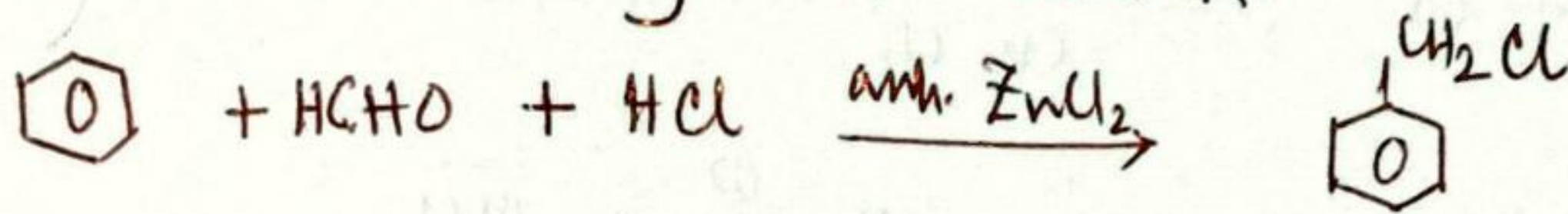
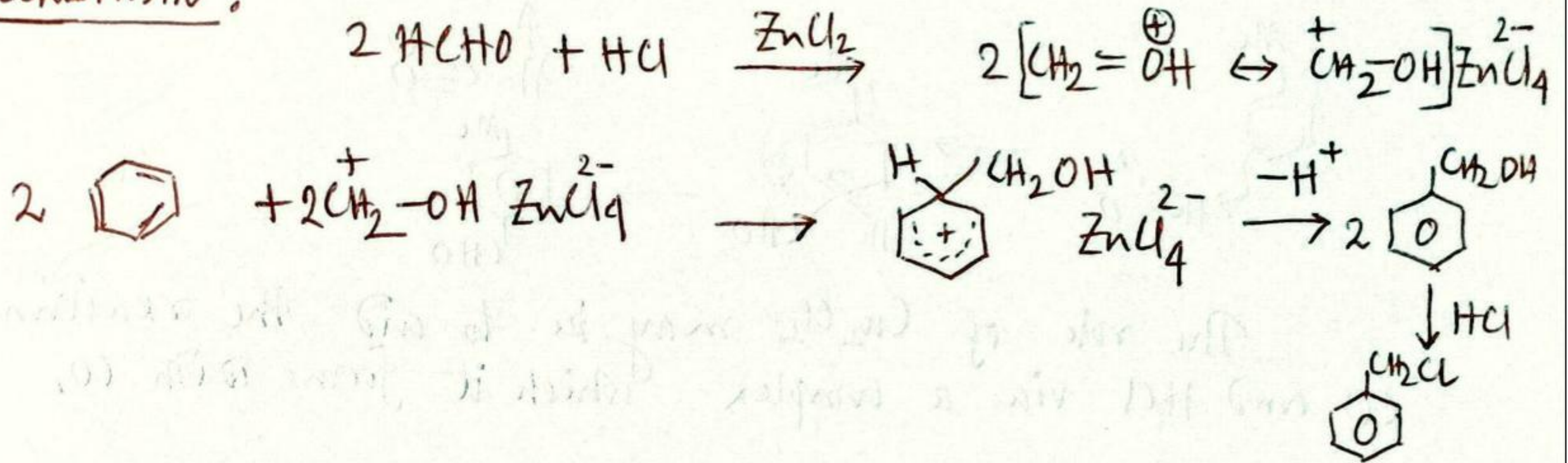


Chloromethylation reaction: When some aromatic compounds are treated with HCHO in the presence of catalysts like ZnCl₂, SnCl₄, AlCl₃ etc. (Lewis acid), one hydrogen atom of the aromatic nucleus get replaced by chloromethyl (CH₂Cl gr.) and the reaction is known as chloromethylation reaction.

