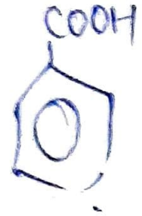
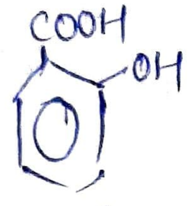
AROMATIC ACID

- → Synthesis
- → Chemical Reaction
- → Uses
- → Acidity, effects of Substituents

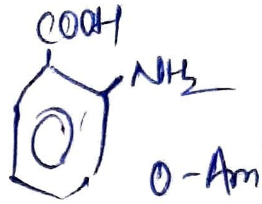
Aromatic acids are compound in which one or more carboxylic acid (-COOH) are attached directly to aromatic ring



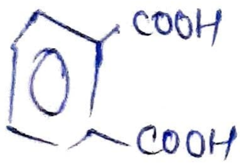
Benzoic acid



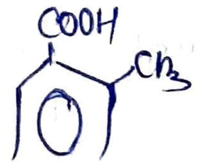
o-hydroxy benzoic acid
(Salicylic acid)



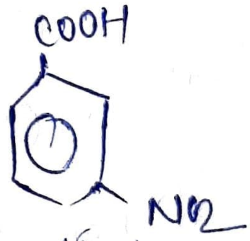
o-Amino benzoic acid
(Anthranilic acid)



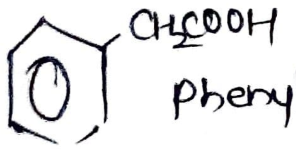
Phthalic acid



o-toluic acid



m-nitro benzoic acid



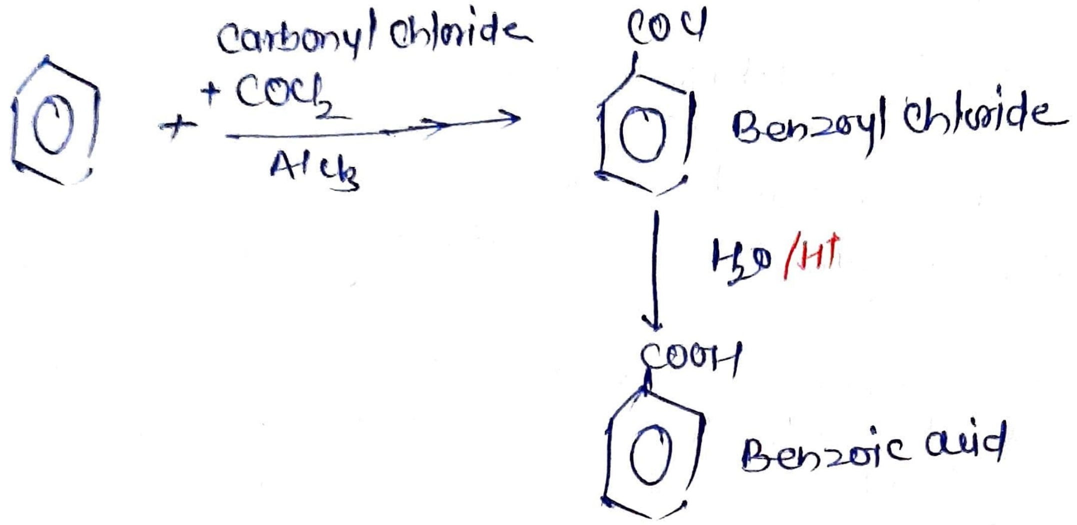
phenylacetic acid - Side chain Aromatic acid

