25th July Thursday

*Chapter: 2 P-2

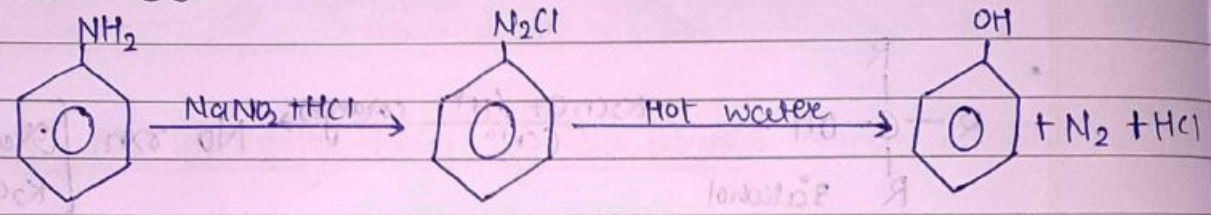
Alcohol, Phenol & Ethers

PHENOL

phenol [C_6H_5OH] [Carbolic Acid]

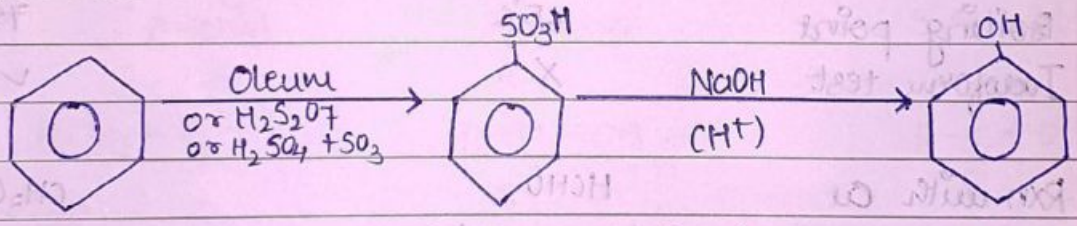
* Preparation:

1.) From Aniline:



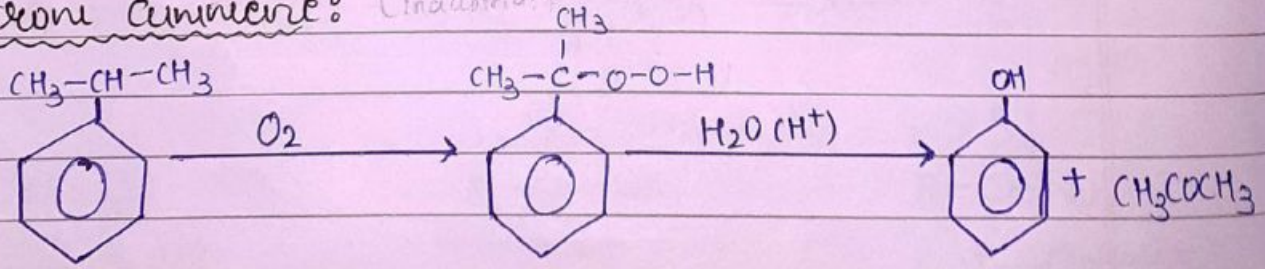
Aniline ($C_6H_5NH_2$) — Benzene diazonium Chloride — Phenol (Carbolic acid)

2.) From Benzene:



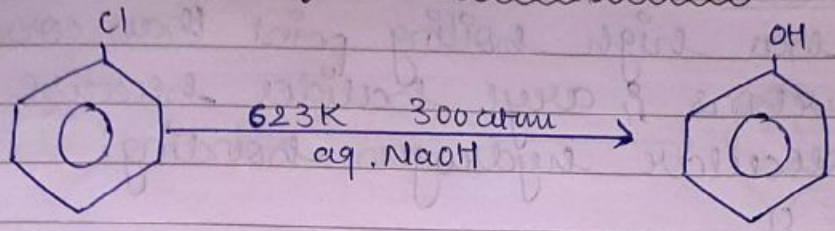
Benzene — Benzene Sulphonic Acid — Phenol

3.) From Cumene:

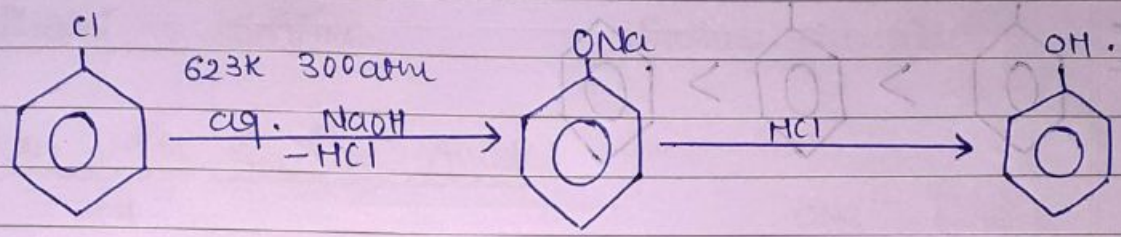


Cumene — Cumene hydro peroxide — Phenol — Propanone

4.) Dow's Process (from chlorobenzene):

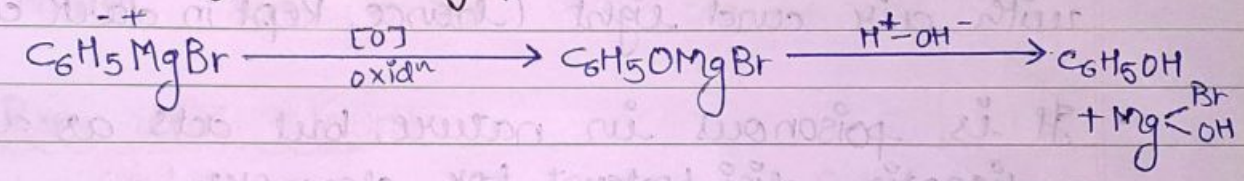


(NSR)

