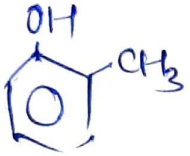
UNIT-2

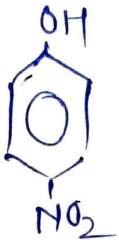
PHENOL

Phenols are compounds containing -OH group attached directly to an aromatic ring.

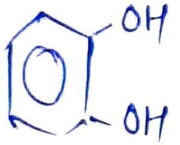
Phenol



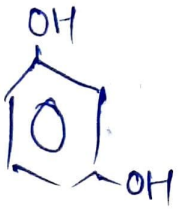
2-methyl phenol (O-cresol)



p-nitrophenol



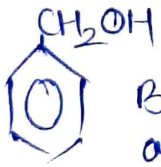
Catechol



Resorcinol

Quinol

Aromatic alcohols - OH gp at side chain are not phenols



Benzyl alcohol

2-phenyl ethanol

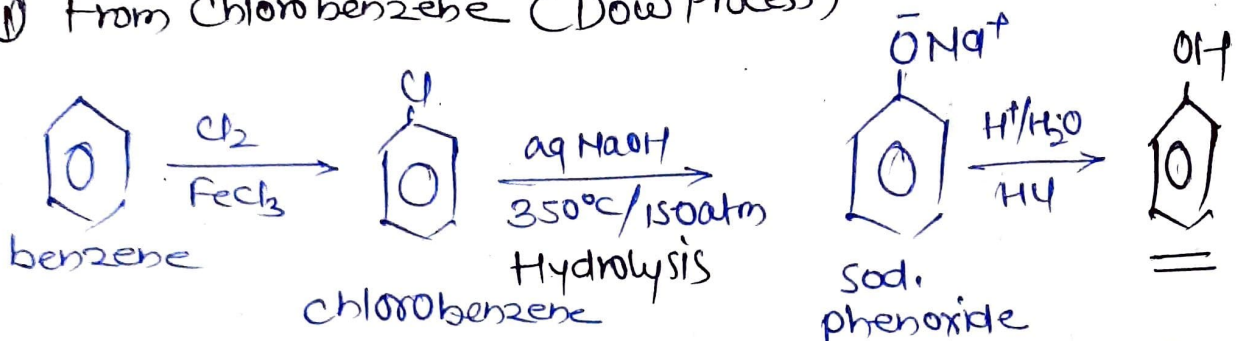
PHENOL 

Physical Properties –

- Pure phenols are colourless liquid & solid, but they are found to contain red tint owing the presence of oxidation product
- Phenols have characteristic Carbolic Odour, which in case of phenol itself is highly toxic
- BP 182°C higher than aliphatic alcohol
- MW : 94 g/mol
- MP : 42°C , IR - OH str - 3200-3650 cm⁻¹
  CO-1 - 1230 cm⁻¹
  OH bending 1400-1300

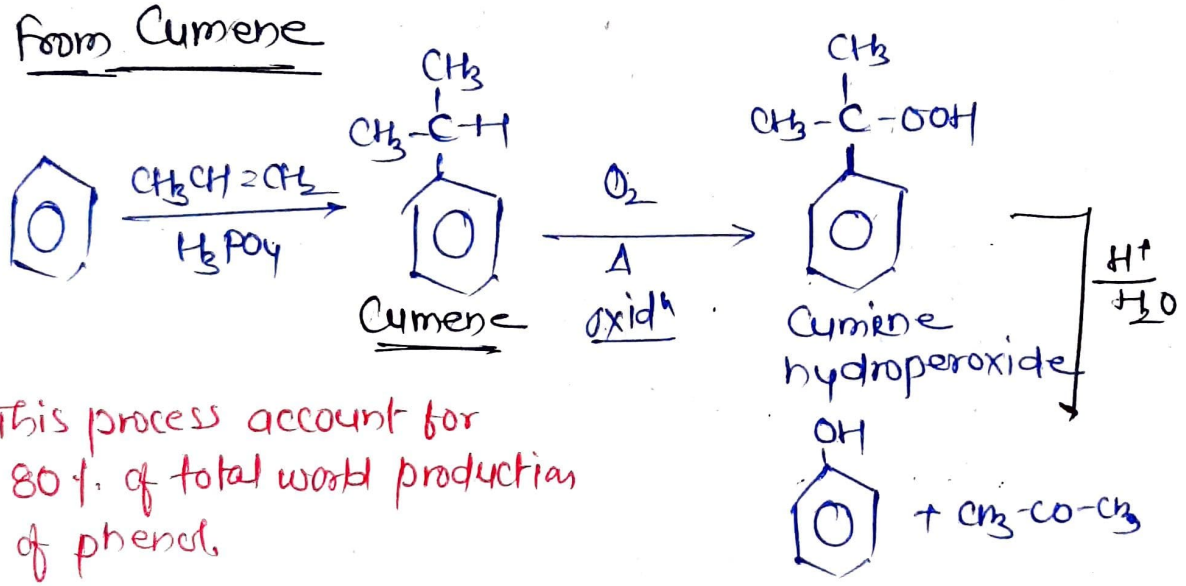
PREPARATION METHOD –

① From Chlorobenzene (Dow Process)



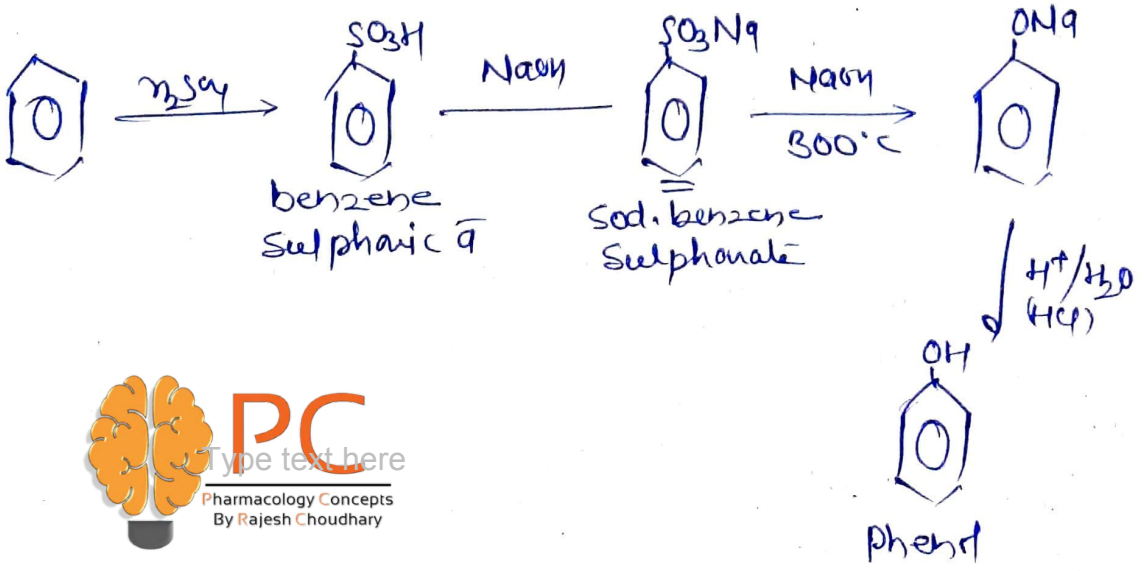
- First introduced in 1928 by Dow Chemical Company of USA.