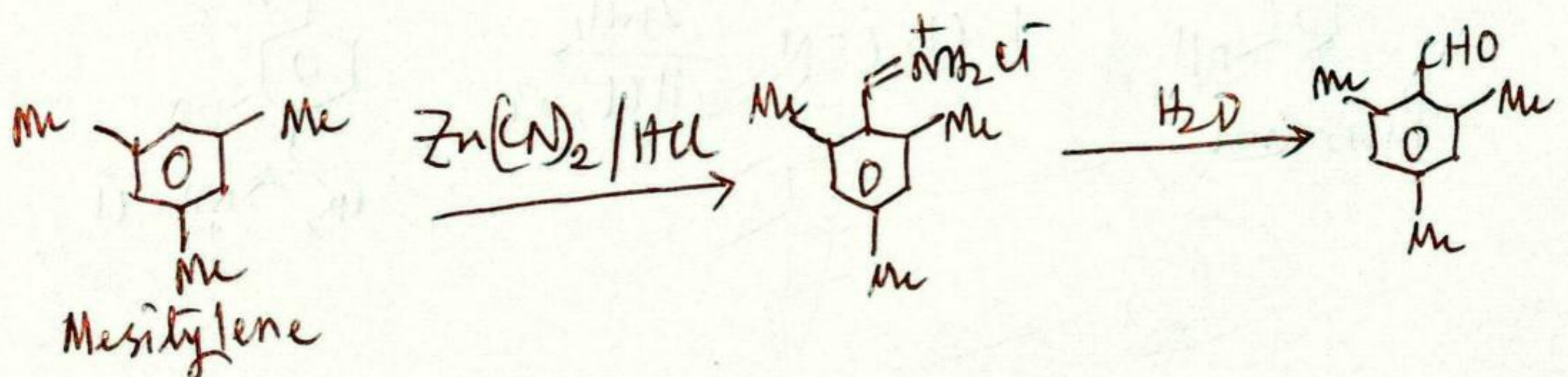
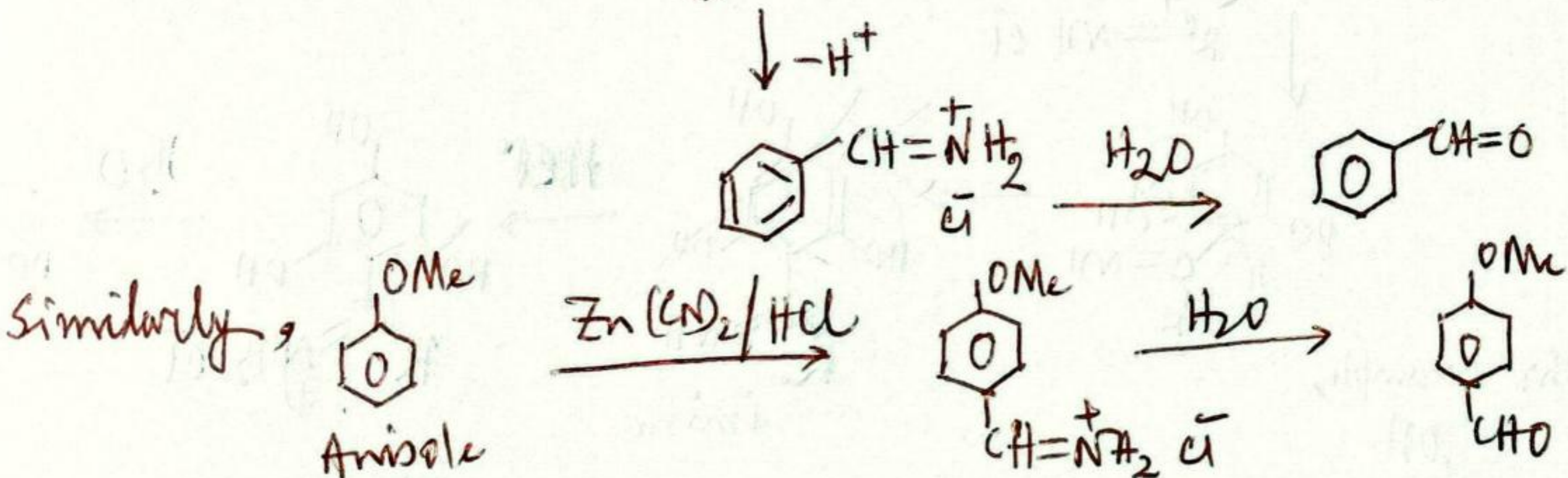
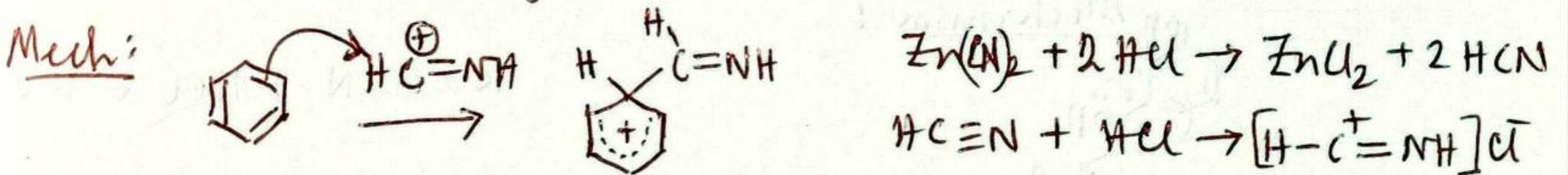


Mechanism:

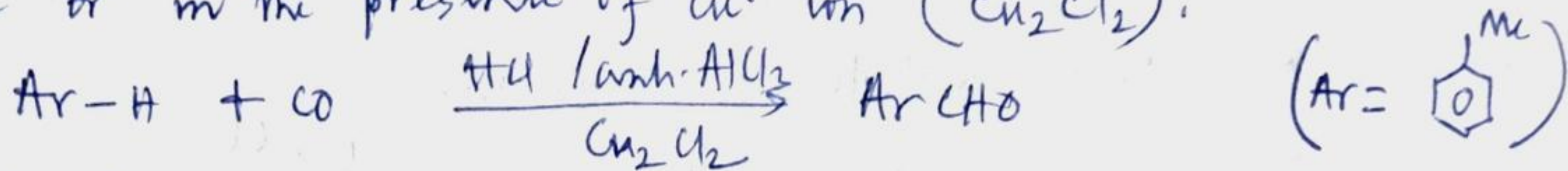


Gattermann (formylation) reaction:

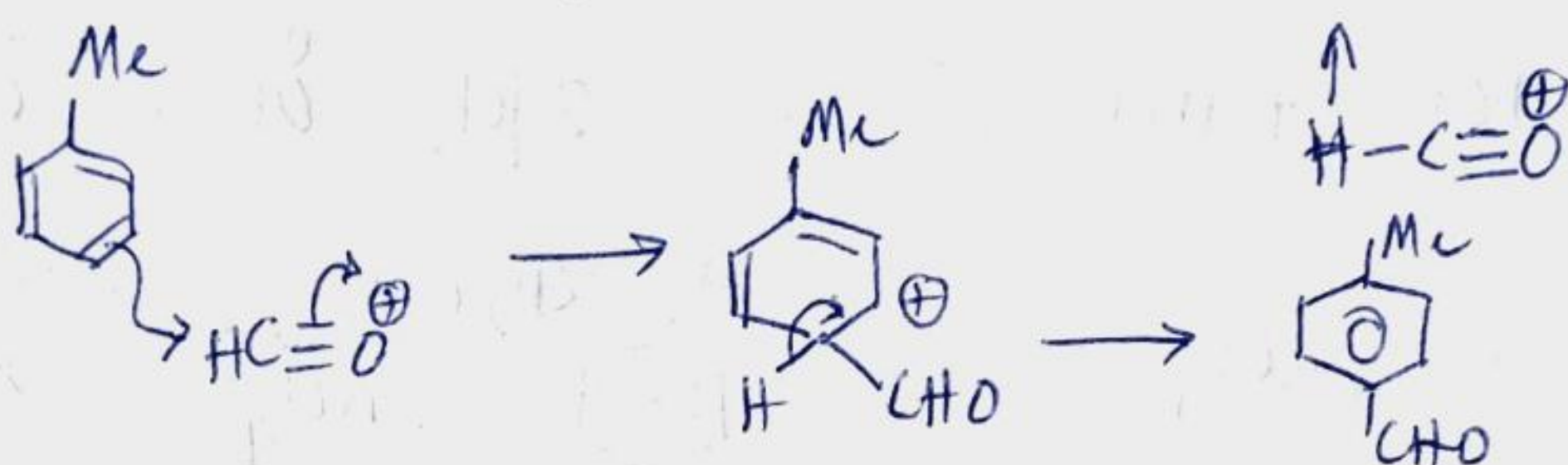
Formylation of activated aromatic ring with Zn(CN)₂/HCl is called Gattermann formylation rxn. This rxn is applied to activated aromatic rings eg. phenols, anisole, mesitylene etc.



① Gattermann-Koch reaction: The formyl group (CHO) may be introduced into aromatic nucleus by treatment of the aromatic compound with CO and conc. HCl in the presence of a Lewis acid like anhydrous $AlCl_3$. The rxn is carried out either under pressure or in the presence of Cu^+ ion (Cu_2Cl_2).

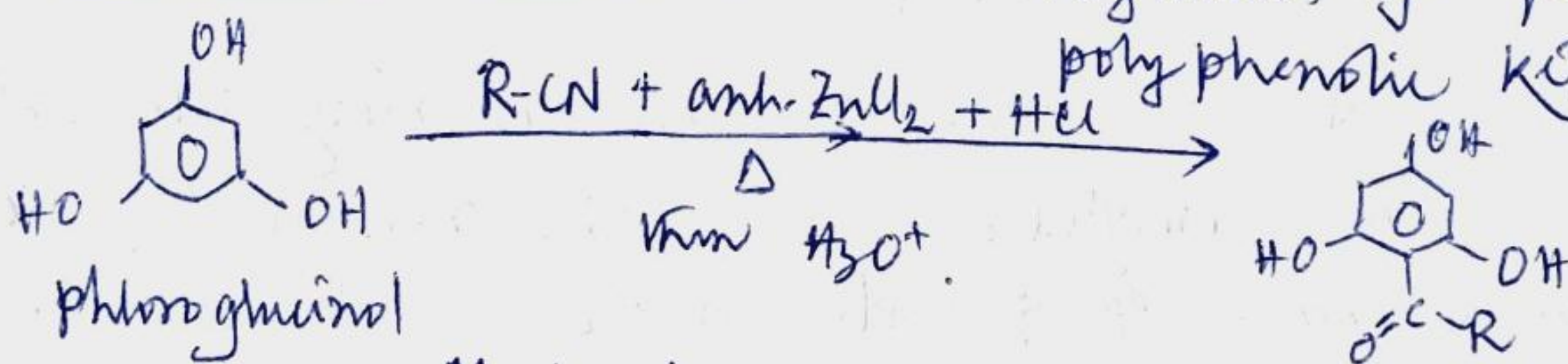


Mechanism:

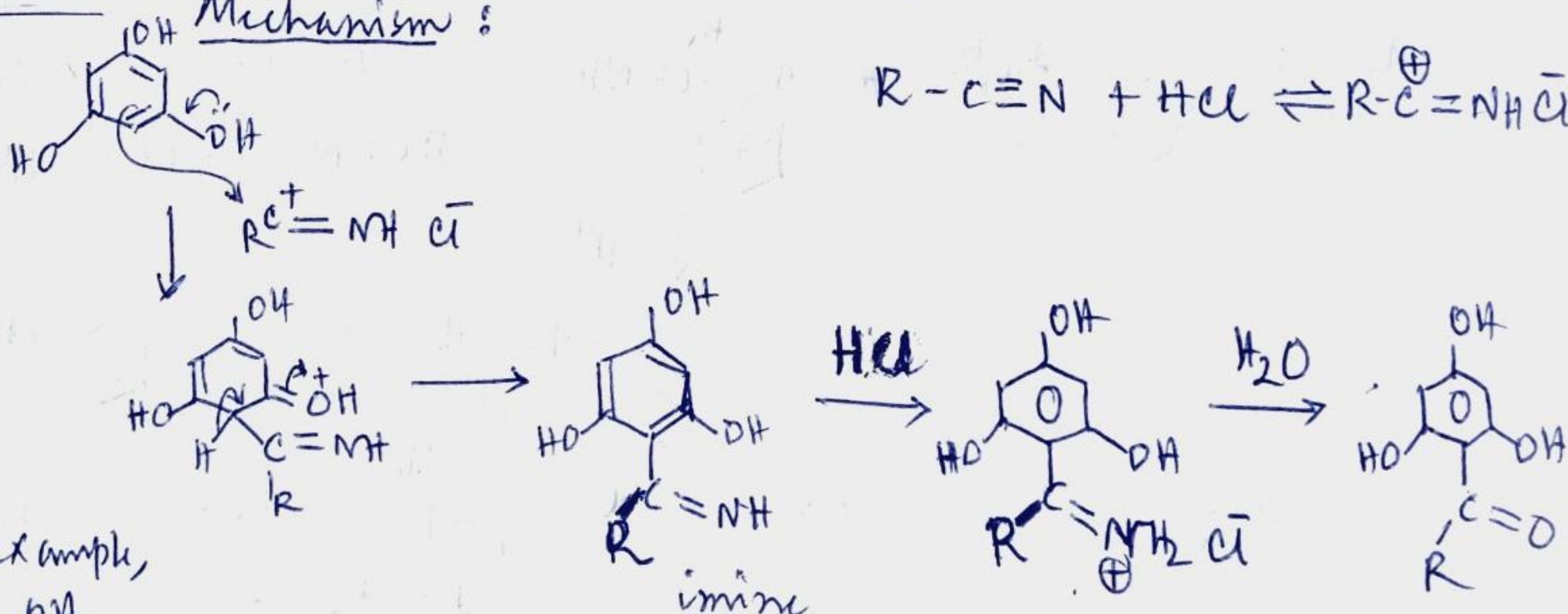


The role of Cu_2Cl_2 may be to aid the reaction between CO and HCl via a complex which it forms with CO.

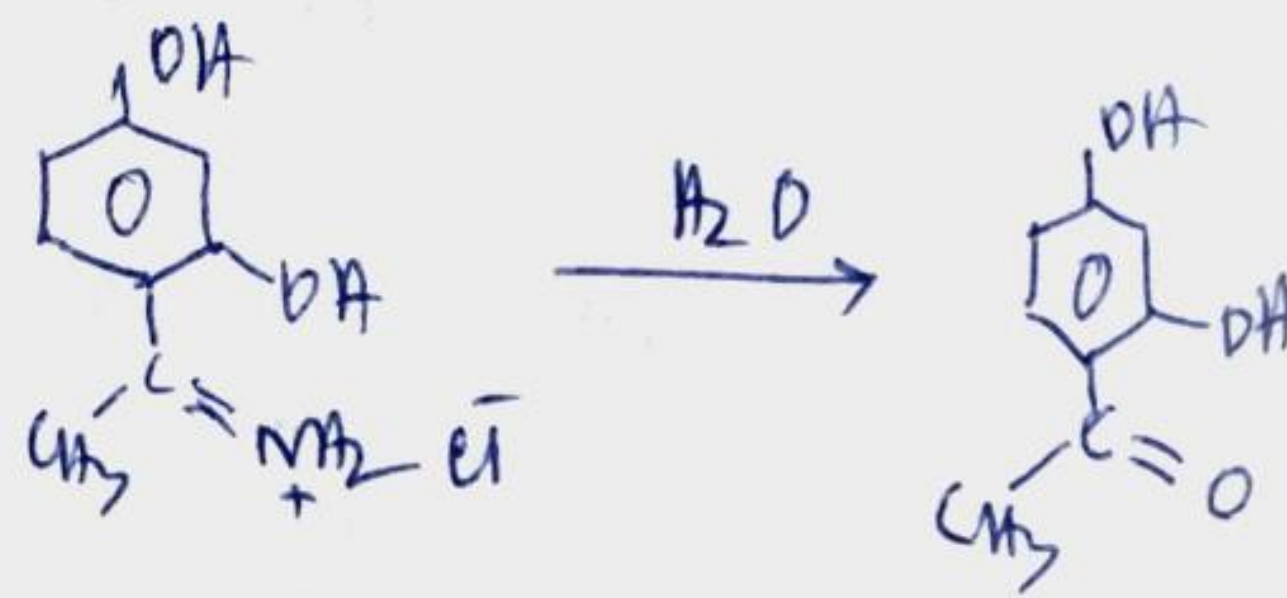
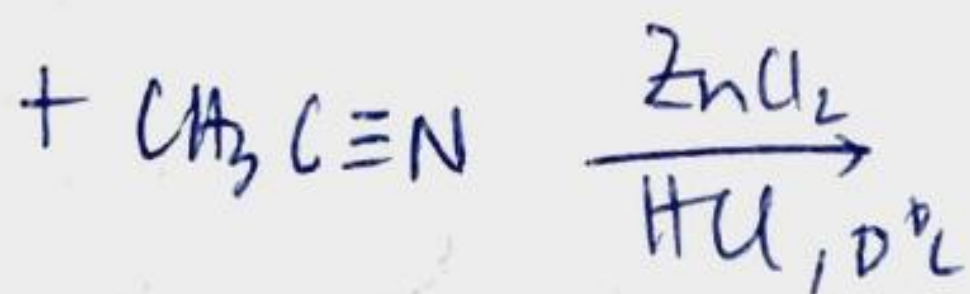
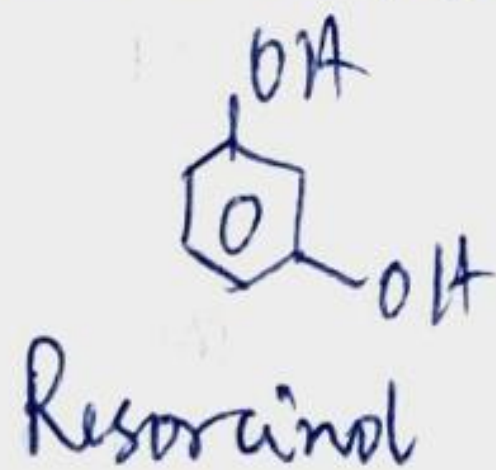
② Houben-Hoesch reaction: Acylation of polyphenolics to have polyphenolic ketones.



