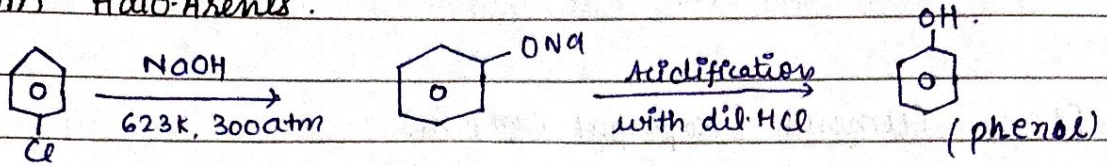
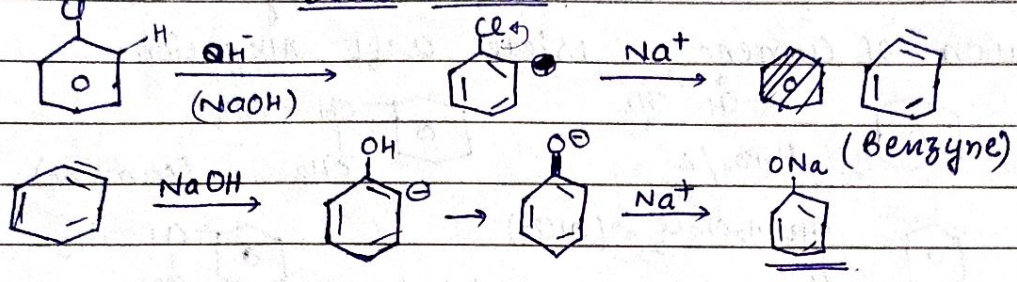


*** PREPARATION OF PHENOLS**

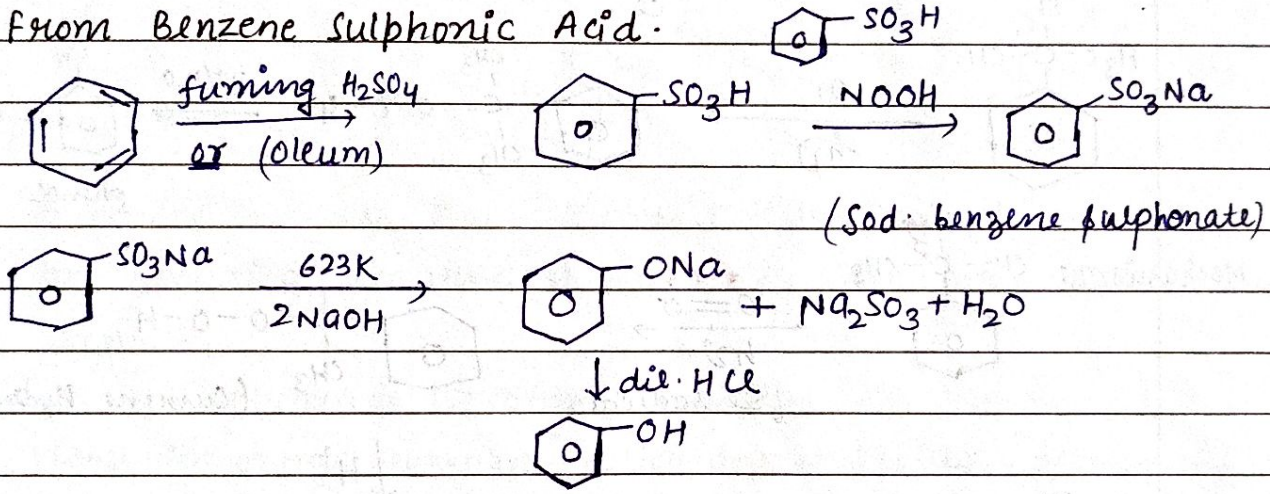
(1) From Halo-Arenes.



Dow's Process

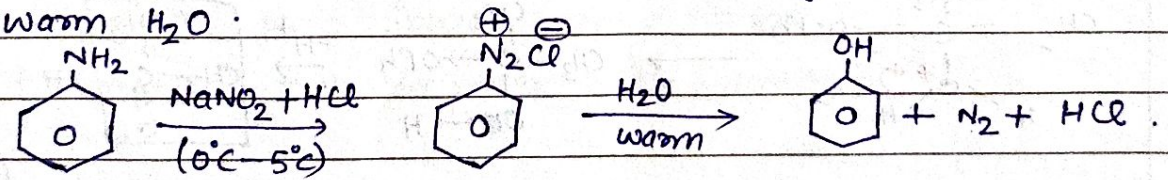


(2) From Benzene Sulphonic Acid.

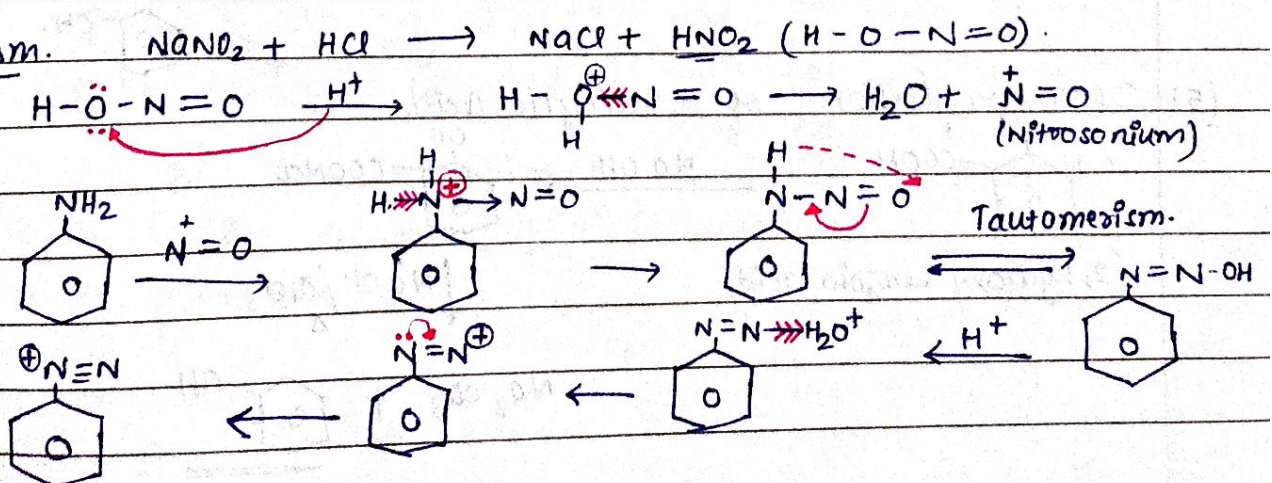


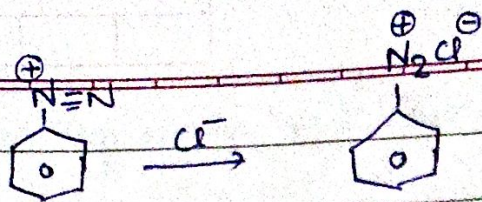
(3) From Diazonium Salts (1° Amine only)

By diazotisation of Aniline followed by hydrolysis with warm H₂O.