② From Cumene

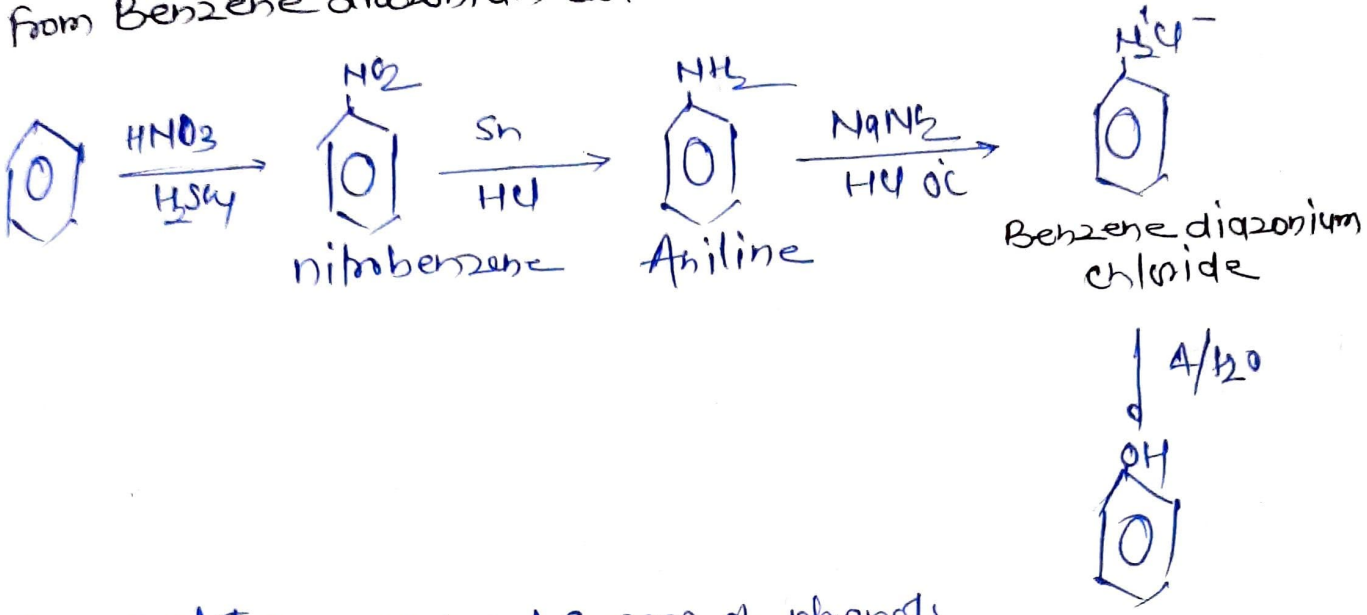


This process account for 80% of total world production of phenol.

③ From Sodium Benzene sulphonate



(4) From Benzene diazonium Salt



nitrobenzene Aniline

(5) From Coal Tar - Natural Sources of phenols

- Middle oil Fraction (170 - 240°C) of coal tar contain phenol, cresol, & naphthalene

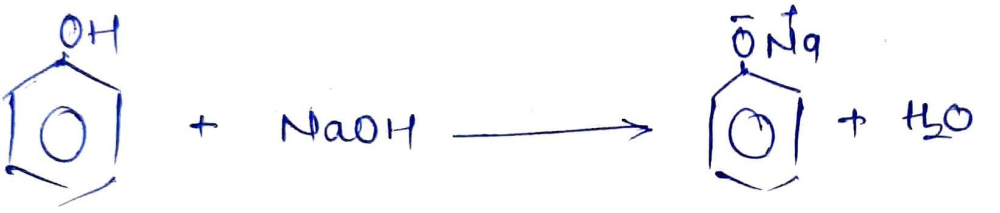
CHEMICAL REACTION OF PHENOL

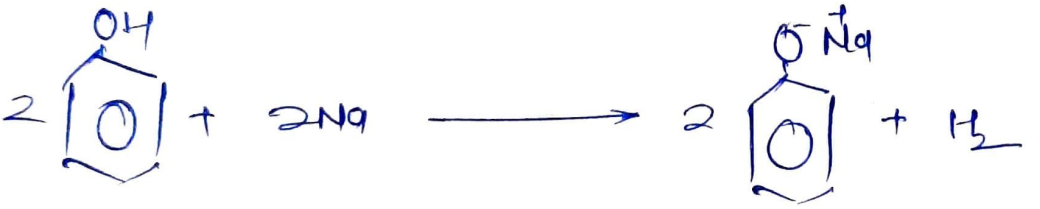
→ Reactn of -OH group
→ Reactn of Benzene ring

(A) Reaction of -OH group

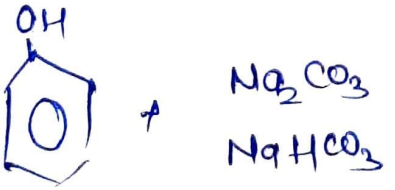
(1) formation of Sod. Salt

- Phenol is acidic in nature, it reacts with Sodium metal & NaOH to form. Salt



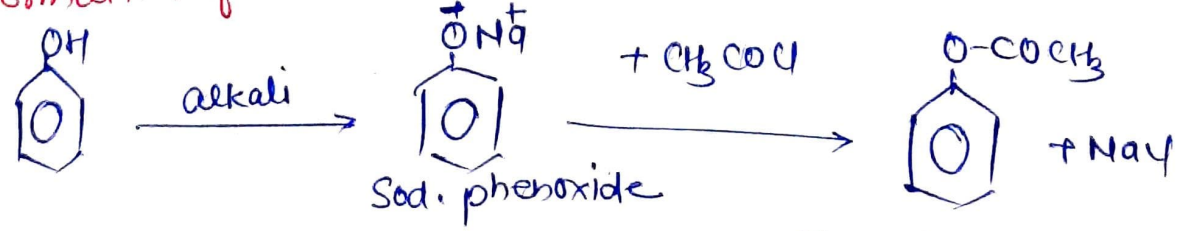


* but Phenol is weaker acid than carboxylic ā, so doesn't react with Sod. Carbonate & Sod. bicarbonate

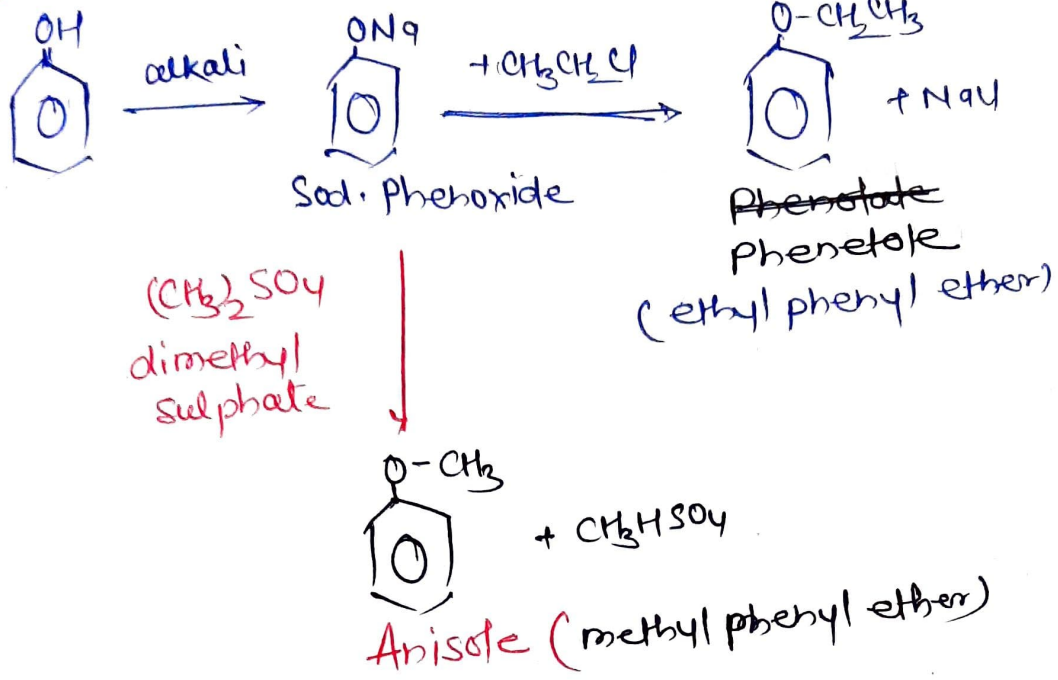


(2) Reactn with $FeCl_3$ → give purple colour due to formation of complex.