Mechanism:

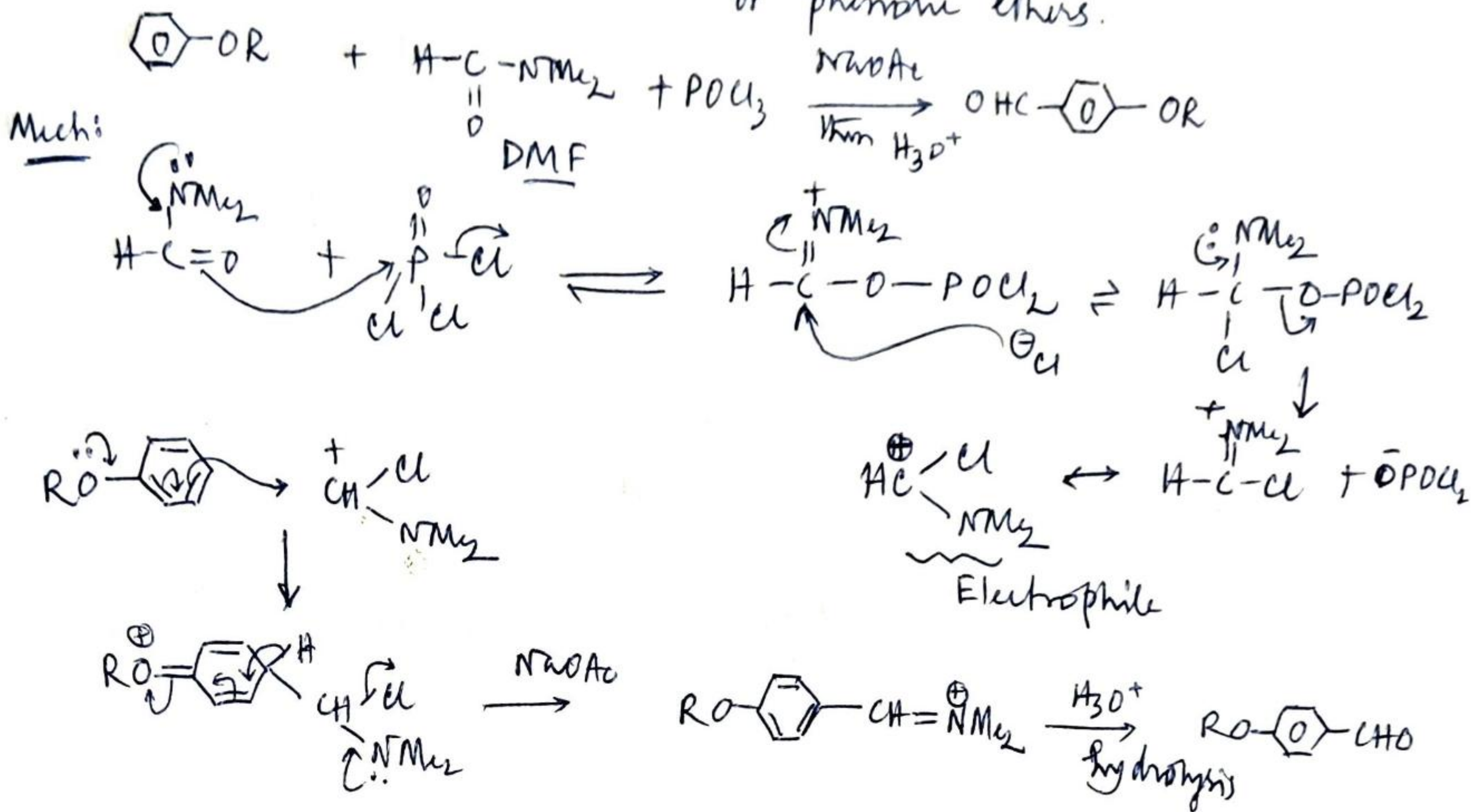


Another example,

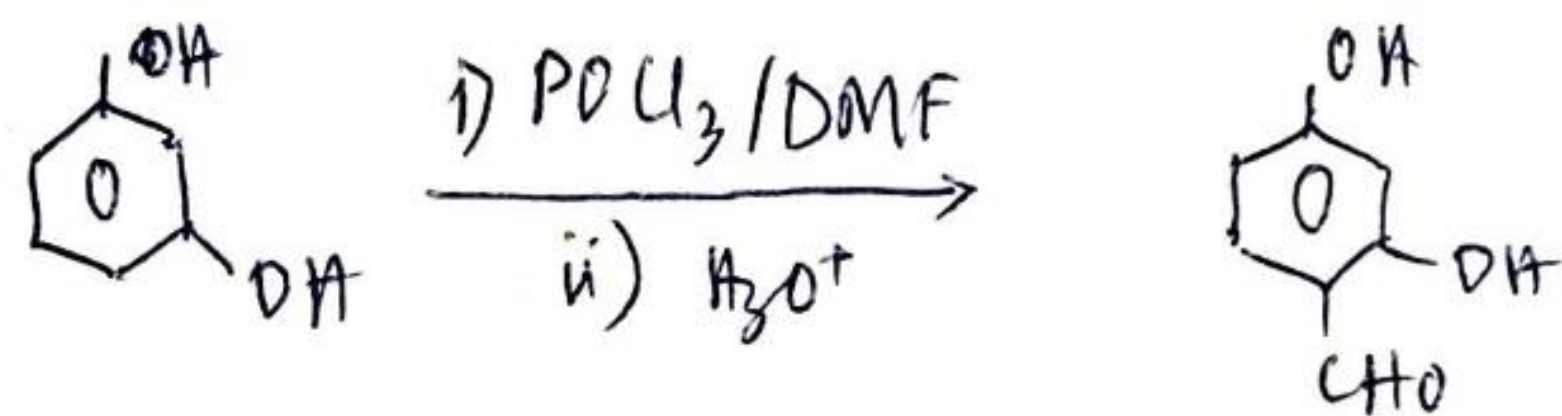


① Vilsmeier-Haack reaction?

for para-formylation of phenols or phenolic ethers.