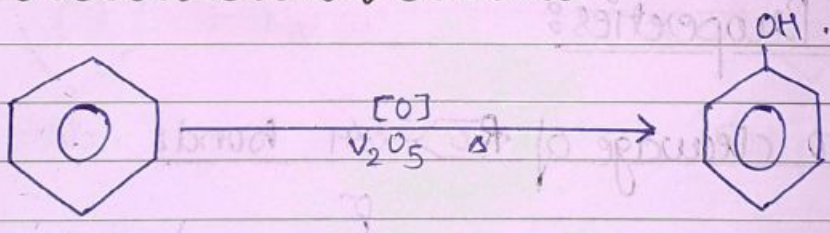


Chlorobenzene Sodium phenoxide. Phenol.

5.) From Grignard reagent:



6.) From Oxidation of benzene:

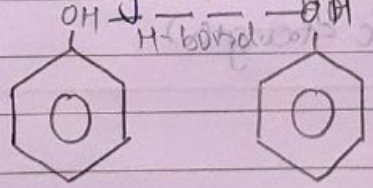


V_2O_5 = Vanadium pentaoxide.

* Physical Properties:

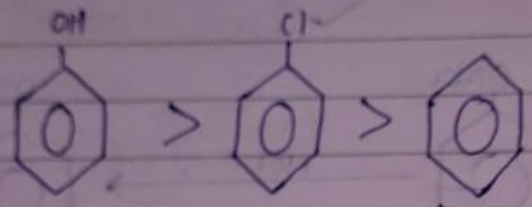
1.) Solubility:

- phenol is slightly soluble in water and is readily soluble in organic solvent.
- phenol is less water soluble than alcohols, as large hydrocarbons (phenyl) parts in.



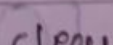
2.) Boiling Point:

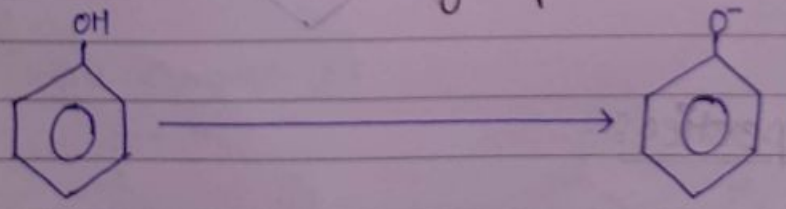
- phenol has high boiling point than corresponding hydrocarbons & aryl halides because of intermolecular hydrogen bonding.

Order: 

- Phenol is a coloured, hygroscopic, crystalline solid.
- It attains pink colour when it comes in contact with air and light (Chance, Kept in dark container)
- It is poisonous in nature, but acts as an antiseptic disinfectant for cleaneres.

* Chemical Properties:

1.) Rxn due to cleavage of  O-H bond: Acidic behaviour



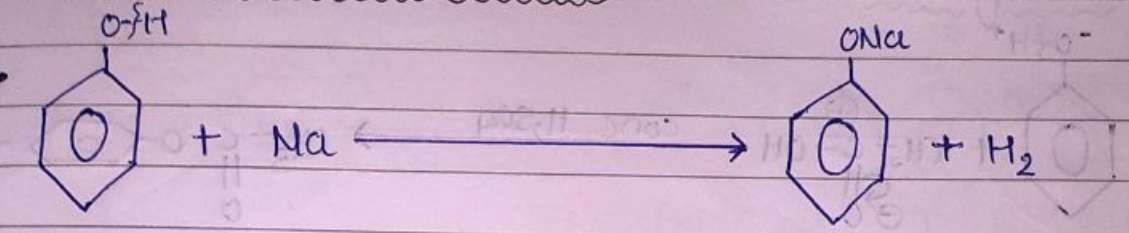
Acid — Phenoxide ion. (conjugated base). (Resonance stabilised).

* NOTE:

- $CH_3COOH > H_2CO_3 >$ phenol $> CH_3OH > H_2O > C_2H_5OH$.
(acidic strength)

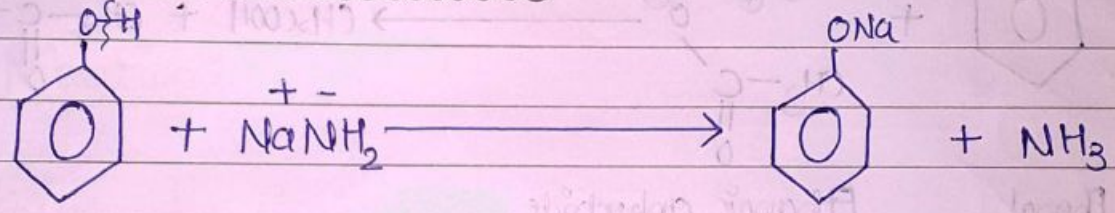
Rxn with metals.