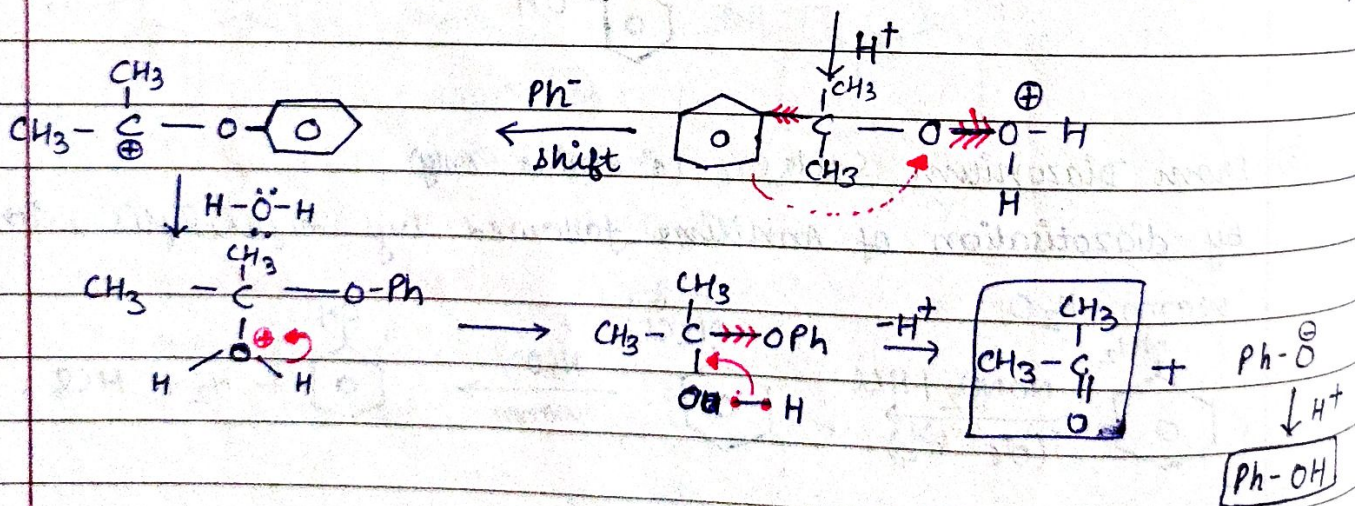
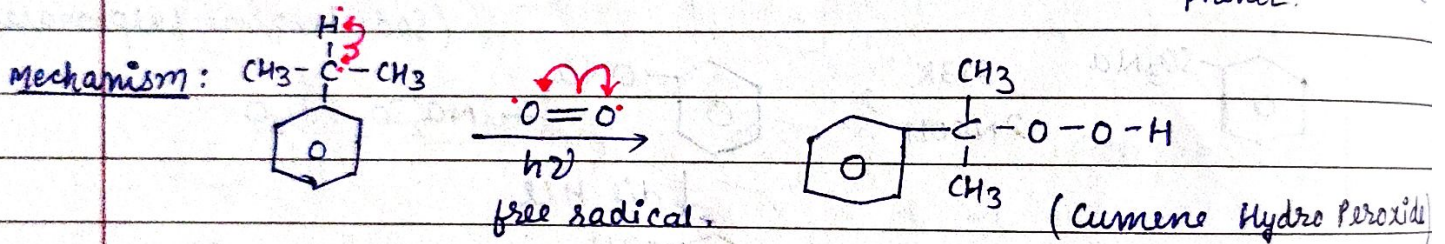
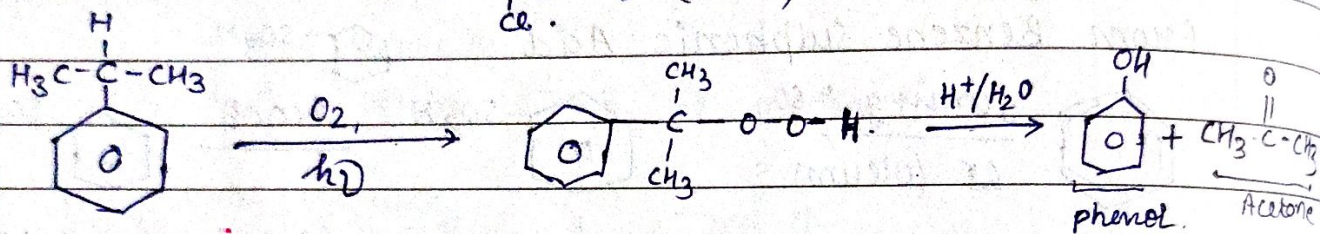
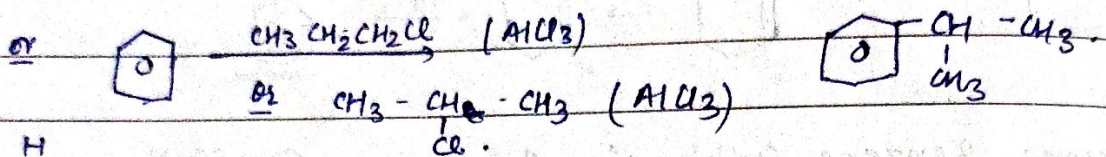
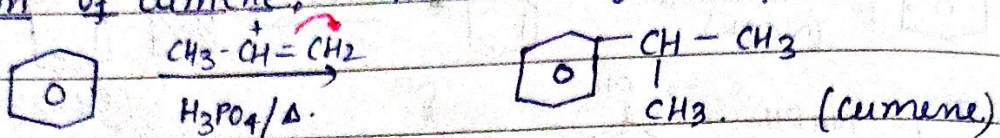
Mechanism.



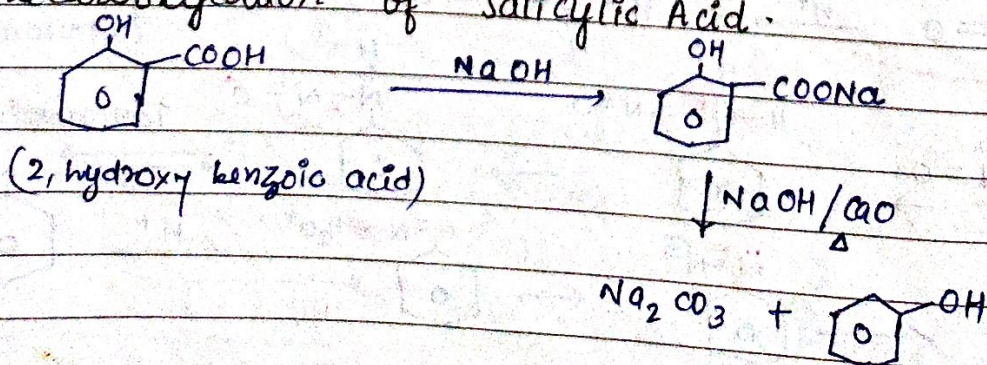


(4) From Cumene (Isopropyl Benzene)

Areal oxidation of cumene followed by Acidic Hydrolysis.
 formation of Cumene: Friedel Craft Alkylation.



