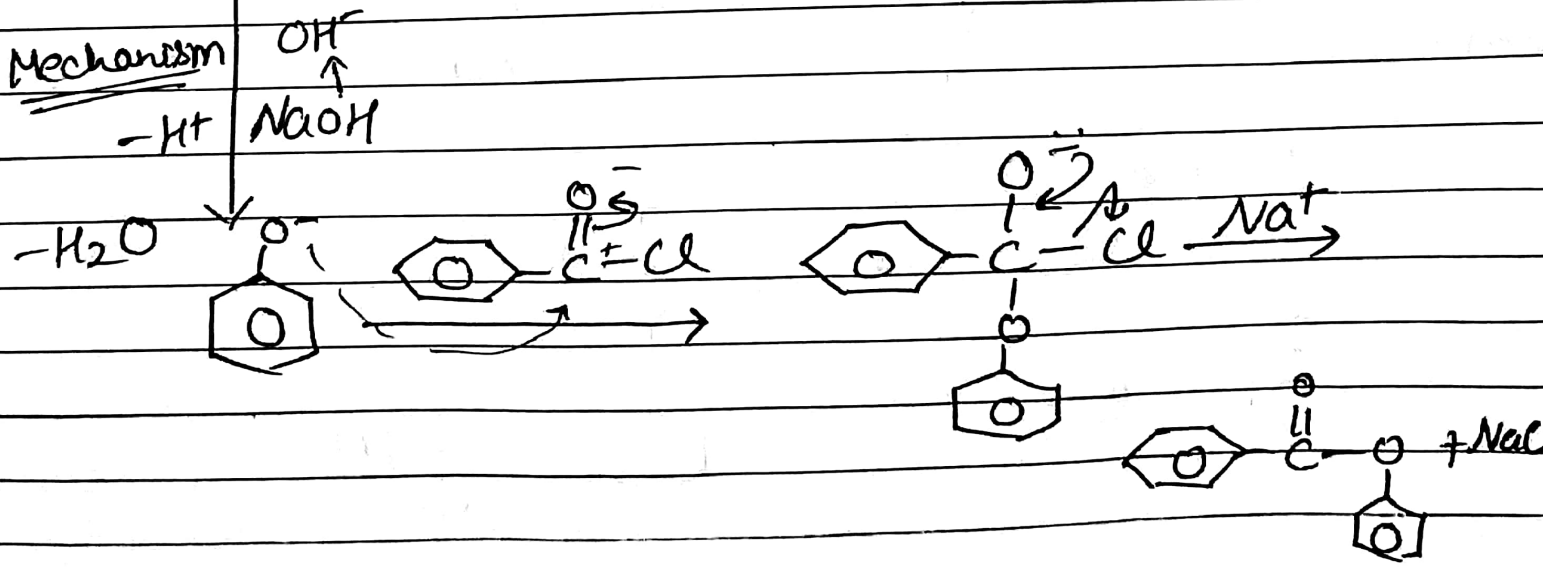
Phenyl esters on treatment with anhydrous $AlCl_3$ in presence of CS_2 (solvent) undergoes Fries rearrangement



(3) Benzoylation :