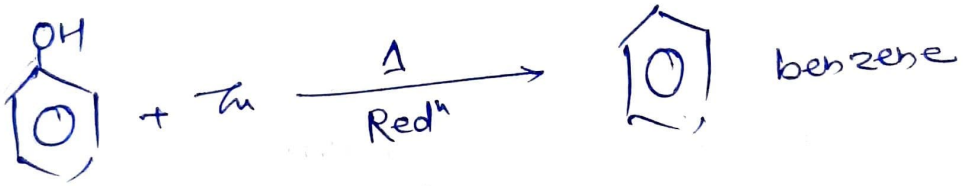
(3) Formation of ester



④ Formation of Ether

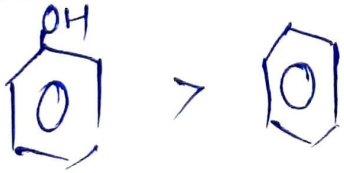


⑤ Reacts with Zinc dust

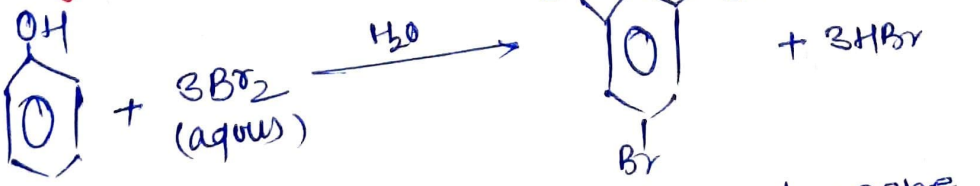


B. Reaction of Benzene ring

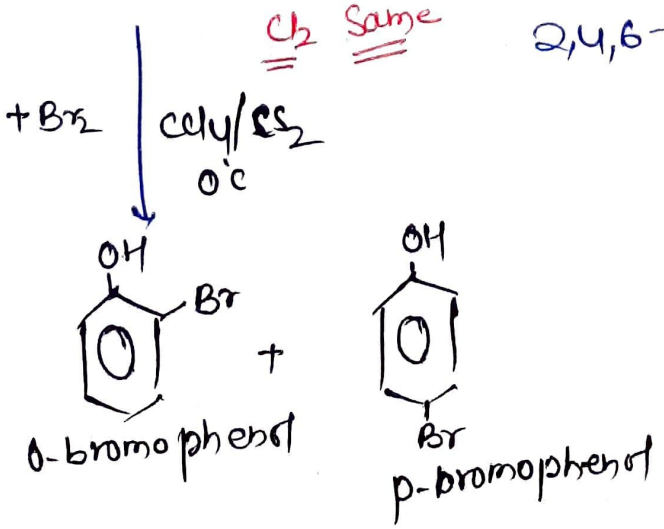
ESR



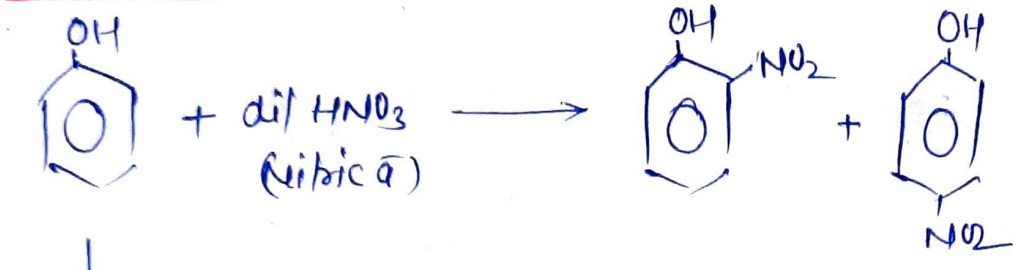
① Halogination



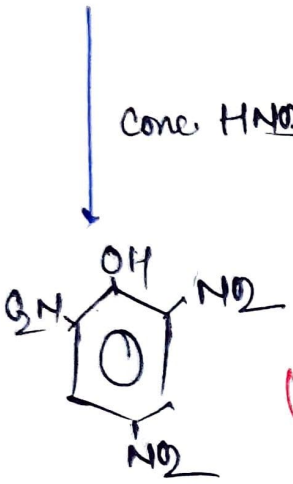
Cl_2 Same



② Nitration

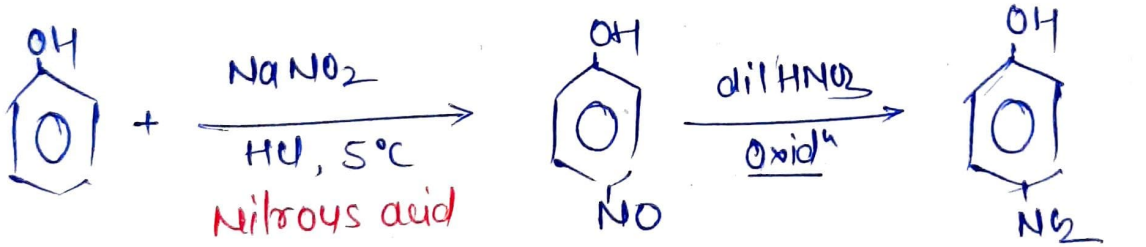


O & p-nitrophenol

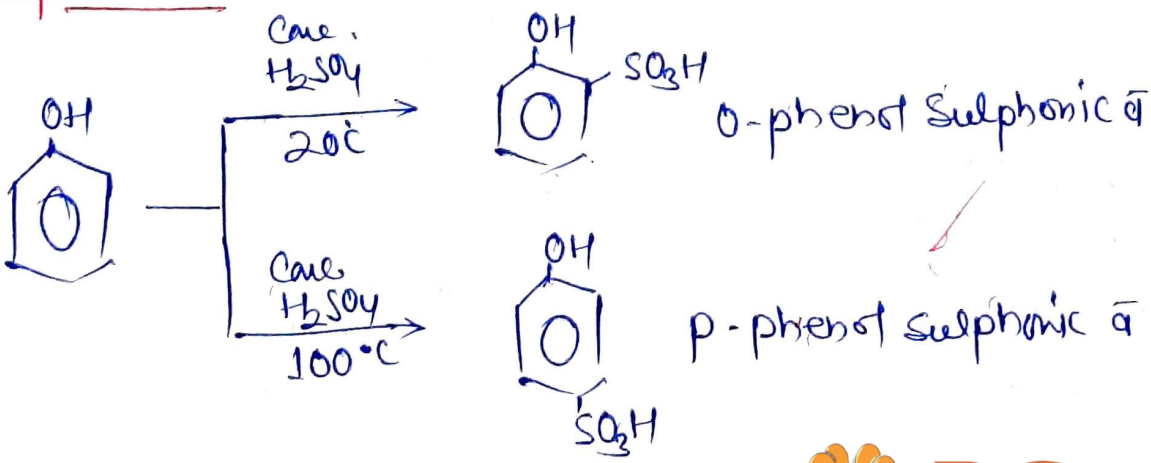


Picric acid
(2,4,6-Trinitrophenol)