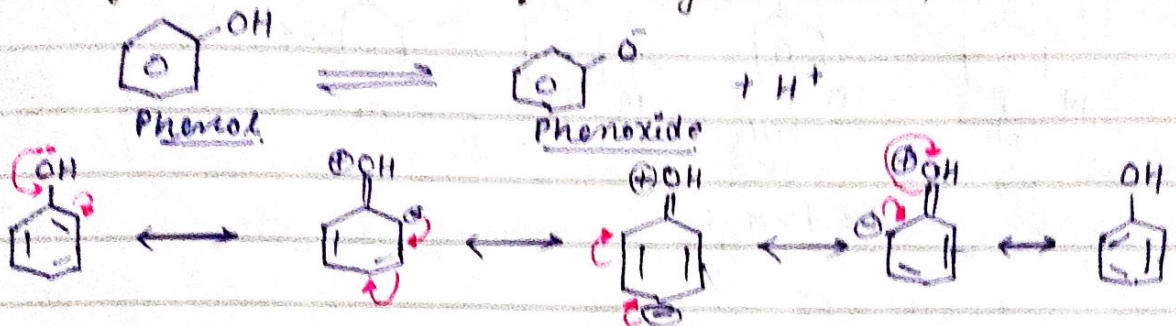
(5) Decarboxylation of Salicylic Acid.



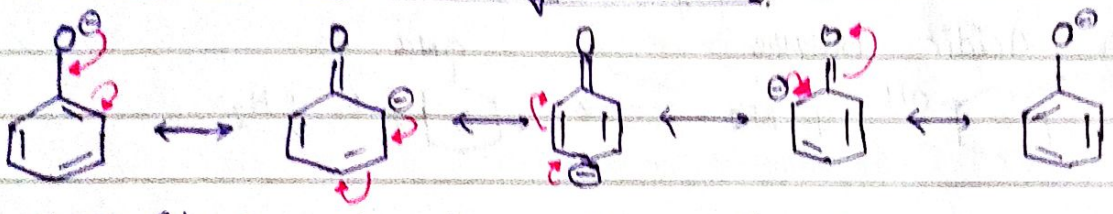
(11) ACIDIC NATURE OF PHENOLS.

Acidic strength: Carboxylic acid > Phenols > Water > Alcohols
 K_a : 10^{-5} 10^{-10} 10^{-14} 10^{-18}

★ ★ Why phenol is acidic? Although it is resonance stabilised.



Phenol has **5** resonating structures.



phenoxide ion also has 5 resonating structures but resonating structures of phenoxide are more stable than phenol.

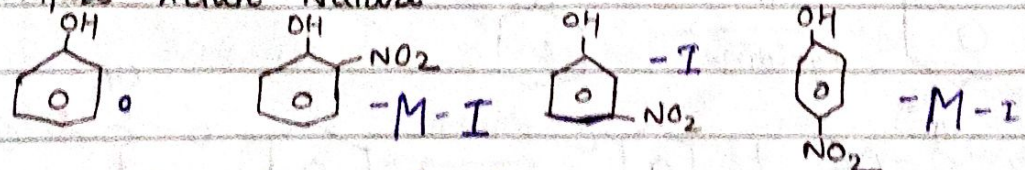
∴ Phenoxide > Phenol (stability)

phenol has "charge separation" which decreases stability of resonating structures.

Effect of substituent on Acidic Nature

- (1) -I or -M group increase acidic nature.
- (2) +I or +M group decreases acidic nature.

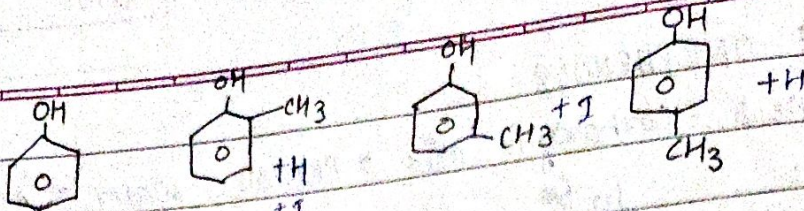
Ex. Compare Acidic Nature.



But in o-nitrophenol, H-bond is present. So, removal of H^+ is difficult.

∴ $d > b > c > a$.

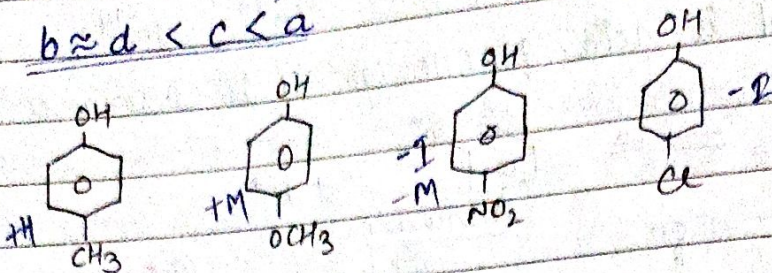
Ex



$b \approx d < c < a$

Jan 2013

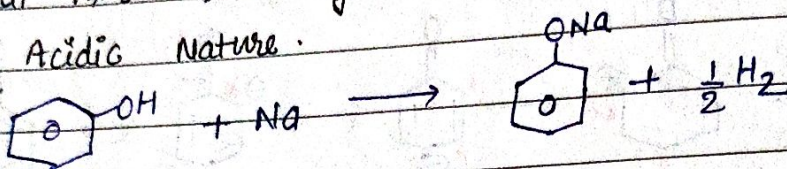
Ex



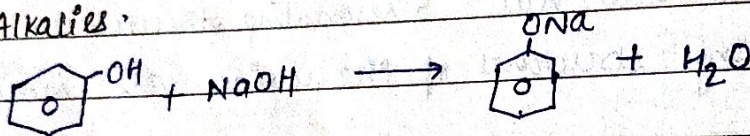
$c > d > a > b$

Chemical Rx^{ns}. Involving Acidic Nature.

1) With Acidic Nature.



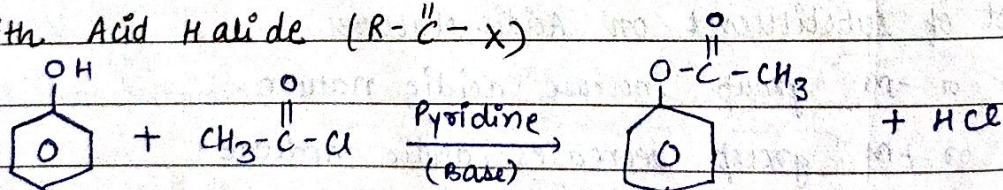
2) With Alkalies.