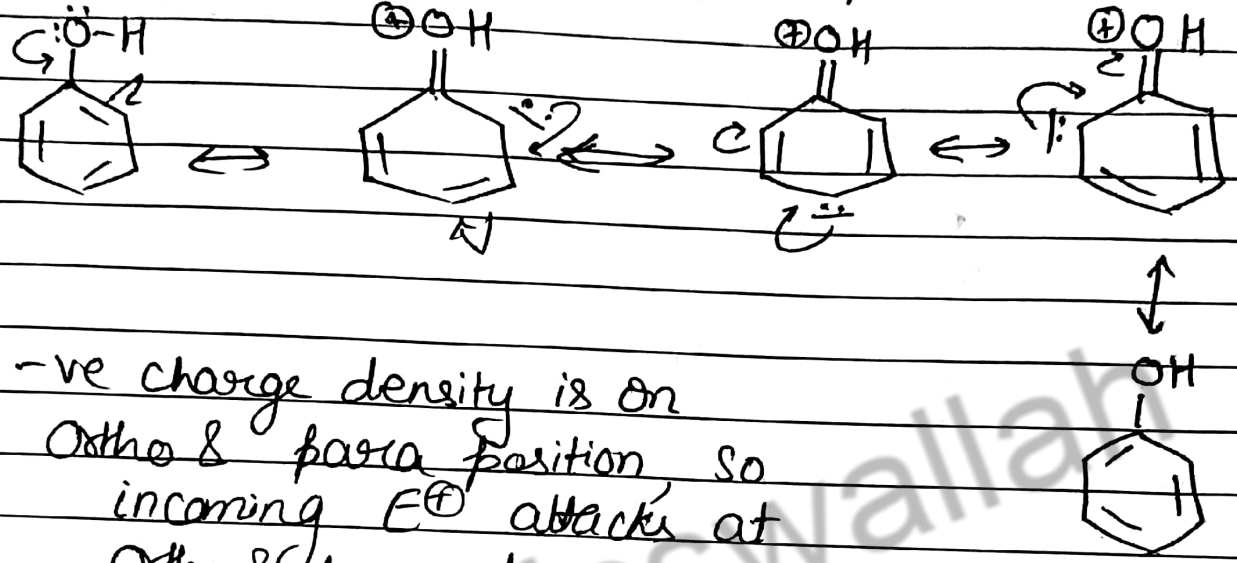
Mechanism



Schotten-Baumann Reaction

(II) Reactions due to benzene Ring : Aromatic $E^{\oplus}$ Substitution

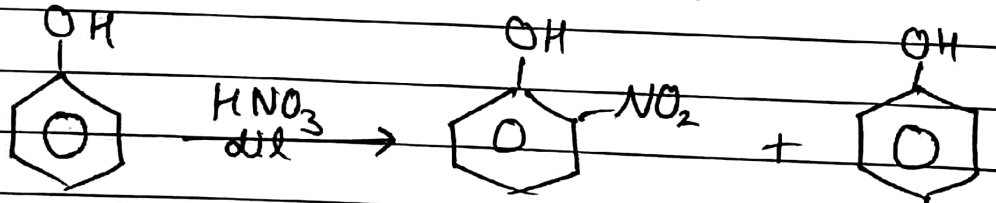
–OH group is an activating group towards $E^{\oplus}$ substitution (at ortho & para positions)



-ve charge density is on ortho & para position so incoming $E^{\oplus}$ attacks at ortho & para positions

(i) Nitration :

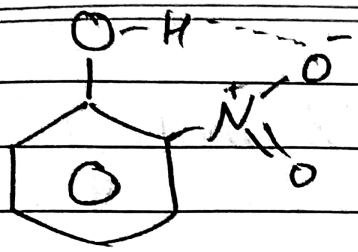
with dil HNO_3 at low temp (25°C ⇔ 298K)



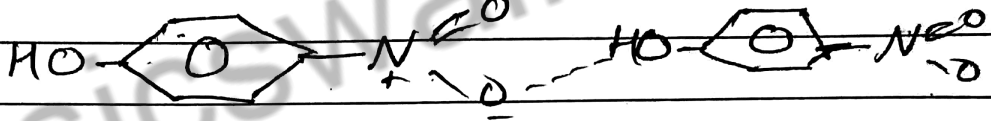
o-nitro phenol (Major) ← due to intramolecular H-bond

p-nitro phenol (Minor)

ortho & para isomers can be separated by steam distillation. O-Nitro phenol is more volatile due to intramolecular H-bonding whereas p-nitrophenol is less volatile due to intermolecular H-bonding.

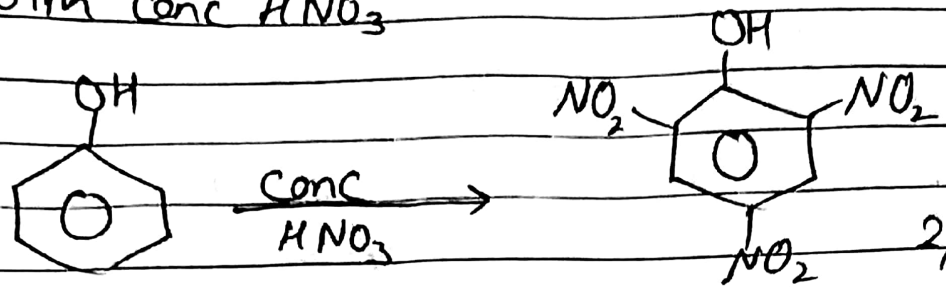


O-nitro phenol (Intramolecular H-bonding)



p-nitrophenol (Intermolecular H-bonding)