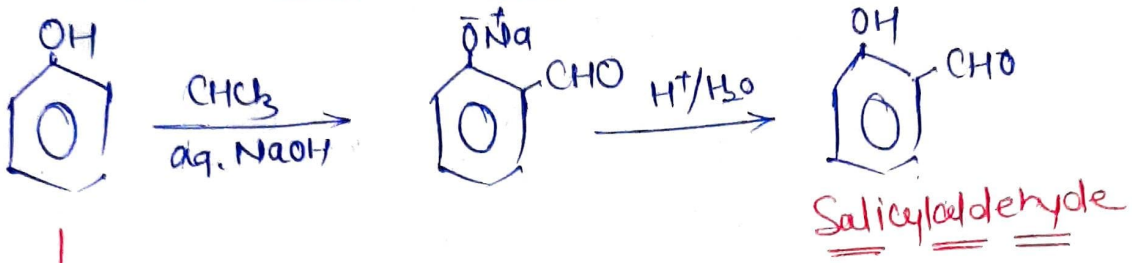
③ Nitrosation



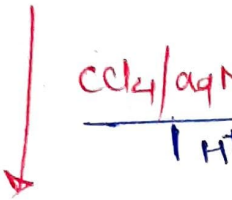
④ Sulphonation

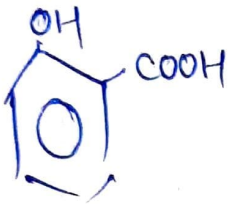


⑤ Reimer-Tiemann Reaction



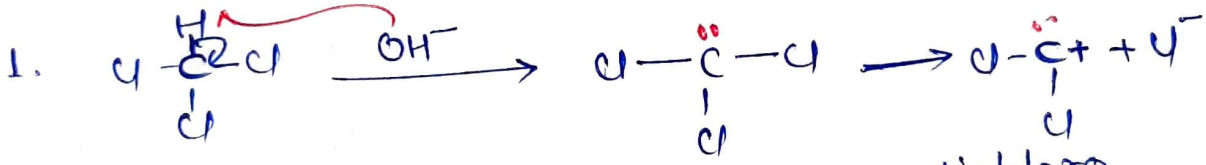
Salicylaldehyde



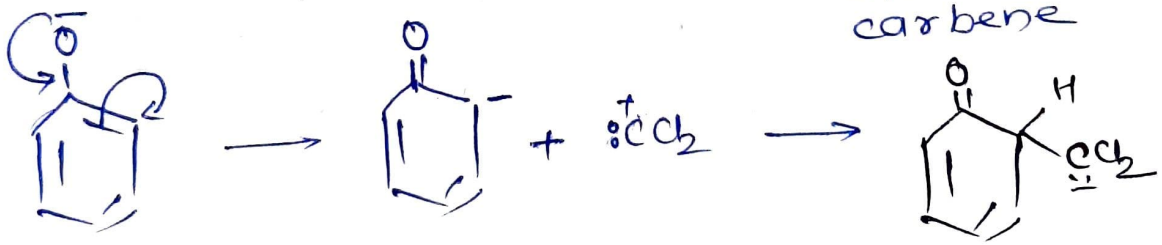


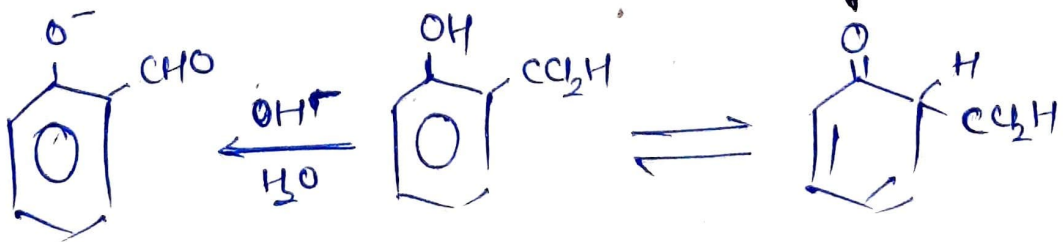
Salicylic acid

Mechanism :→

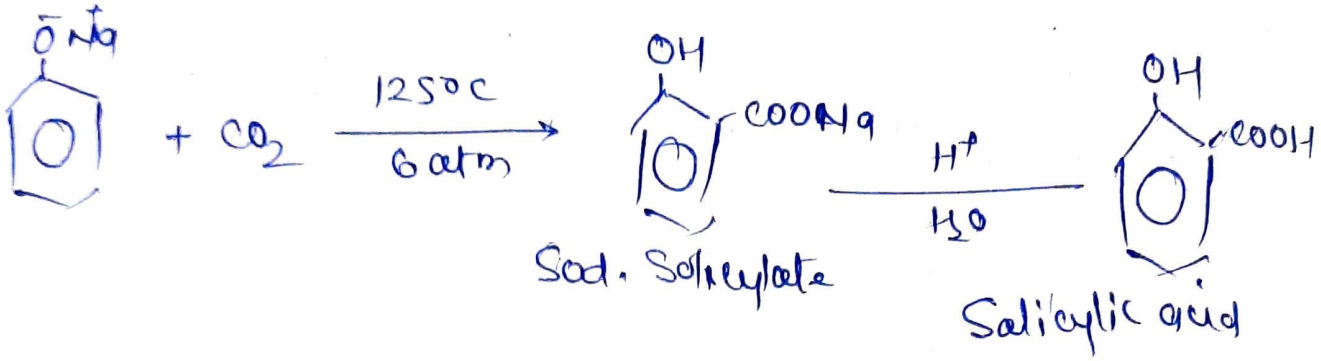
1. 

dichloro carbene

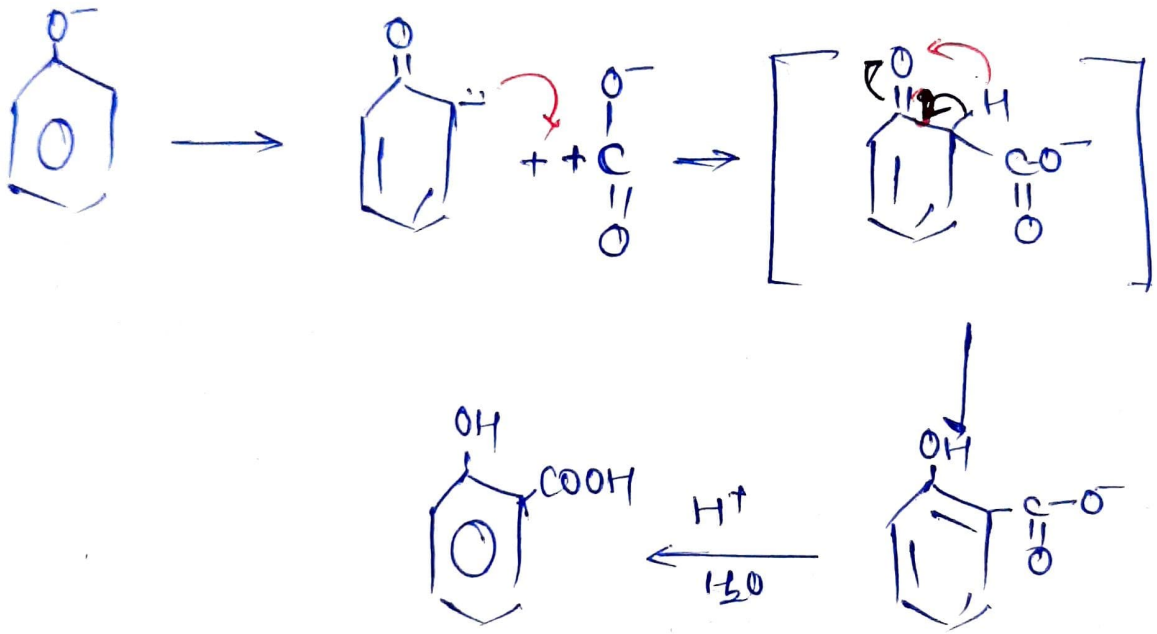
② 



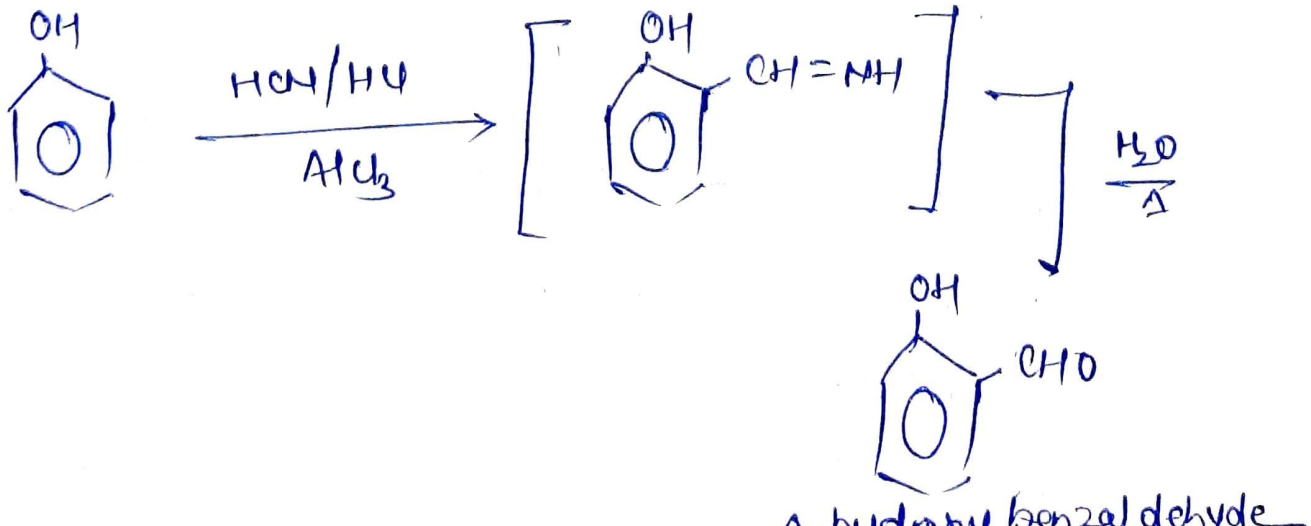
⑥ Kolbe Reaction — ~~Salty~~ Salicylic a