★★ Phenols don't give CO₂ on rxⁿ with M HCO₃ or M CO₃. but carboxylic acids evolve CO₂

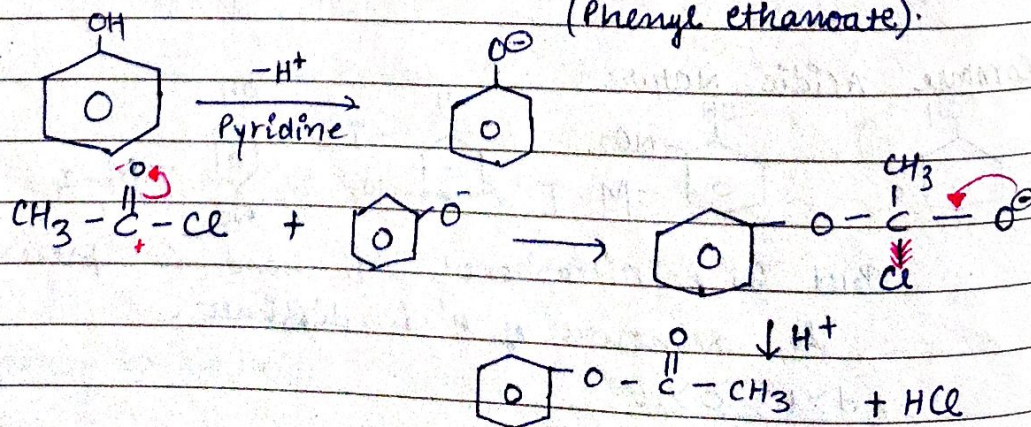
⊕ ESTERIFICATION: formation of Phenyl Esters

1) With Acid Halide (R-C(=O)-X)

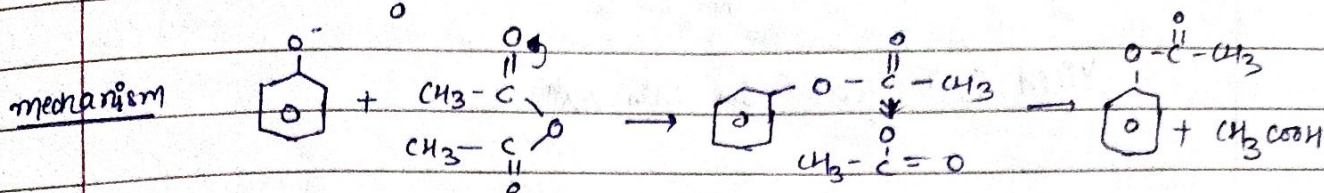
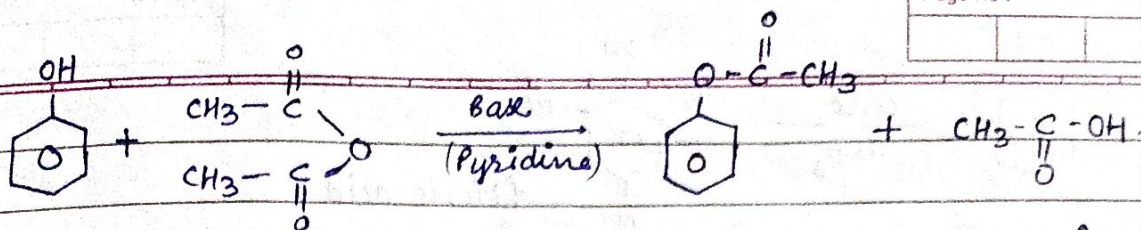


(Phenyl ethanoate).

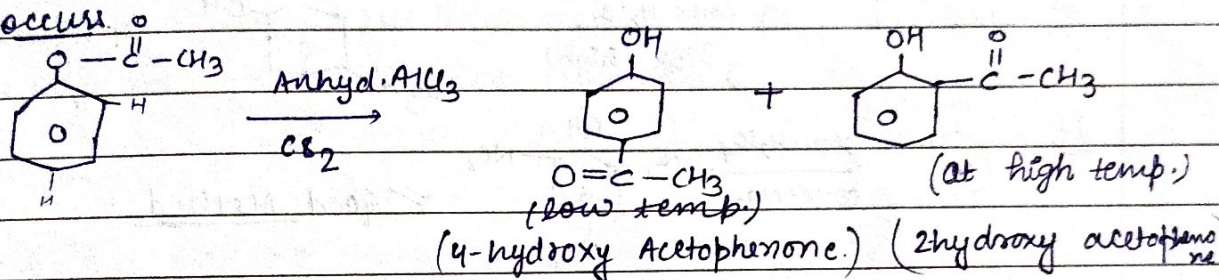
mechanism



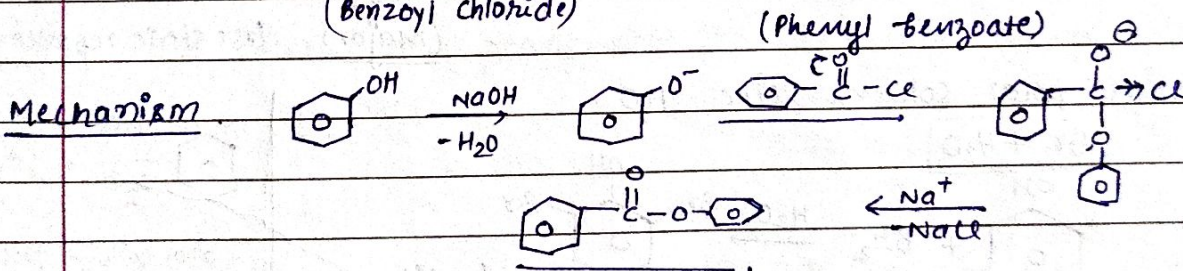
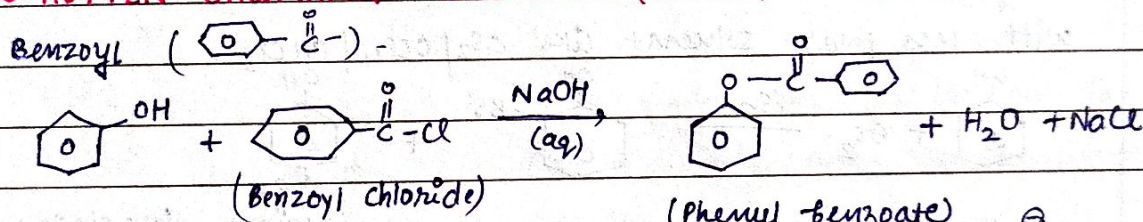
2) With Acid Anhydride. (R-C(=O)-O-C(=O)-R')



⊕ **FRIES REARRANGEMENT** When phenyl esters are treated with anhydrous $AlCl_3$ in presence of CS_2 , 'Fries rearrangement' occurs.