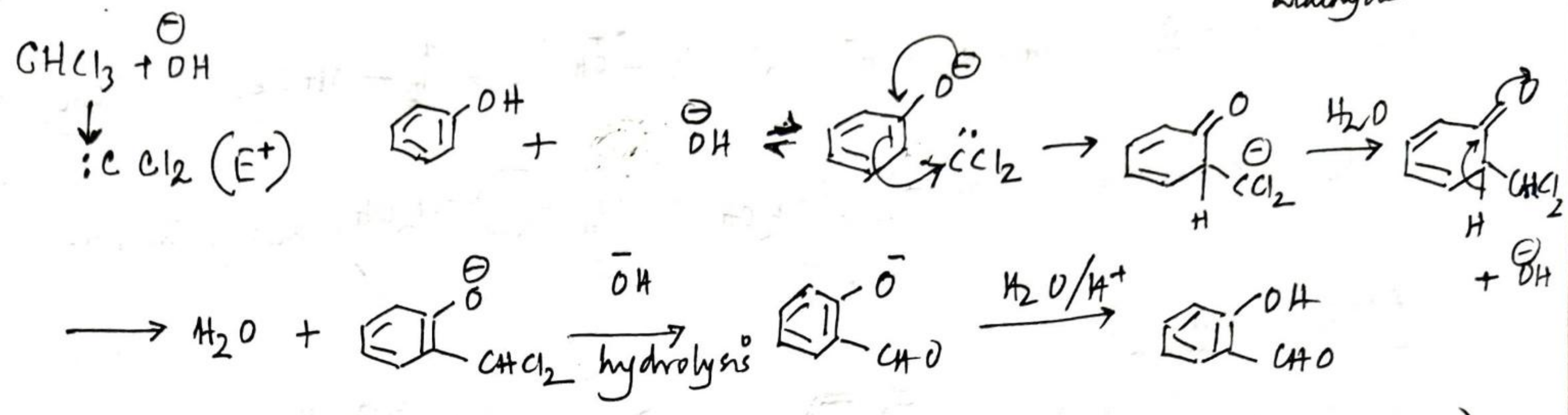
more eg,
NBSU



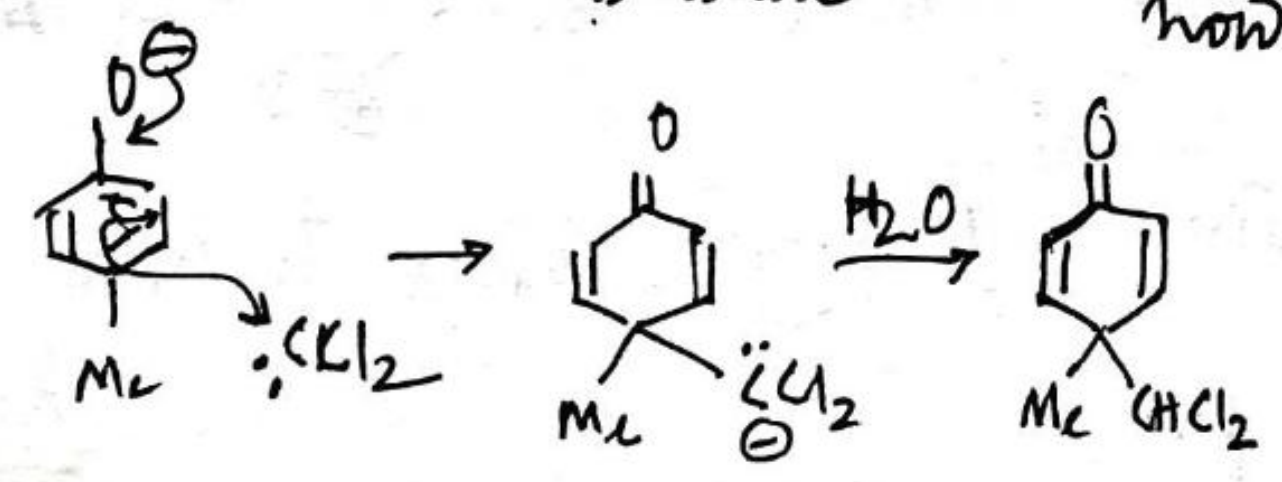