Mechanism -

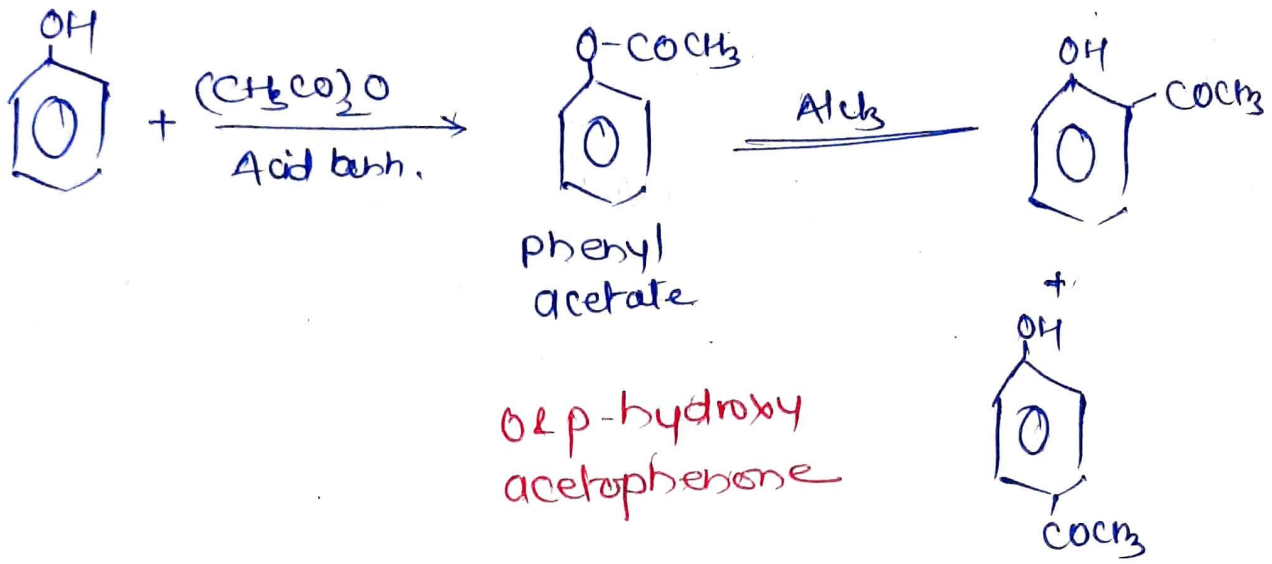


⑦ Gatterman Reaction — Salicylaldehyde Formed



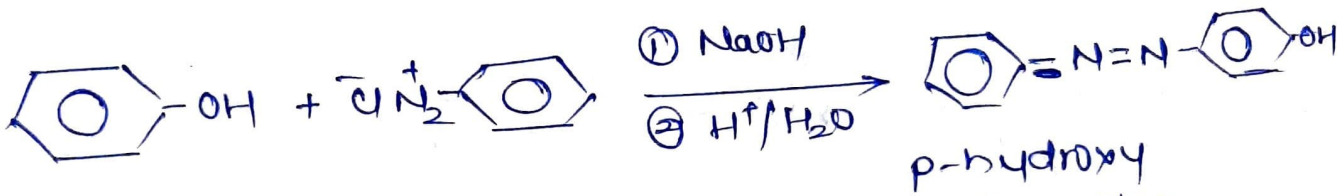
o-hydroxy benzaldehyde

8. Fries Rearrangement



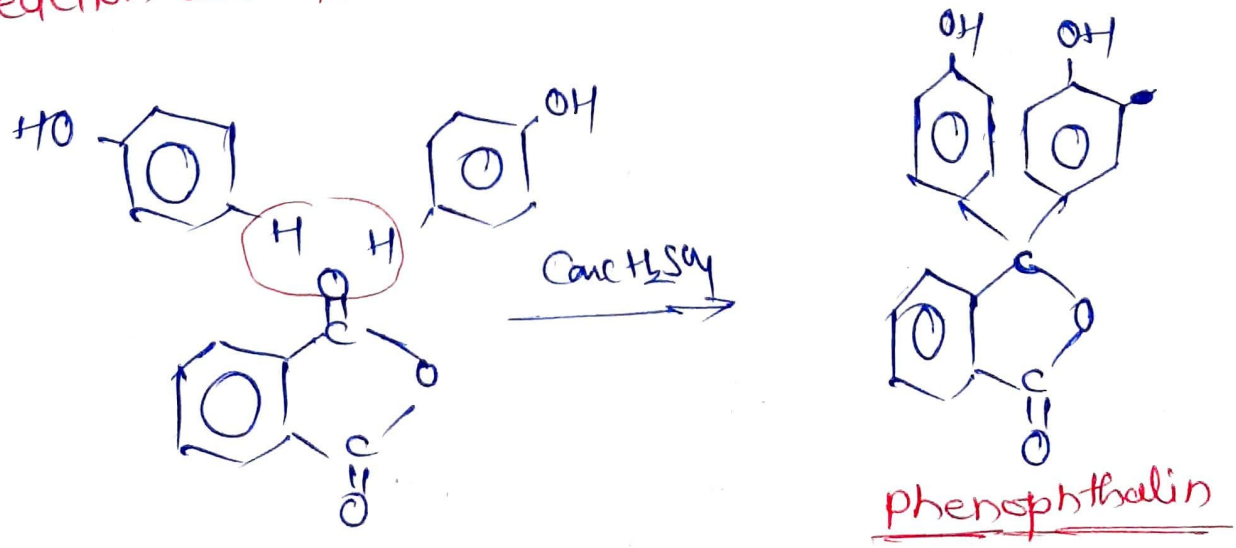
o & p-hydroxy acetophenone

(9) Reaction with Benzadiazonium chloride



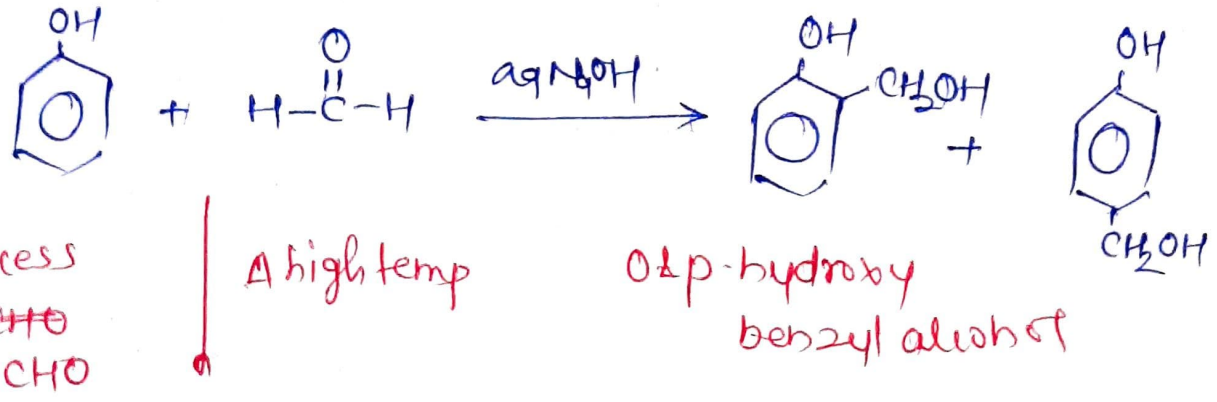
p-hydroxy azobenzene (dye)