With conc HNO_3

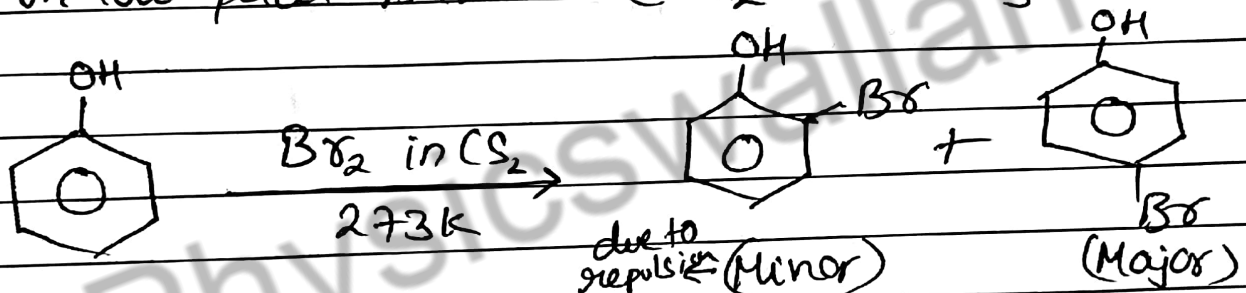


2,4,6-trinitro phenol
(picric Acid)
(poor yield)

To get good yield of Picric Acid, we use another method → (under sulphonation topic)

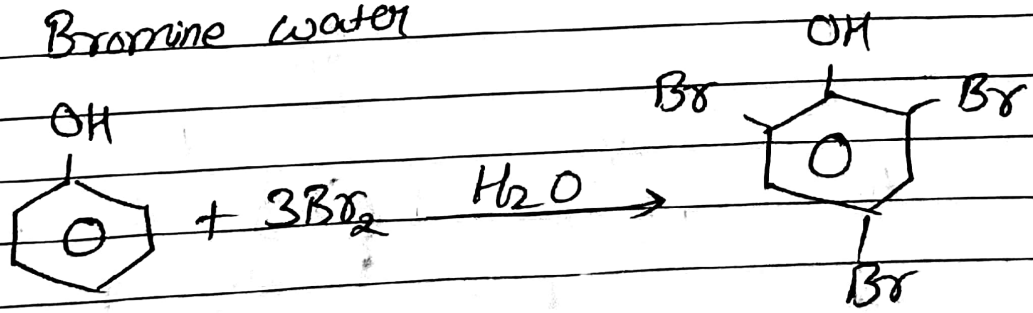
② Halogenation:

i) In low polar solvents (CS_2 OR $CHCl_3$ OR CCl_4)



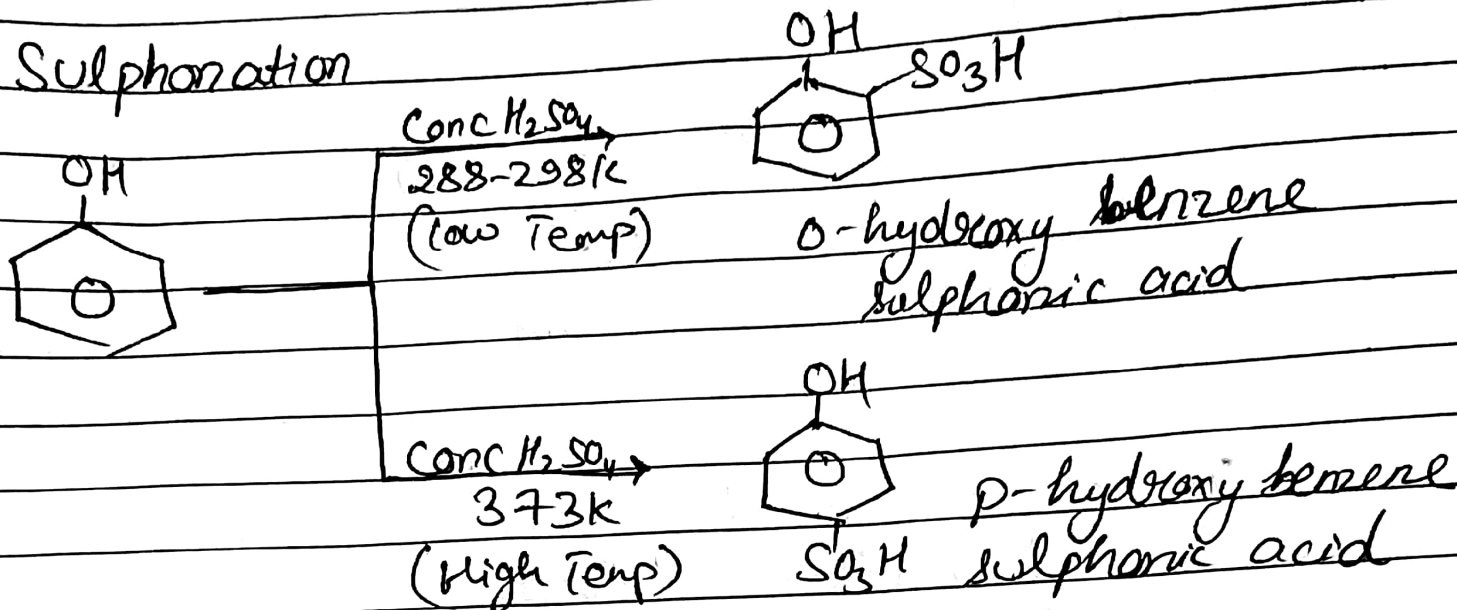
No need of Lewis Acid (such as $AlBr_3$ OR $FeBr_3$) as -OH group is itself highly activating