(A) Rxn with Sodium metal:



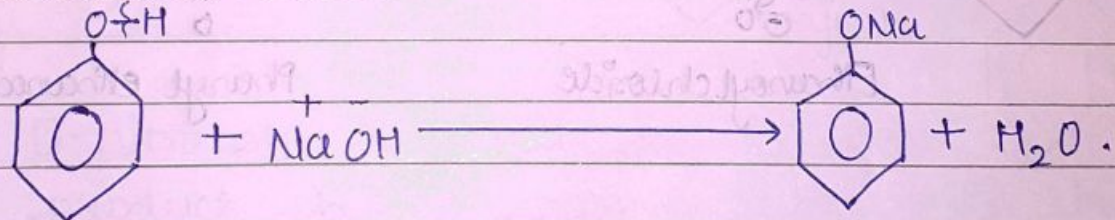
Phenol Sodium Sodium phenoxide

(B.) Rxn with Sodium Amide:



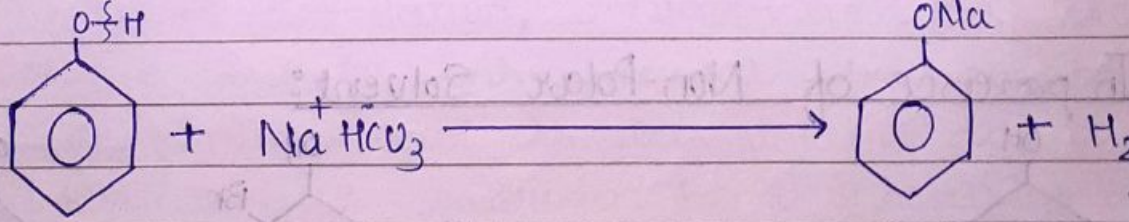
Phenol Sodium amide Sod. phenoxide

(C.) Rxn with NaOH:



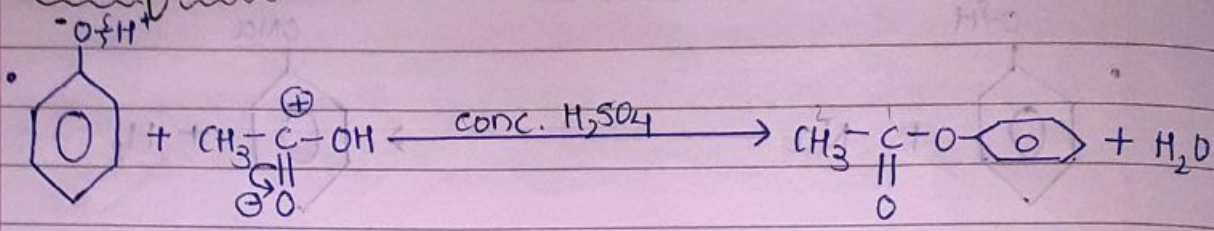
Sod. phenoxide

(D.) Rxn with Sodium bicarbonate:

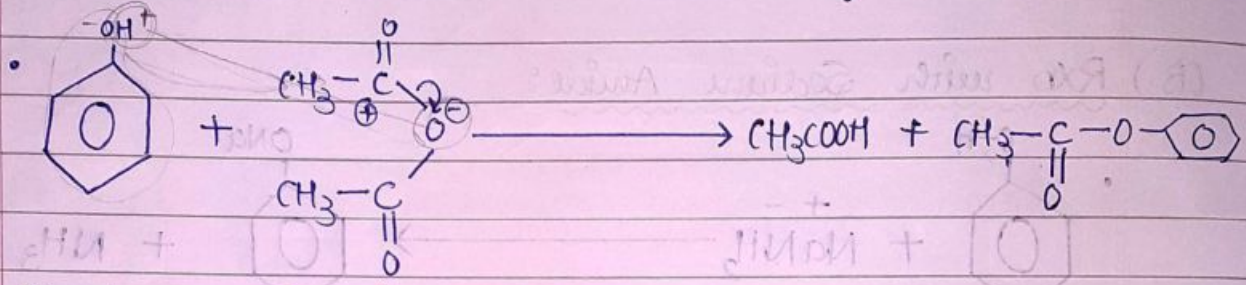


Weak acid Sod. phenoxide. Strong acid

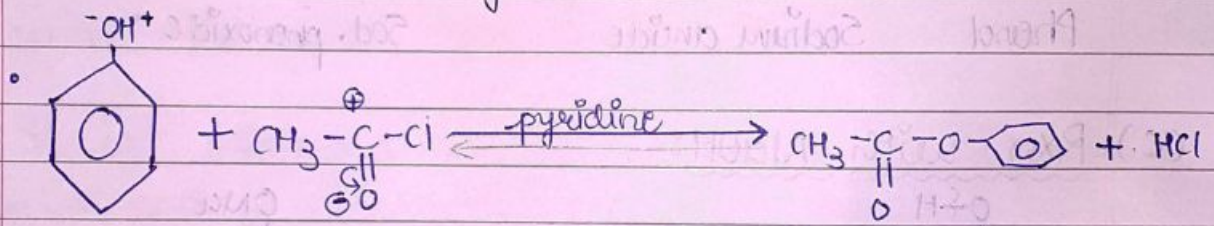
(E.) Esterification:



Phenol Ethanoic acid Phenyl ethanoate



Phenol Ethanoic anhydride.