10) Reaction with Phthalic Anhydride



Phenolphthalin

(11) Reactn with formaldehyde



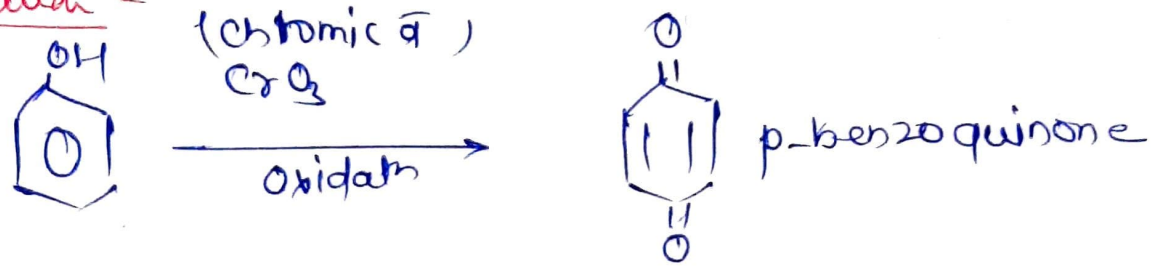
excess HCHO

Δ high temp

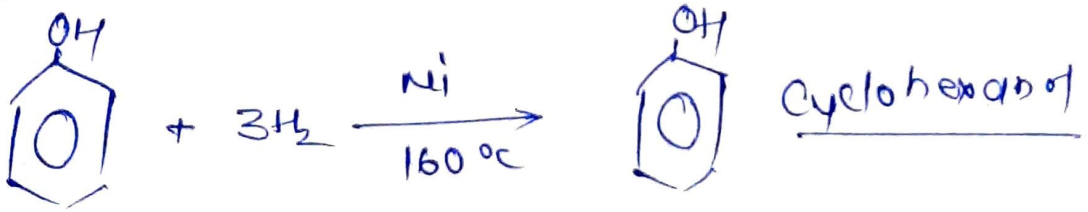
o & p-hydroxy benzyl alcohol

Hard thermosetting Plastic, Bakelite

(12) Oxidation –



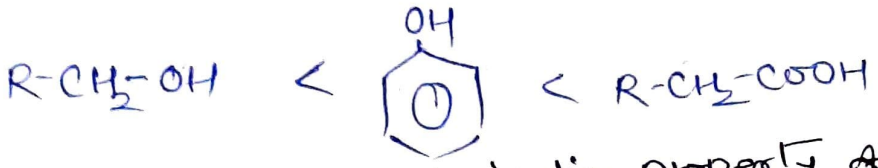
(13) Hydrogination



Uses –

(1) Bakelite
(2) formatn of Salol, Aspirin, Detol
(3) dyes - phenolphthalein
(4) Explosives – picric acid
(5) wood preservative, herbicide, nylon, Antiseptic etc.

ACIDITY OF PHENOLS



Acidity is depends upon ionization property of compound in aqous solution. (H^+ donating property)

Described by Acidity constant

$$Ka = \frac{[RCOO^-][H_3O^+]}{RCOOH}$$

↓

describe the relative strength

* Alq. alcohol

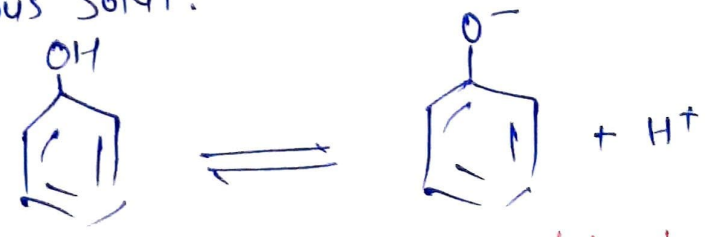
$HOH > R-OH > R_2CH-OH > R_3C-OH$ = less acidic

Strong acids will have higher numerical value of Acidity constant

Order of Acidity Constant -

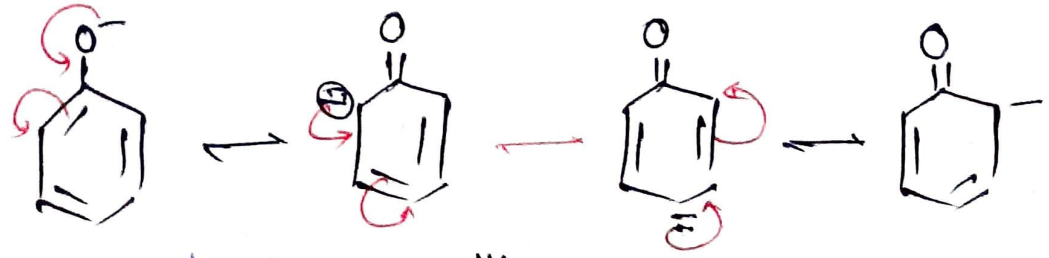
		Ka (approx)
Phenol	Ar-OH	10^{-19}
Alcohol	R-OH	10^{-18}
Carboxylic a.	R-COOH	10^{-5}
Carbonic a.	H_2CO_3	10^{-7}

Phenols are acidic due to formation of stable phenoxide ion in aqous solut^n.

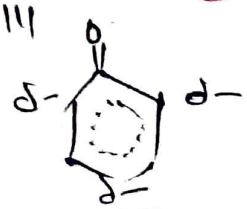


Phenol — Phenoxide ion

Phenoxide ion is stable due to resonance



↳ delocalized -ve ion

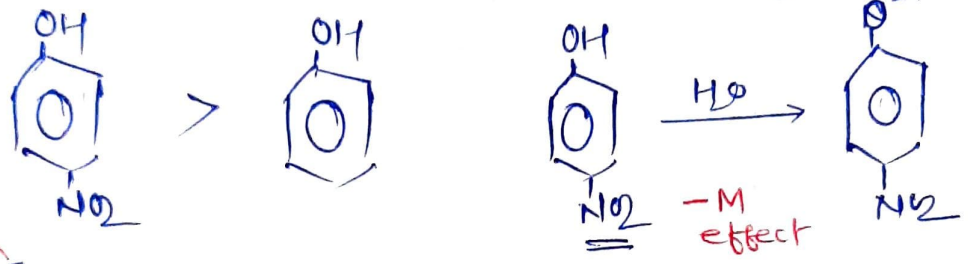


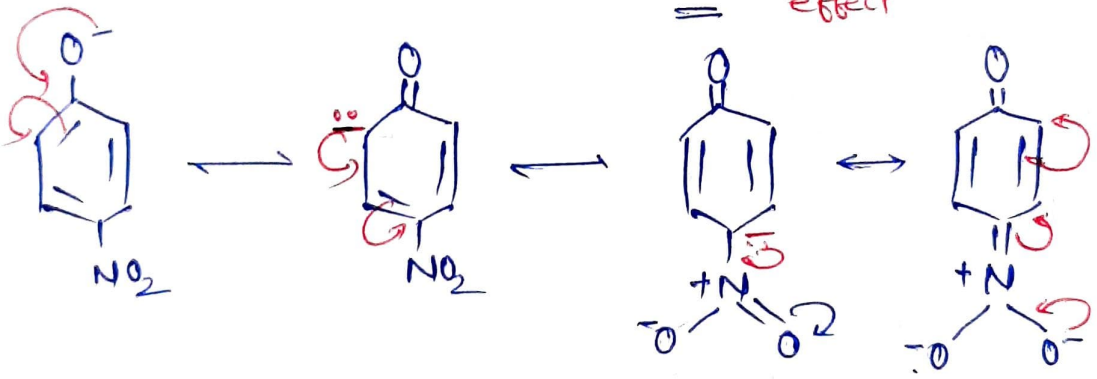
* but No Resonance is possible in alkoxide ion (RO^-) derived from alcohol (it has localized -ve el)

Effects of Substituents on Acidity

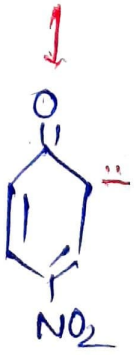
① Electron (el^-) withdrawing Substituents – (–Cl, –CN, ~~–COOH~~, NO_2, –CHO, –COOH) ⇒ ↑ the strengthening of aromatic ring acidity due to ~~↑ el density~~ it enables ~~to~~ the ring to withdraw more el^- from phenoxy oxygen.

eg.