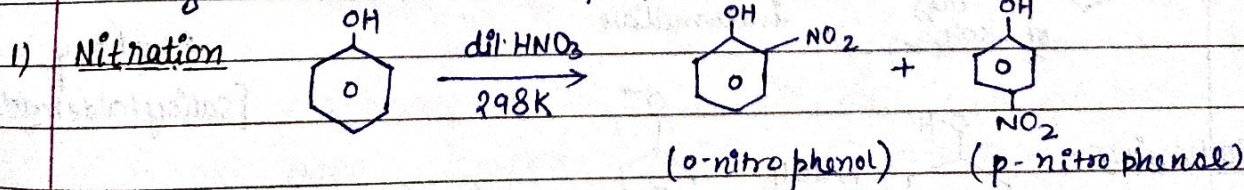
⊕ **SCHOTTEN-BAUMANN REACTION (BENZOYLATION)**



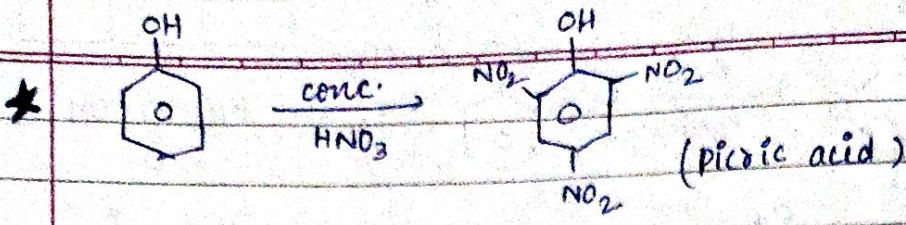
⊕ **REACTION OF PHENOL DUE TO BENZENE RING**

Aromatic Electrophilic substitution

$\bar{O}H$ group is activating towards E^+ substitution. e^- density increases at o & p position.

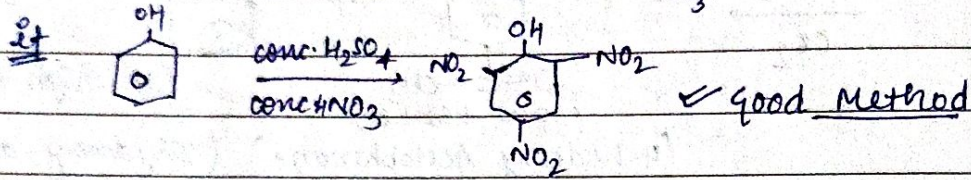
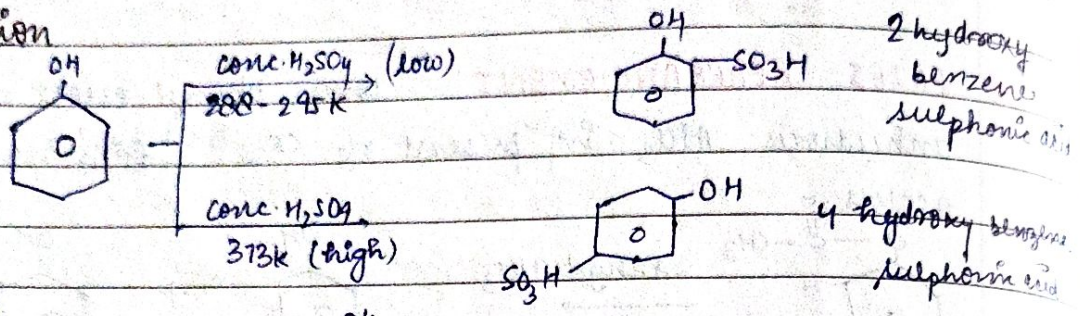


ortho & para can be separated by steam distillation.
o-nitrophenol is more volatile due to intra molecular H-bond & p-nitrophenol is less volatile due to inter molecular H-bond.



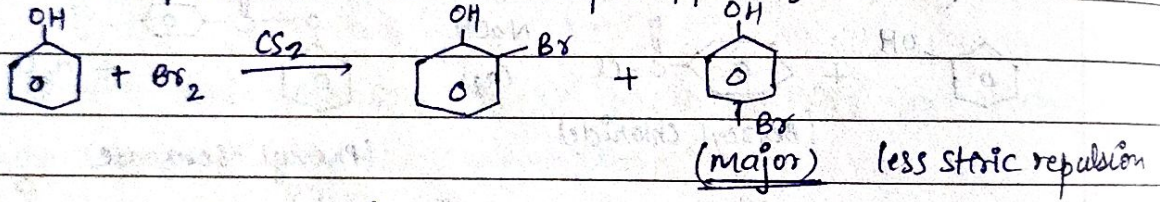
Yield isn't good in this rxn.

2) Sulphonation

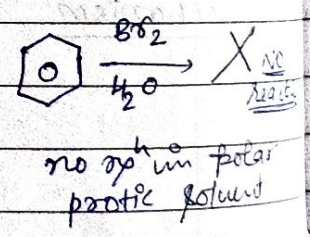
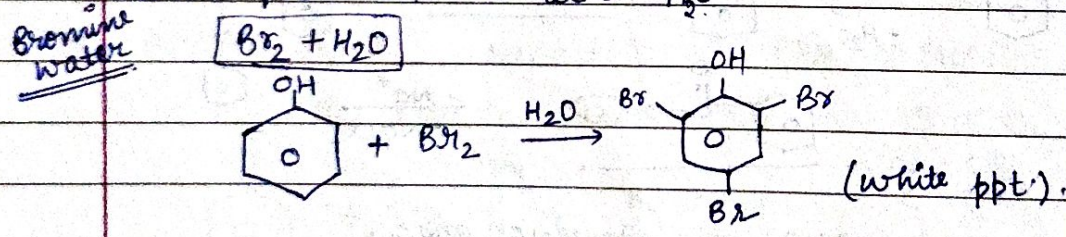


3) Halogenation

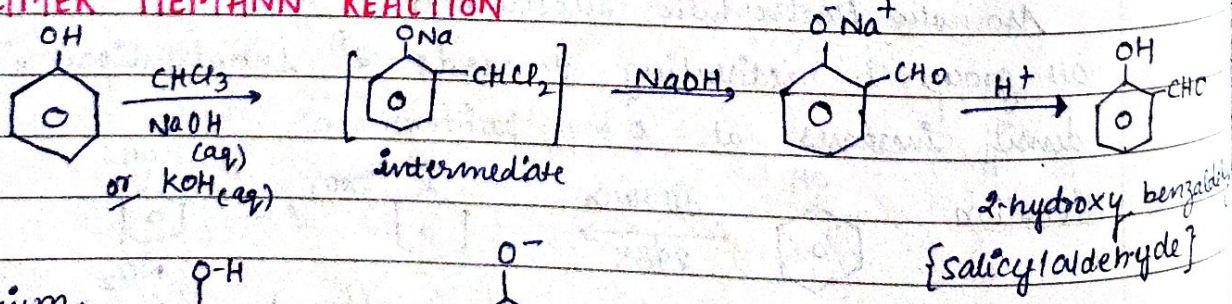
with less polar solvent like CS2 / CCl4 / CHCl3.