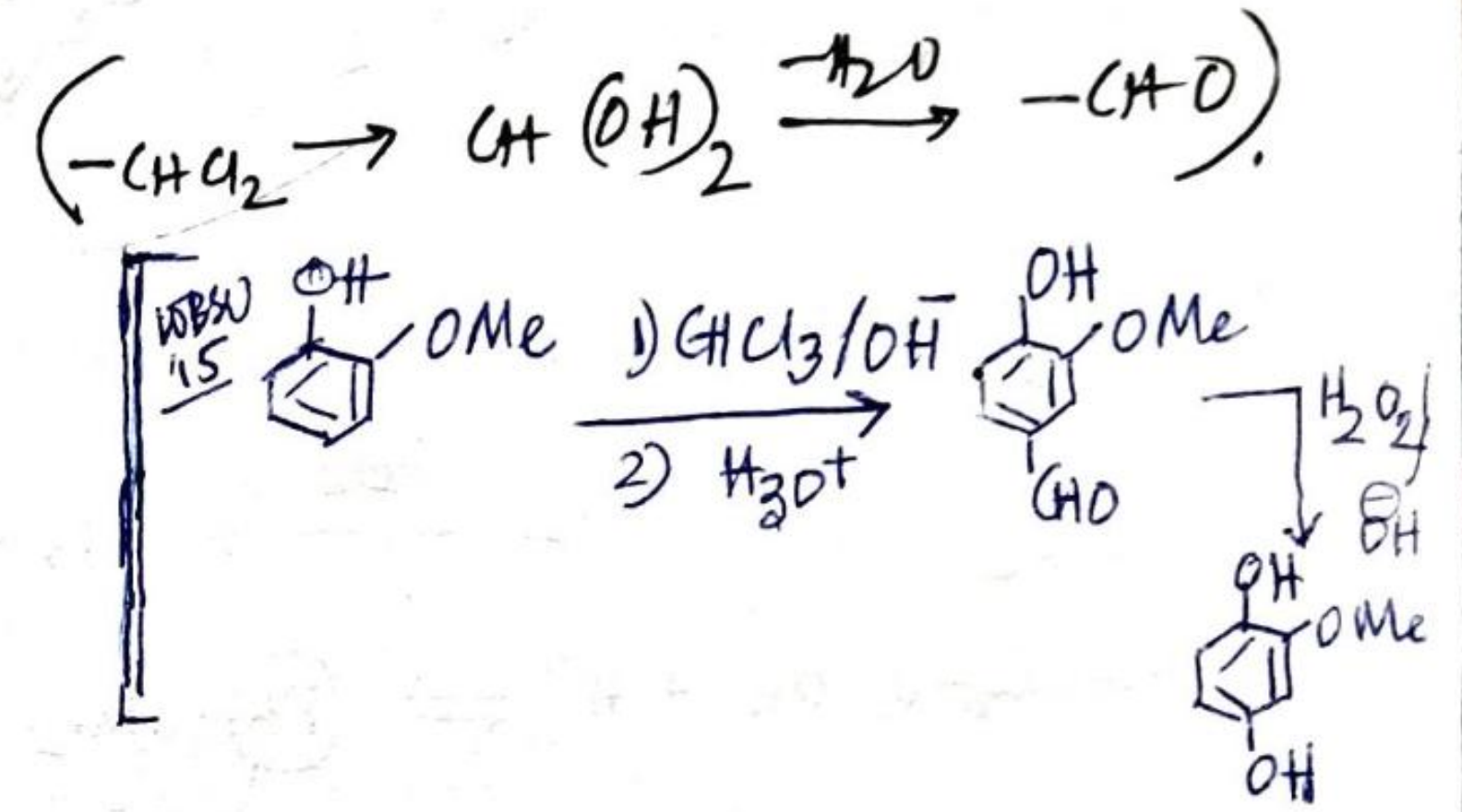
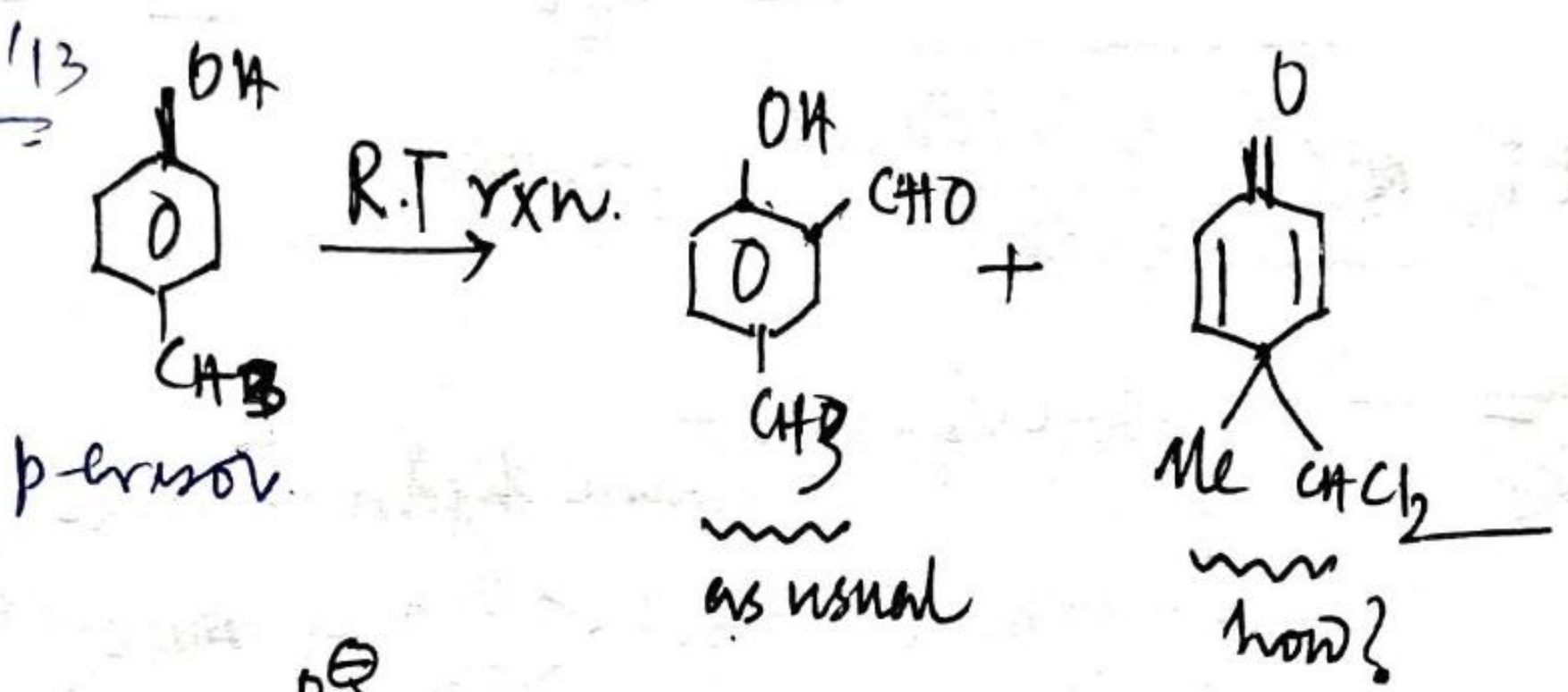
(DMF = Dimethyl formamide)