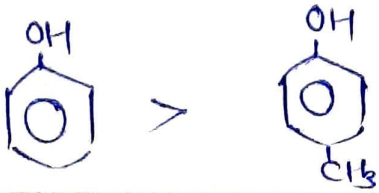
Resonance forms of p-nitrophenoxide ion



② Effect of Electron-Releasing Substituents

– ($-CH_3$, $-CH_2$, $-OCH_3$, $-NH_2$) Electron releasing group on the aromatic ring is acid weakening. It strengthens the negative (-ve) charged on phenoxide ion and inhibits the charge delocalization due to Resonance

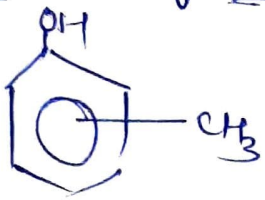
This destabilises the phenoxide ion & result in a weaker acid.



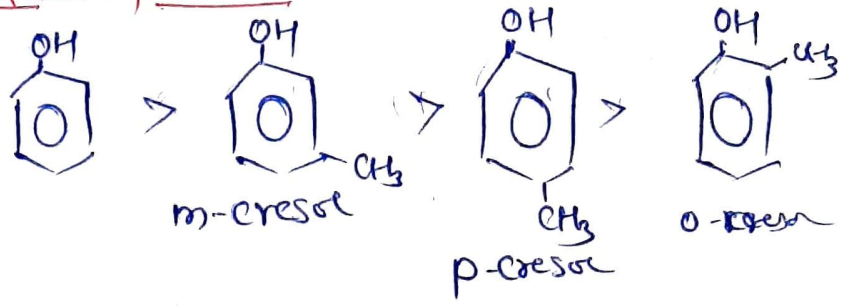
p-cresol

In Case of cresol - +Inductive effect by $-CH_3$

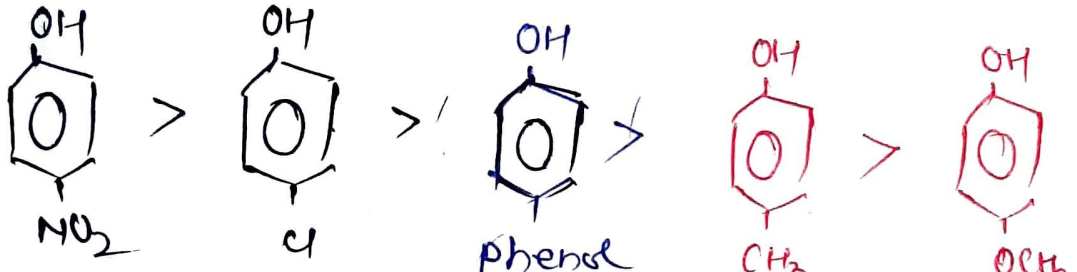
- ↑ -ve charge in phenoxide ion



Acidity order

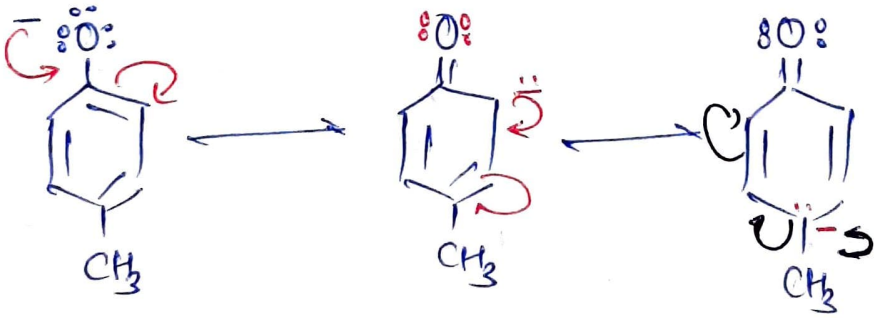


Acidic order



pKa = 7.2 | 9.2 | 10 | 10.26 | 10.27

Resonance Effect



Negative charge next to an e^- doner is Bad.

QUALITATIVE ~~QUANTITATIVE~~ TEST FOR PHENOL

① Iron(III) chloride ($FeCl_3$) test

$$Ar\text{-}OH + FeCl_3 \longrightarrow Fe(OAr)_3 + 3HCl$$

purple colour complex

↳ A red, blue, green, or purple coloured observed.

② Pyridine Test for water-insoluble phenol

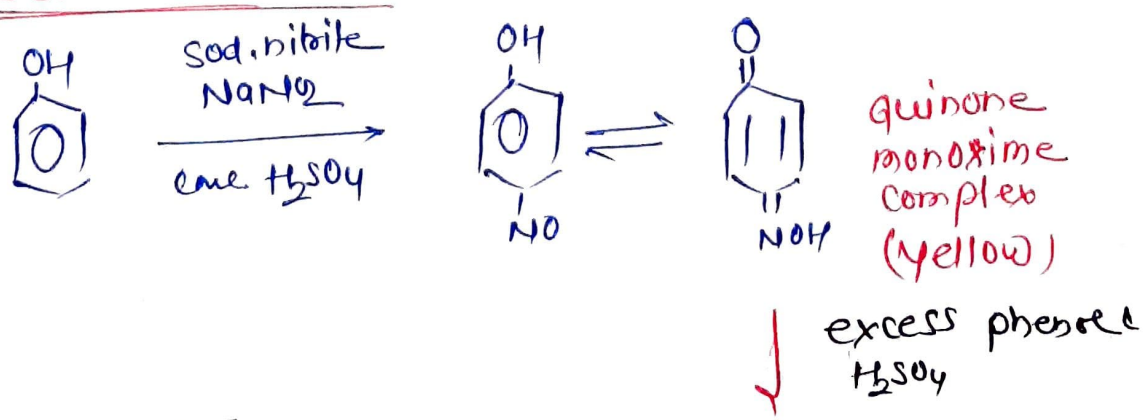
By addⁿ of pyridine & stirring will produce a color if phenol or enols are present

⇒ with $FeCl_3$

Phenol, Resorcinol, o/p-cresol	-	violet & Blue colour complex
Catechol	-	Green
Hydroquinone	-	violet / Transient blue col
Pyrogallol	-	Blue rapidly changing to Red.

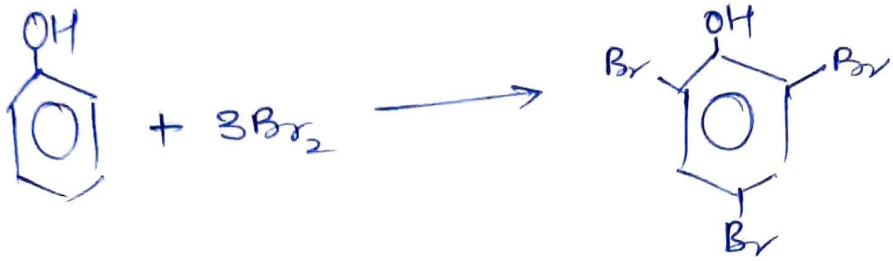
③ Litmus test - ~~Red~~ Litmus paper turn ~~blue~~ Red / Blue

④ Libermann's test :-



⑤ Bromine Water Test

Phenol + Br_2 water (brown colour) → Tribromophenol (white ppt)