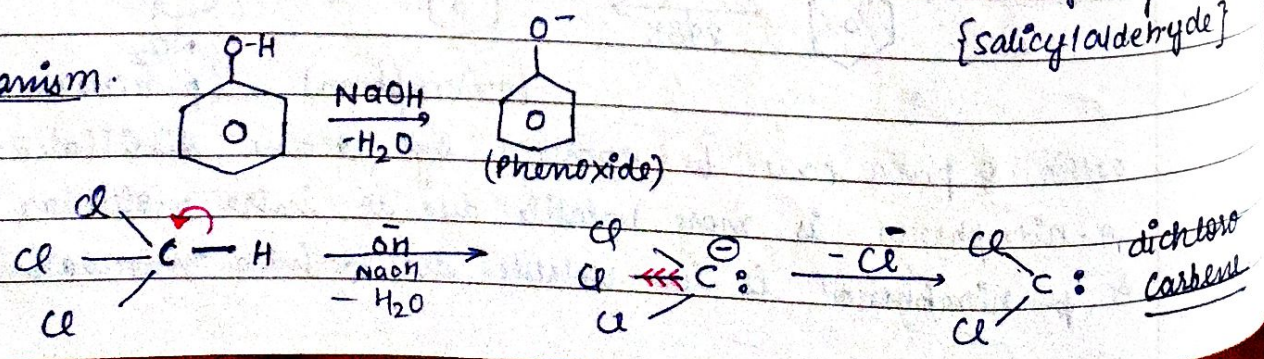
with polar solvent like H2O.



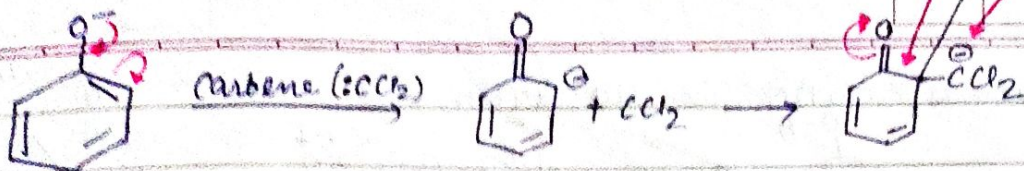
⊕ REIMER-TIEMANN REACTION



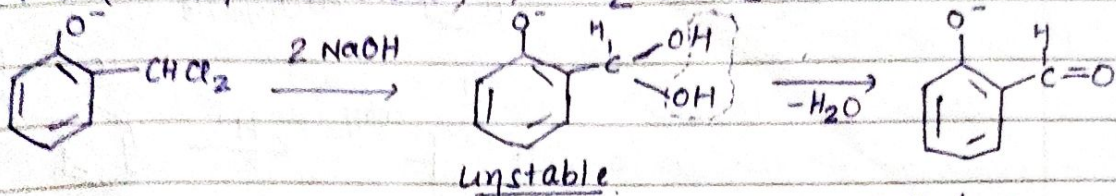
Mechanism:



Carbene is e^- deficient. (Neutral electrophile)



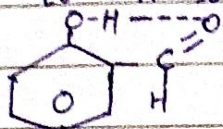
* $\ominus > \ominus^+$ (nucleophilic nature) \Rightarrow $:CCl_2$ attacks on \ominus not on \ominus^+ .



(salicylaldehyde) $\xrightarrow{H^+}$

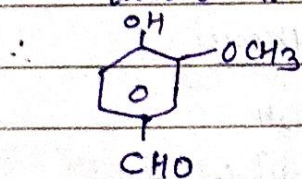
Q why ortho-para substitution takes place & not para??

1) due to H-bonding at ortho position.

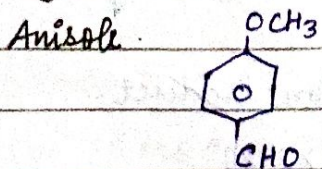


2) \bar{O} has +M, +I. at o-position, +I effect is more than para-position. \Rightarrow e^- density increases more at ortho

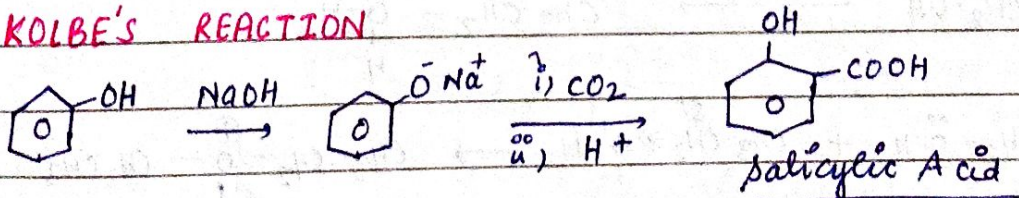
Ex. In case any one ortho position is pre-occupied, ortho substitution doesn't take place due to steric hindrance.



Ex. OCH_3 has +M, -I. so, at ortho, -I is more. \Rightarrow e^- density more at para position.