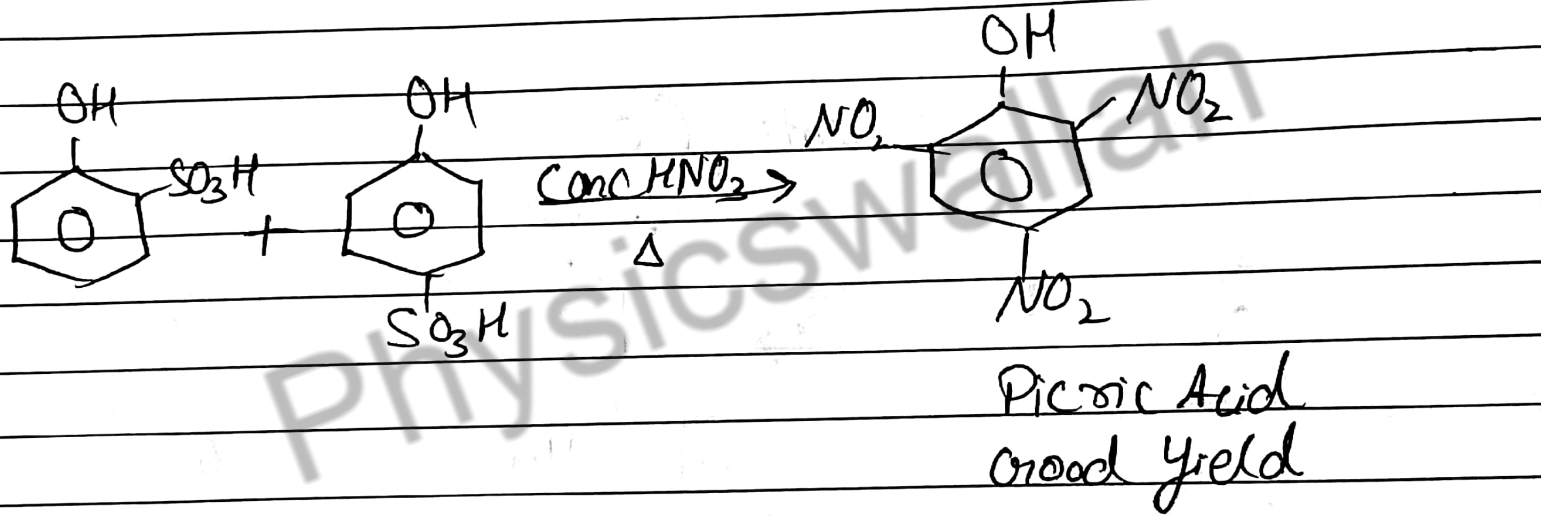
ii) Bromine water



2,4,6-tribromo phenol
(white ppt)

③ Sulphonation





④ Friedel Craft Reaction:

i) Alkylation