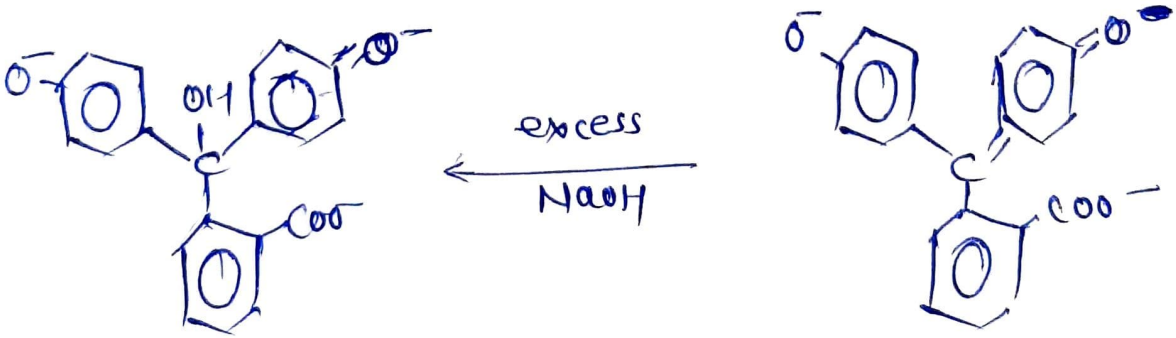


⑥ Phthalein Dye Test

Phenol + phthalic acid → Phenolphthalein (colourless)

NaOH

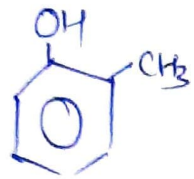
Pink



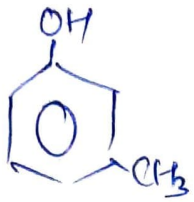
excess NaOH

Colourless

CRESOL



O-cresol



m-cresol

p-cresol

⇒ Hydroxy toluene

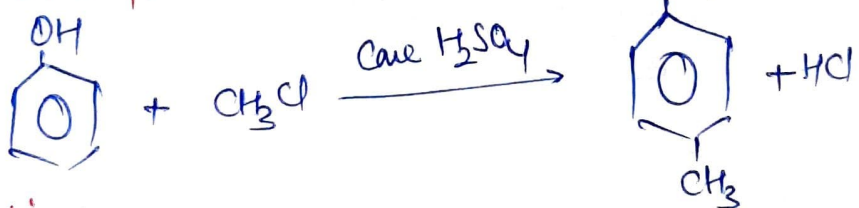
⇒ MF : C_7H_8O

⇒ MW = 108.14 g/mol

⇒ IUPAC Name 2/3/4-methyl phenol
2/3/4-hydroxy toluene

Preparation

① By methyl chloride



Properties :-

⇒ Colourless crystal / Thicker liquid / greasy looking solid

⇒ Soluble in strongly alkaline water

2) BP = 191 °C

2) MP = 29.8°C / 11.8°C

USES :-

① Mixture of cresol used as disinfectants, preservatives, & wood preservative

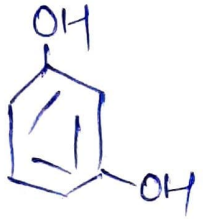
② O-cresol used as a solvent, disinfectant, & chemical intermediate

③ m-cresol is used to produce certain herbicide, & products of antioxidants.

④ p-cresol is used largely in the formation of antioxidants & in the fragrance & dye industries.

RESORCINOLS

= It is also known as Resorcin

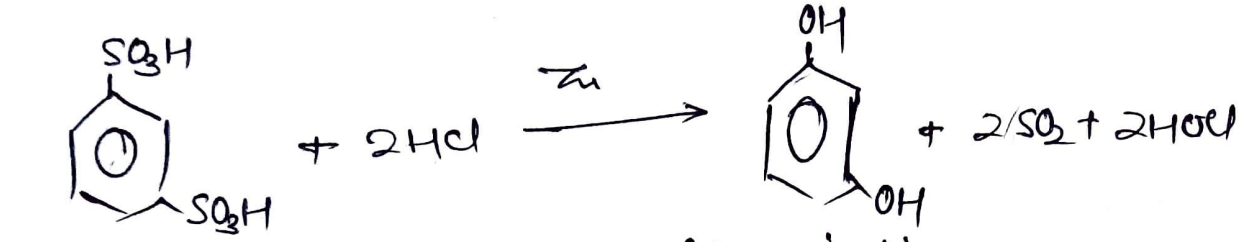


: Benzene-diol

: MF : $C_6H_6O_2$

: MW : 110 g/mol

: IUPAC : 1,3-benzenediol



Benzene-meta-disulfonic acid

(Resorcinol)

Property -

2) white solid, turn pink on exposure to air, light, & iron in appearance

=) mp : 110°C, BP : 277 °C

=) Faint in odour

=) Soluble in water & organic compound.

Use -

(1) used as Antiseptic & disinfectant

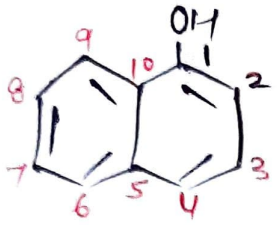
(2) used in treatment of gastric ulcer

(3) used in treat external Vaginal itching & irritation

(4) used in the product of diazo dyes & plasticizer as a UV absorber in resin

(5) used as analytical reagents.

Naphthol



1-Naphthol

2-naphthol, β-naphthol

→ Naphthalene-1-ol

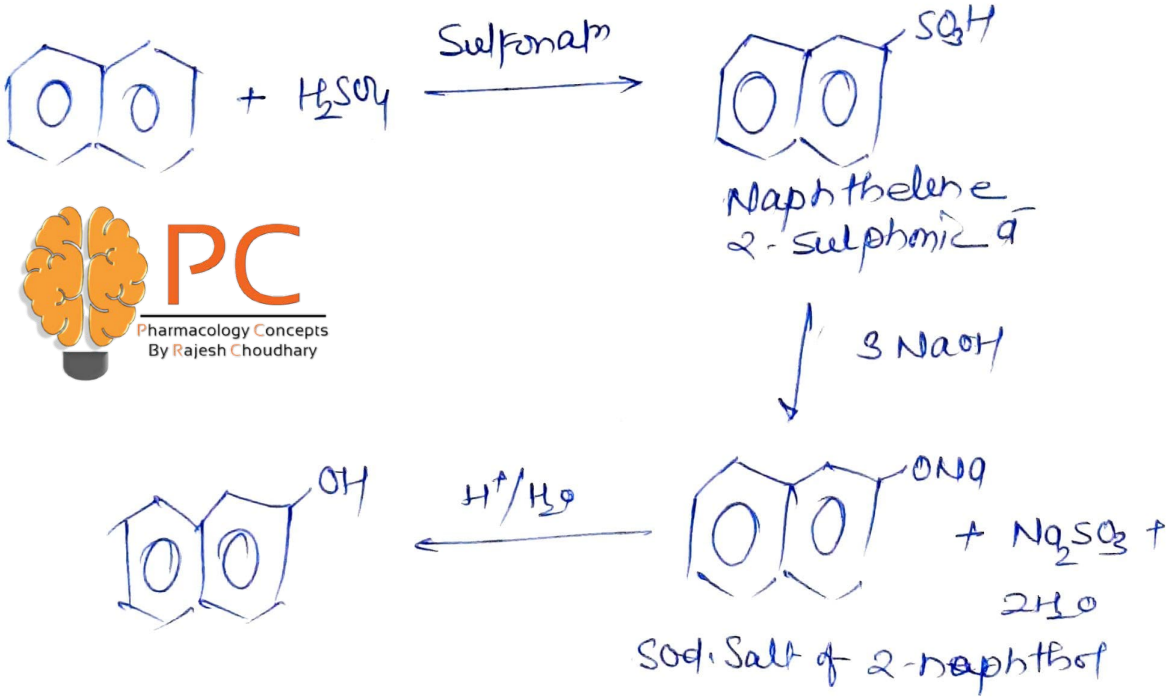
naphthalene-2-ol

=) Naphthalene homologous of phenol

2) MF: $C_{10}H_8O$

2 MW = 144.17 g/mol

= Two isomer 2 & 1-naphthol



PC
Pharmacology Concepts
By Rajesh Choudhary

Properties –

1. Colourless or white solid / crystal
2. MP: 95 – 96 °C (α-naphthol)
3. BP: 278-280 °C
4. Sn soluble in water & soluble in organic compound.

Uses –

1. used as biomarker for livestock & human exposed to polycyclic aromatic hydrocarbon
2. For Molish reagent, & variety of test
3. Synthetic precursor to insecticide, drug (Nadolol)
4. Preparation of azo dyes.