⊕ **KOLBE'S REACTION**

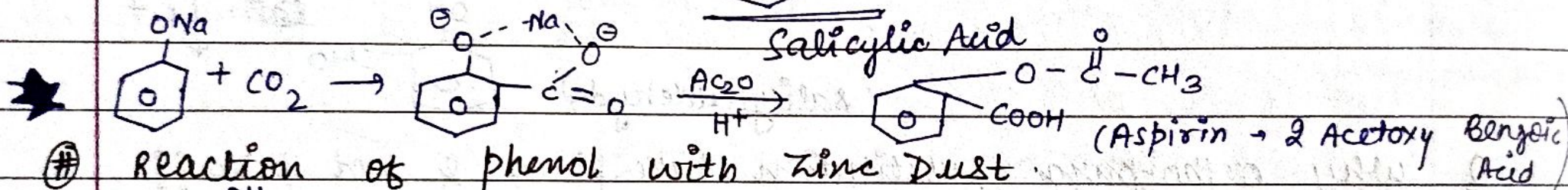
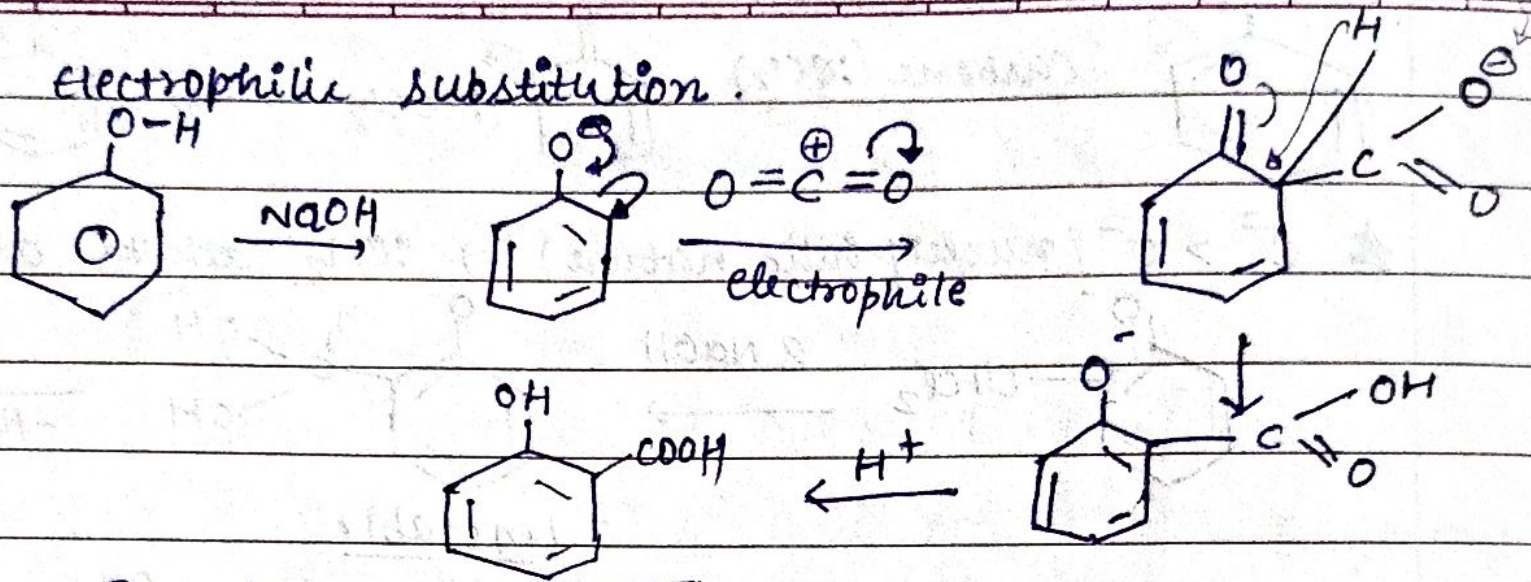


(2 hydroxy benzoic Acid)

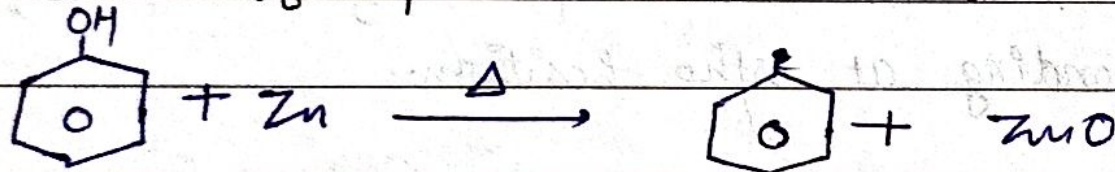
★ With KOH, para product is major. due to chelation effect in case of NaOH. due to large size of K^+ , chelation is not possible.

it is electrophilic substitution.

Mechanism

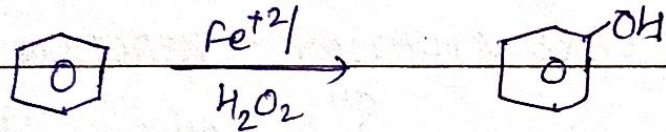
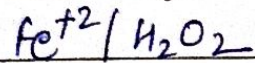


⊕ Reaction of phenol with Zinc Dust.

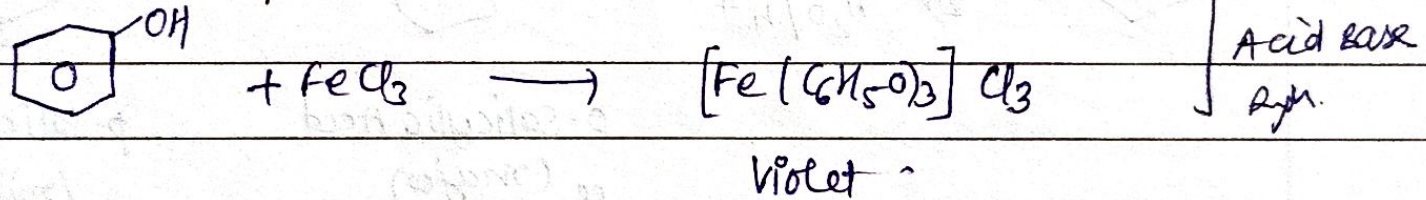


Benzene.

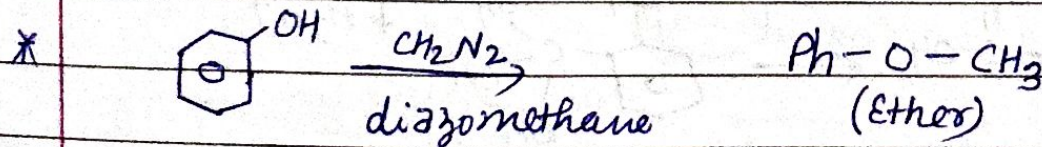
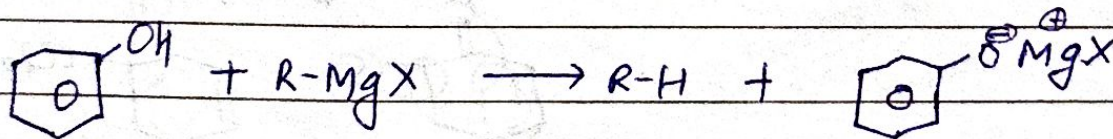
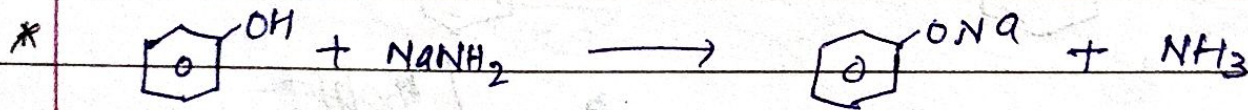
* Preparation of Phenol using 'FENTON REAGENT'