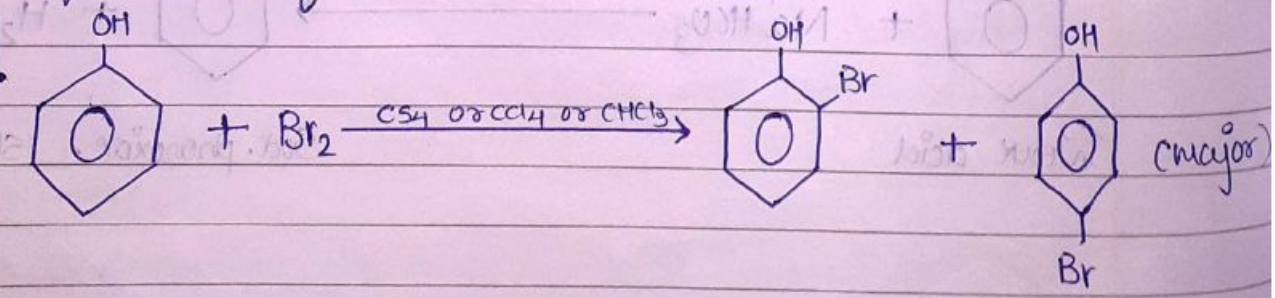


Ethanoyl chloride Phenyl ethanoate

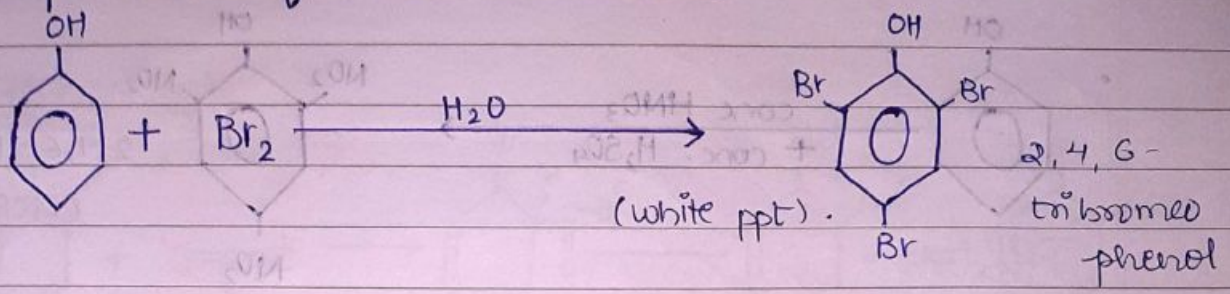
2.) Electrophilic Substitution Reaction:

(A.) Bromination:

1.) In presence of Non-Polar Solvent:



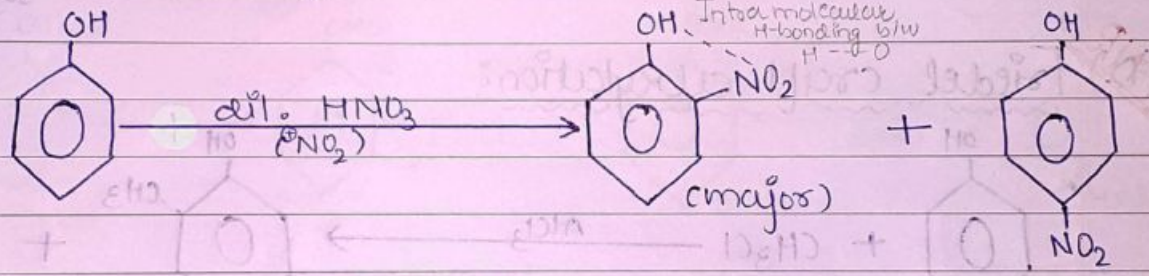
2.) In presence of Bromine water:



* Identification test for phenol.

(B.) Nitration:

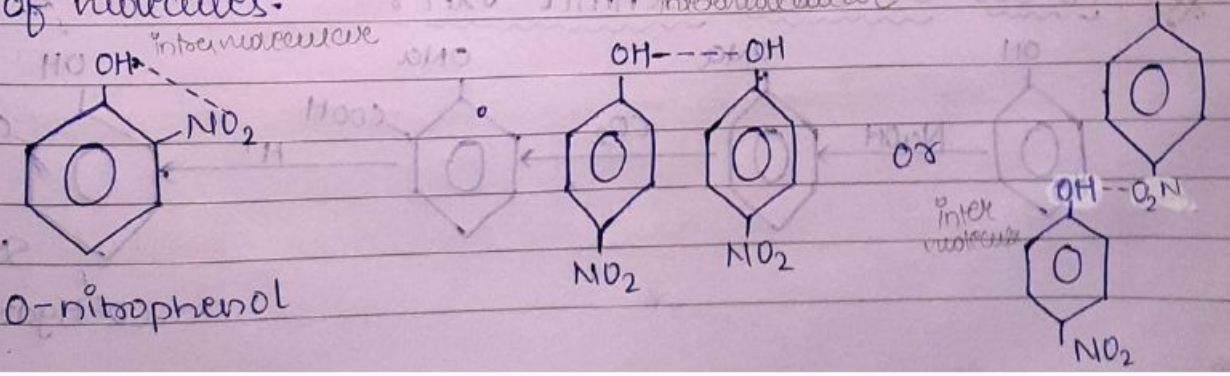
1.) With dil. HNO_3:



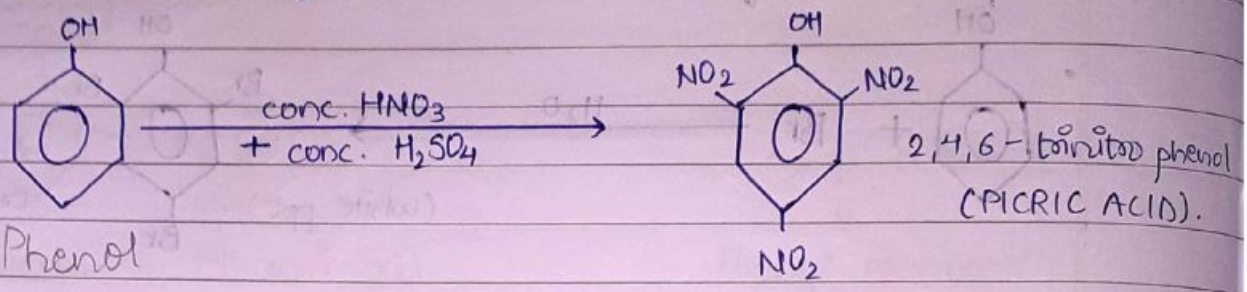
* O-nitro phenol will be major product bcz of "intramolecular H-bonding".

Q:⇒ During nitration of a phenol how can we separate out O-Nitrophenol & p-Nitrophenol?