Keimer - Siemann rxn: Phenol + NaOH + CCl₃ $\xrightarrow[\text{etc.}]{\Delta, \text{thin } H^+}$ Salicyl-aldehyde + O=Cc1ccccc1O

O-Formylation of phenols

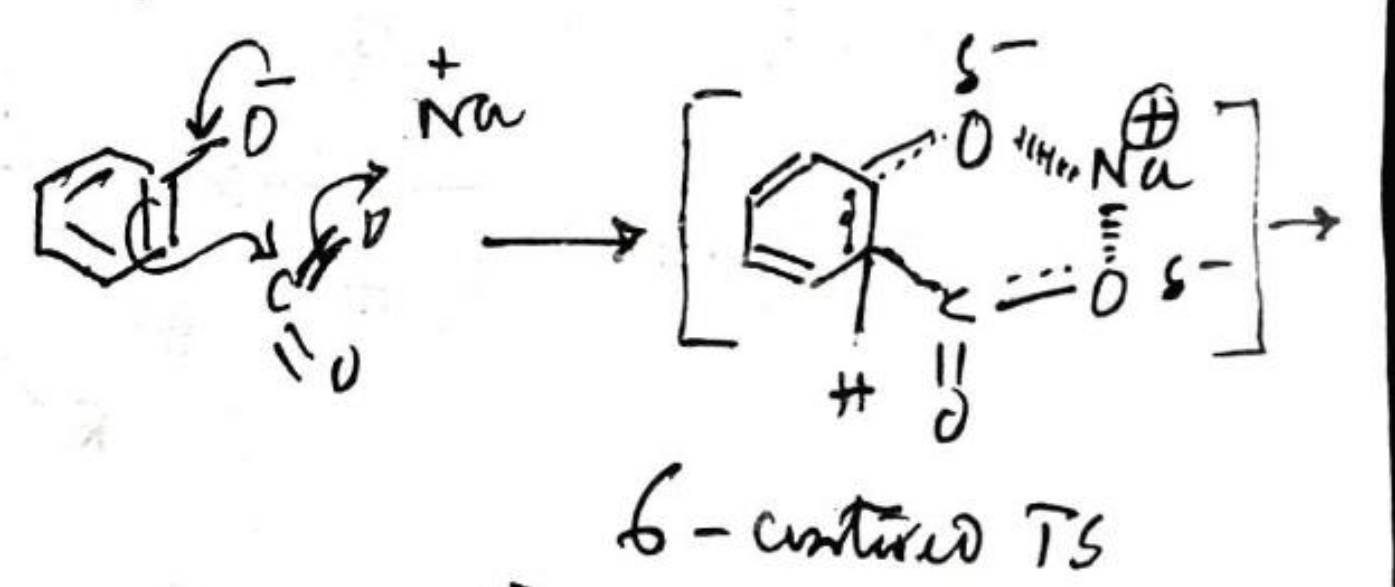
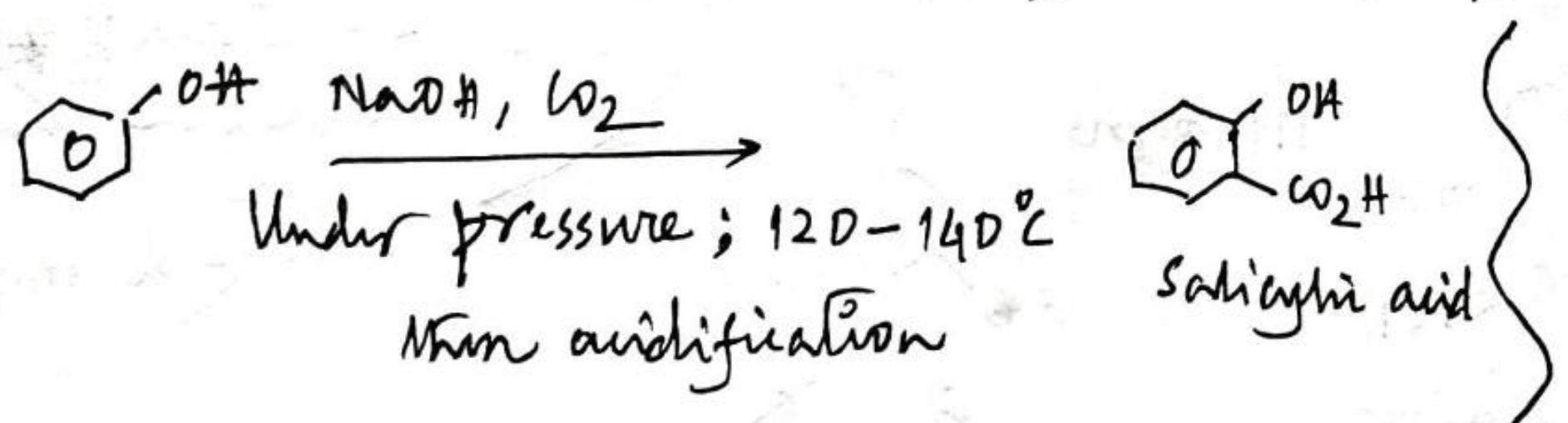


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This ppt cannot aromatise due to lack of para hydrogen.
Also -CHCl₂ gr. is not hydrolyzed presumably due to its insolubility in alkali.

Kolbe-Schmitt rxn: Carboxylation of phenols.



If KOH is used, the para ppt becomes major. K^+ is much larger in size than Na^+ and hence cannot be accommodated in the 6-centered TS as above. So the rxn does not proceed through the above pathway and simple electrophilic substn. occurs at para position.