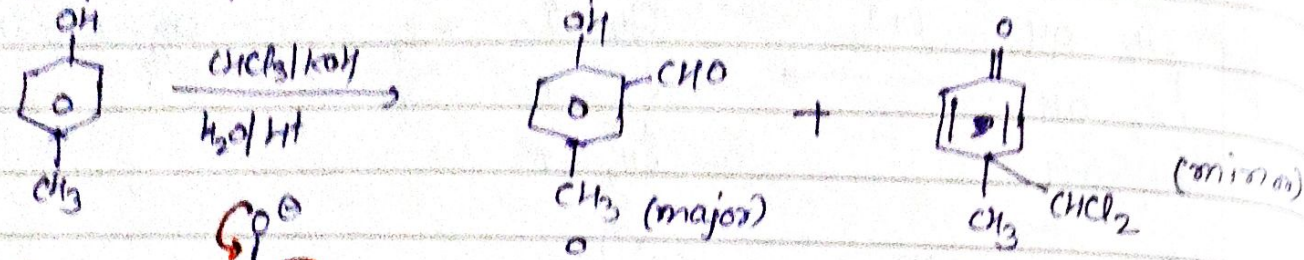
* Neutral FeCl_3 / Test



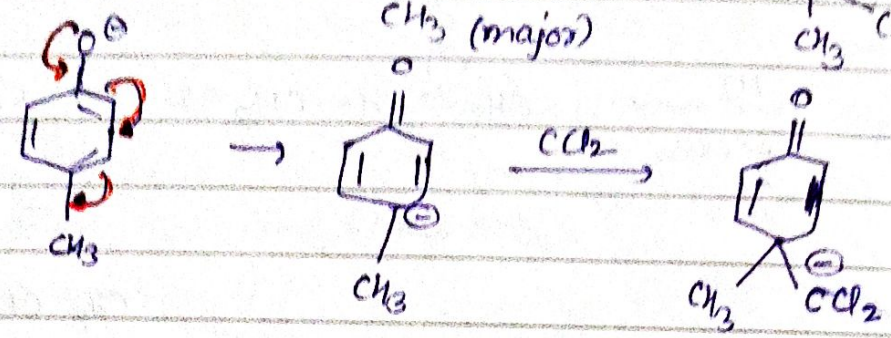
This test is given by enol, phenol & its derivative.



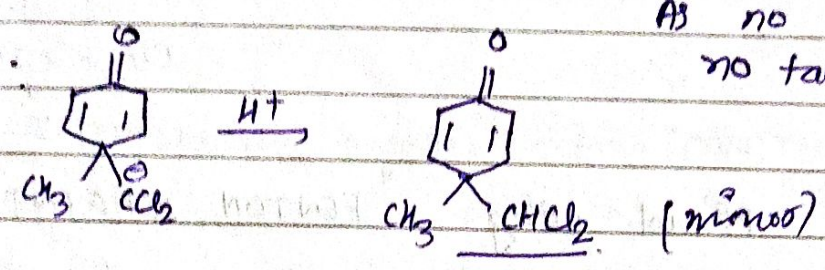
* If para position is occupied in Reimer-Tiemann \rightarrow



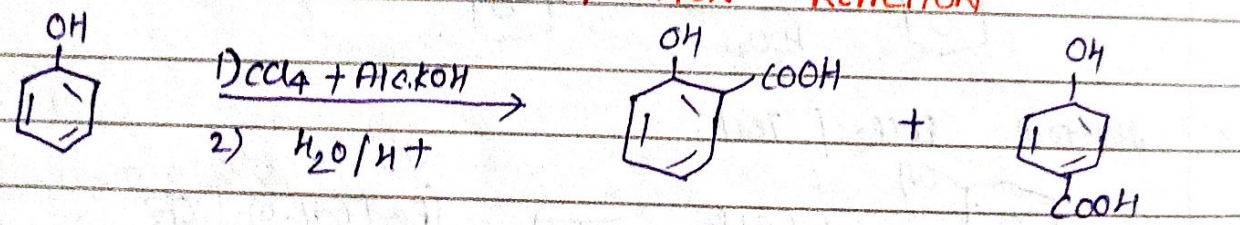
Mechanism:



As no α -H present no tautomerism possible.

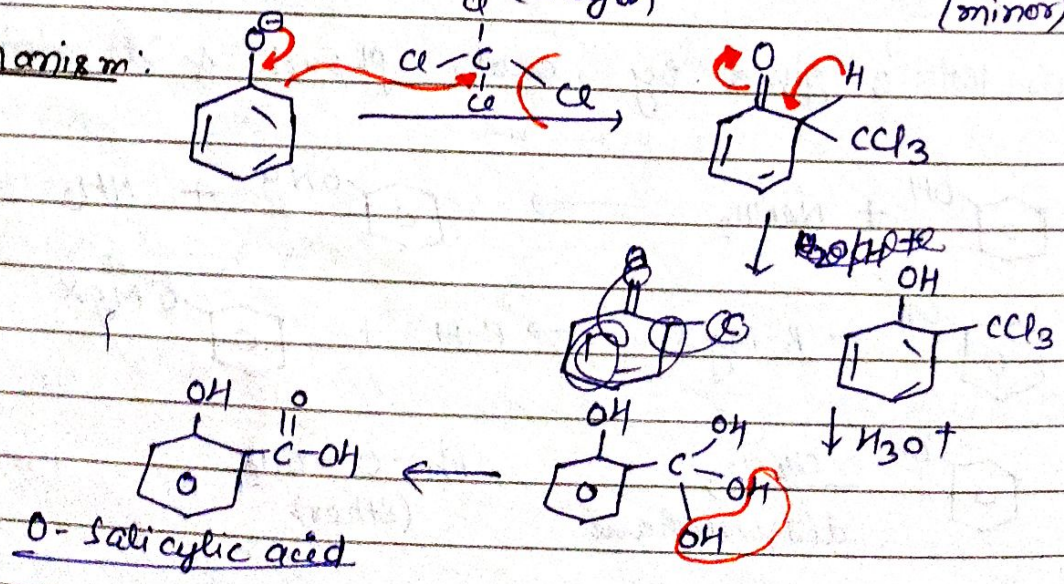


REIMER TIEMMEN CARBOXYLATION REACTION

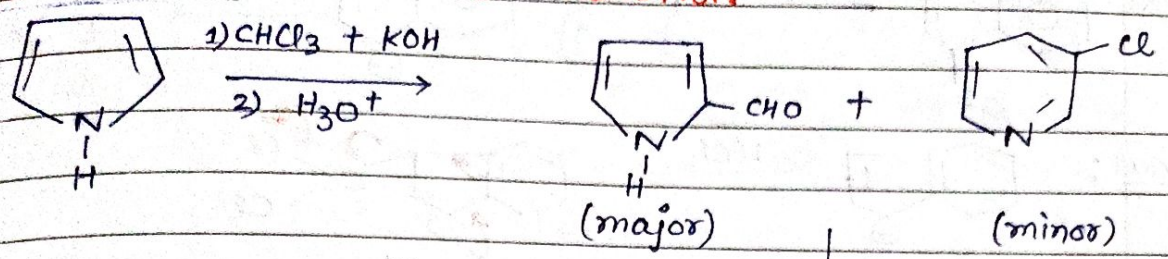


o-Salicylic Acid (major) p-Salicylic Acid (minor)

Mechanism:



Adv 2013 **ABNORMAL RIEMER TIEMANN REACTION**



Normal Riemer Tiemann product | Abnormal Riemer Tiemann product