⟹ By Steam distillation. O-nitrophenol is steam volatile due to intramolecular hydrogen bonding while p-nitrophenol is less volatile due to intermolecular hydrogen bonding causing association of molecules.



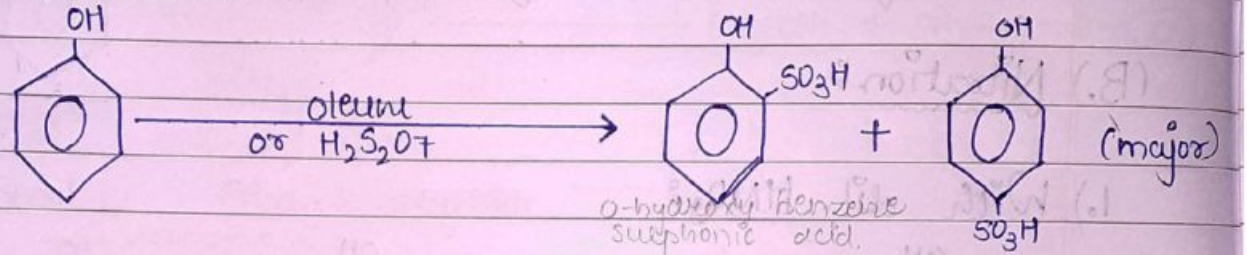
2.) With conc. HNO_3:



Phenol

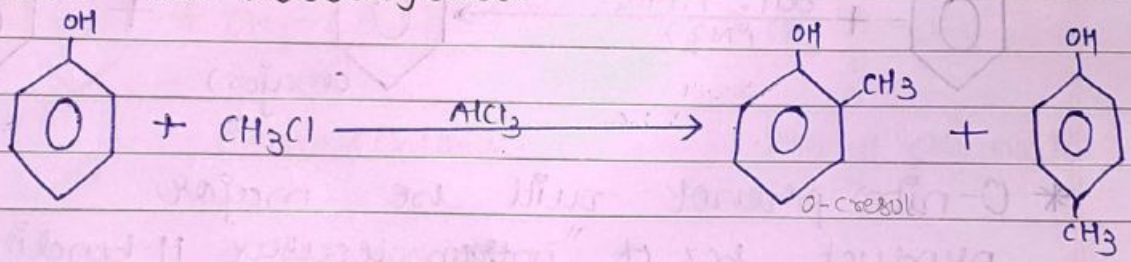
2,4,6-trinitro phenol (PICRIC ACID).

(c.) Sulphonation:



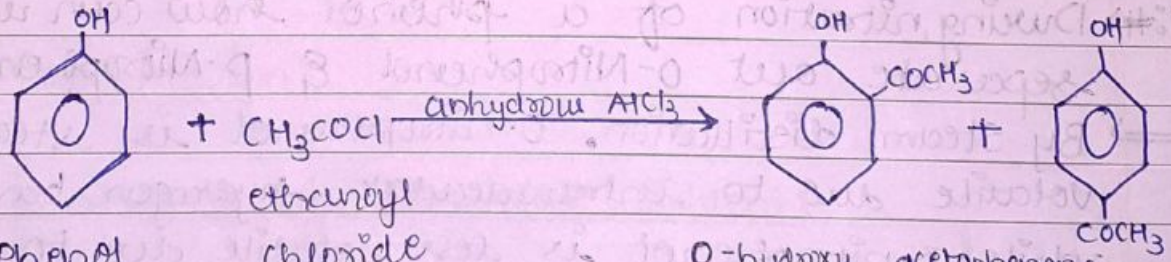
o-hydroxy Benzene sulphonic acid.

(d.) Friedel craft alkylation:



o-cresol

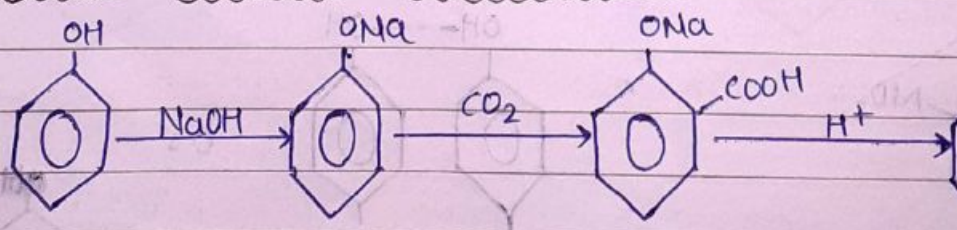
(e.) Friedel craft acylation:



Phenol — ethanoyl chloride — O-hydroxy acetophenone

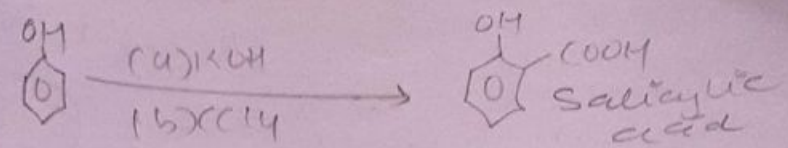
IMP for Boards

(f.) Kolbe's or Kolbe Schmit rxn:



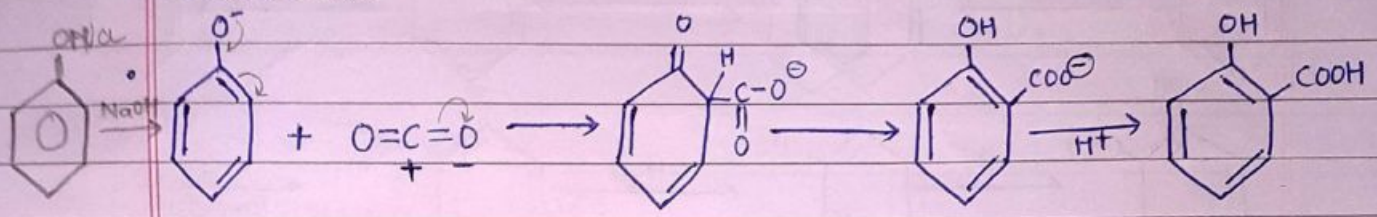
Salicylic acid
(O-Hydroxy benzoic acid)

we can make aspirin

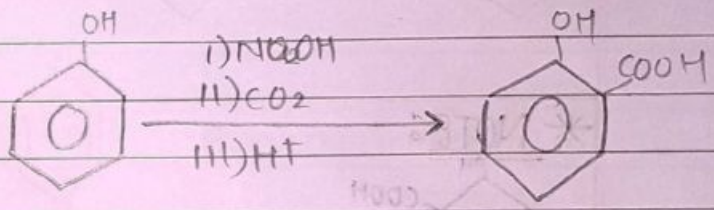
* 

- here, CO_2 acts as an electrophile

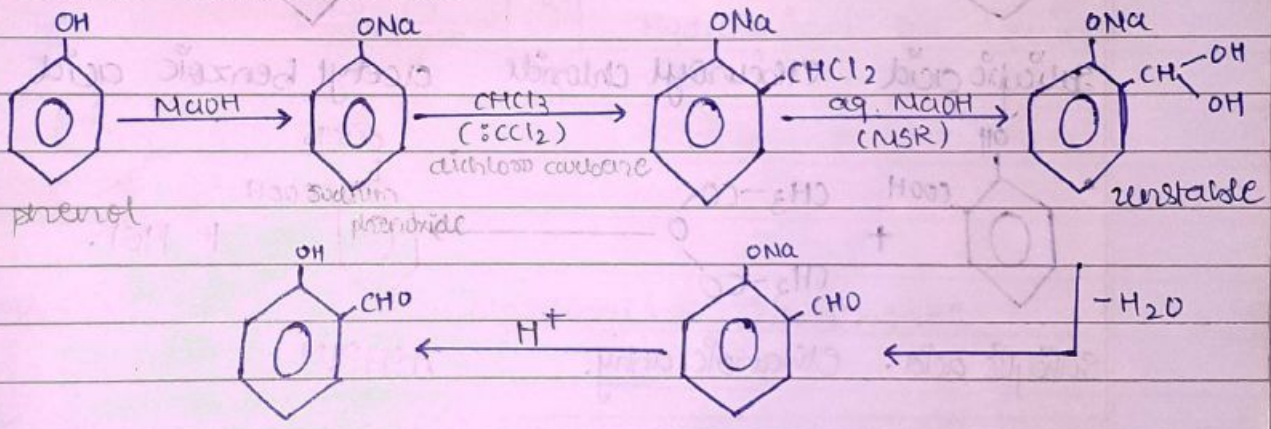
Mechanism:



can be written as:



(6) Reimer Tiemann rxn:



Salicylaldehyde

Mechanism:

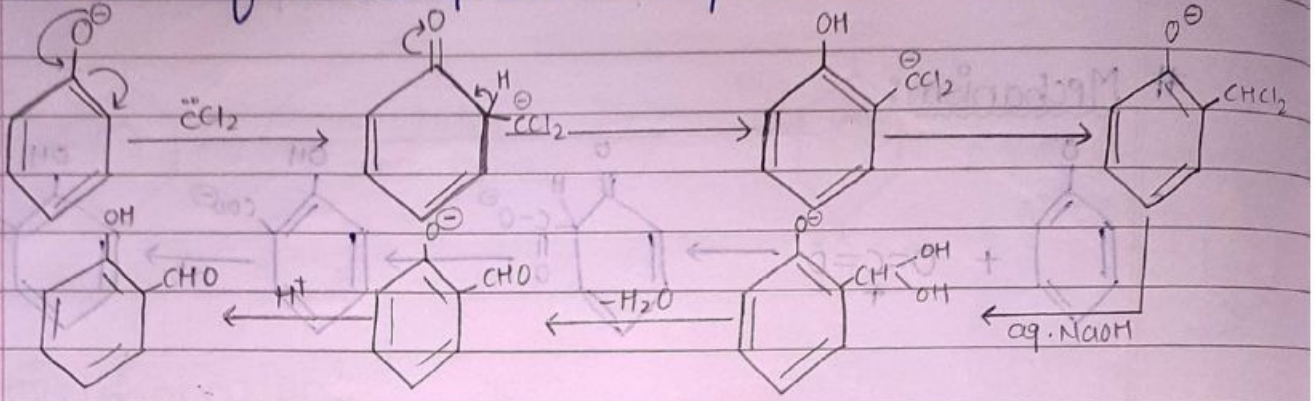
step:1. formation of electrophile (:CCl_2 dichloro carbene)

$$CHCl_3 \xrightarrow[-HCl]{\alpha\text{-elimination}} \ddot{C}Cl_2$$

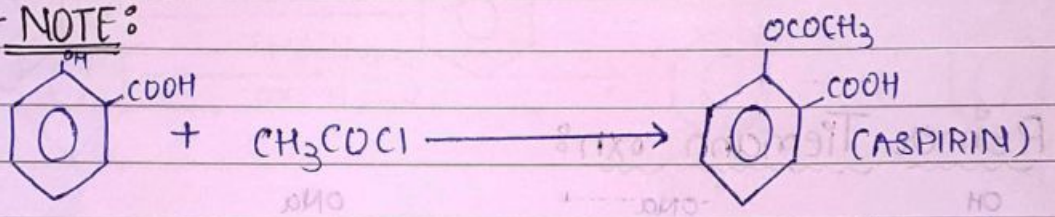
~~step:2 attack of electrophile on phenoxide ion.~~

following mechanism is not in boards

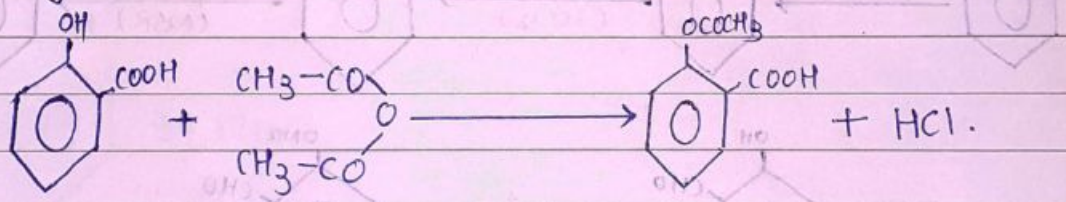
step:2 attack of electrophile on phenoxide ion.



* NOTE:



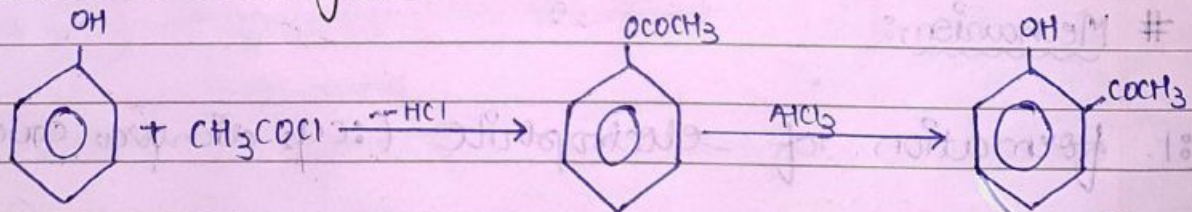
salicylic acid ethanoyl chloride acetyl benzoic acid



salicylic acid. ethanoic anhy. ASPIRIN

Some other rxn's

(1.) Fries Rearrangement:

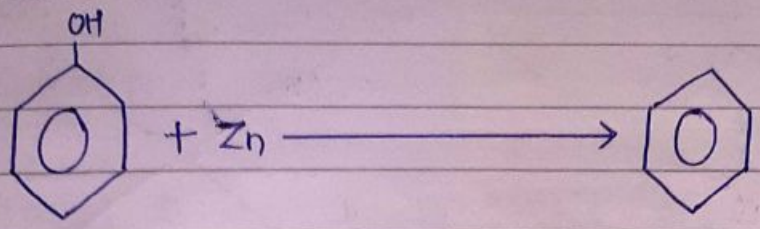


or $C_6H_5-OCOCH_3$ (ester)

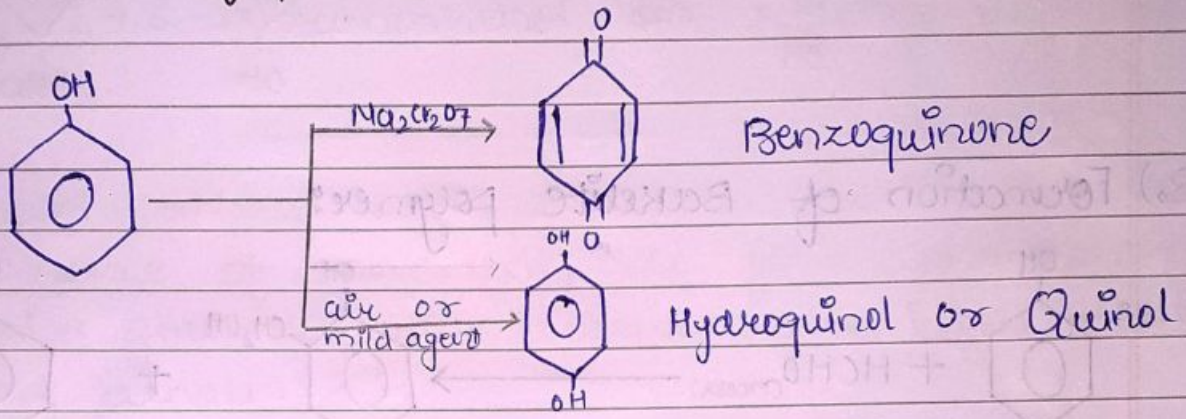
or C_6H_4(OH)($COCH_3$)

- friedel craft took $AlCl_3$ dir. jisse O & P position milta
- fries took anhy. first.

(II.) Rxn with Zinc:

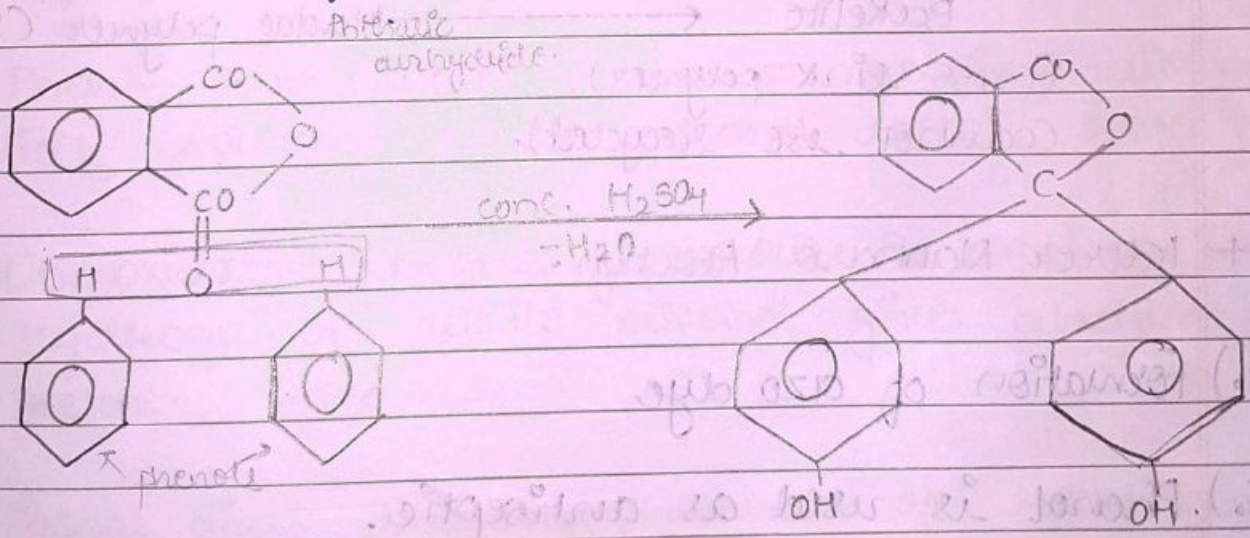


(III.) Oxidation of phenol:



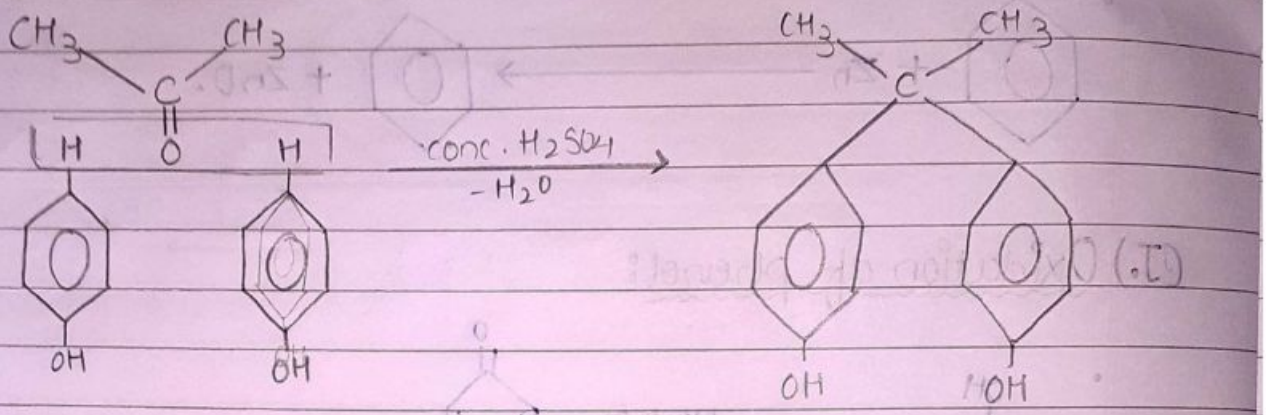
* Uses of phenol:

1.) Formation of phenolphthalein indicator:

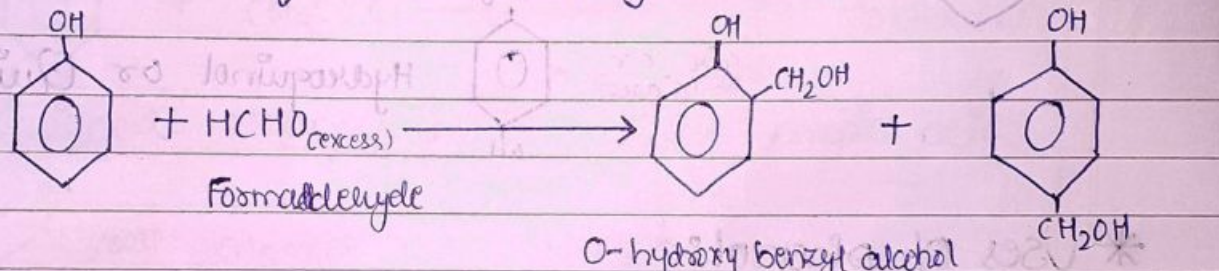


- it is colorless in acidic medium.
- pH = 8.3 (pink colour attain)

2.) Formation of Bis-phenol A indicator: (rxn with acetone)



3.) Formation of Bakelite polymer:



Bakelite ⟵ Novolac polymer (linear)

(cross link polymer)
(cannot be recycled).

→ Iederer Manrase Reaction.

4.) Formation of azo dye (coupling rxn)

5.) Phenol is used as antiseptic.

6.) For drug manufacturing i.e. Aspirin, Salol, Phenacetin

7.) used as preservative for ink.

* Test of phenol:

- Phenol gives out violet colour with neutral $FeCl_3$ solution.

- Phenol turns blue litmus paper to red.

- Aqueous solution of phenol gives white precipitate of 2,4,6-tribromophenol on reacting with bromine water.

- Phenol combines with phthalic anhydride in the presence of conc. H_2SO_4 to form phenolphthalein which gives out pink colour when introduced to any alkali.

* Difference b/w Phenol and Alcohol:

- Phenol is more acidic than alcohol because of phenoxide ion's resonance.

- Phenol gives violet colour on reacting with neutral $FeCl_3$ solution while alcohol doesn't react to it.

- On oxidation, phenol gives out Benzoquinone or Hydroquinol while alcohol gives aldehyde and Ketone.

- Phenol gives triphenyl-phosphate on reacting with PCl_5 whereas alcohol results in alkyl halide.

- $C_6H_5OH + PCl_5 \longrightarrow C_6H_5Cl + POCl_3 + HCl$
- $3\ C_6H_5OH + POCl_3 \longrightarrow (C_6H_5)_3PO_4 + 3HCl$

Triphenyl phosphate.