BENZOIC ACID

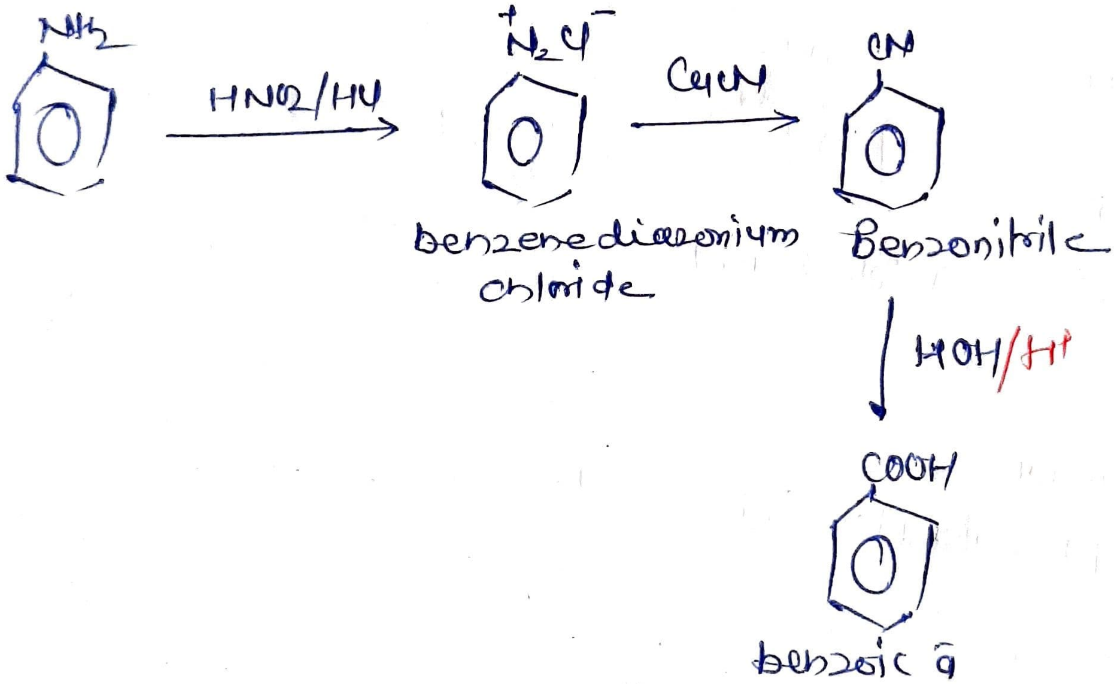
- → $C_7H_6O_2$
- → Colour less solid
- → mp - 122°C
- → Soluble in hot water, ether, ethanol, benzene
- → Acidic ⇒ $C_6H_5COOH > CH_3COOH$
  $K_a = 6.3 \times 10^{-5} > 1.7 \times 10^{-5}$

Preparation Method

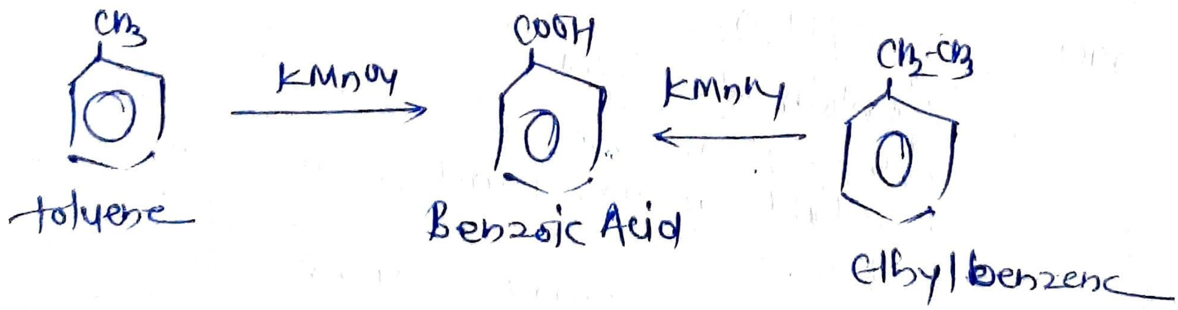
① Friedel-Crafts Reaction :-



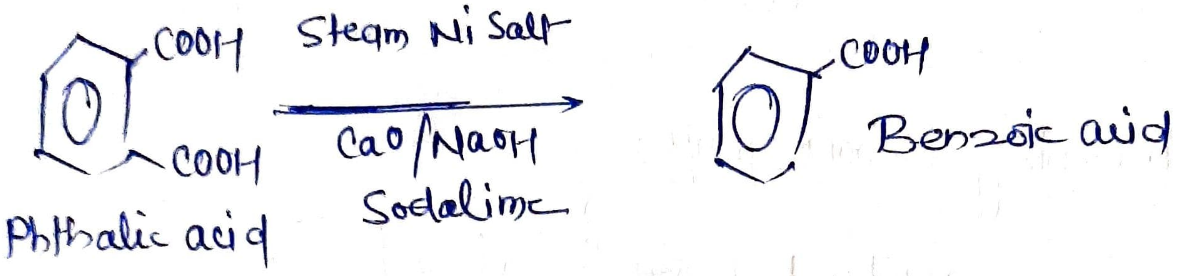
② Sandmayer Reaction



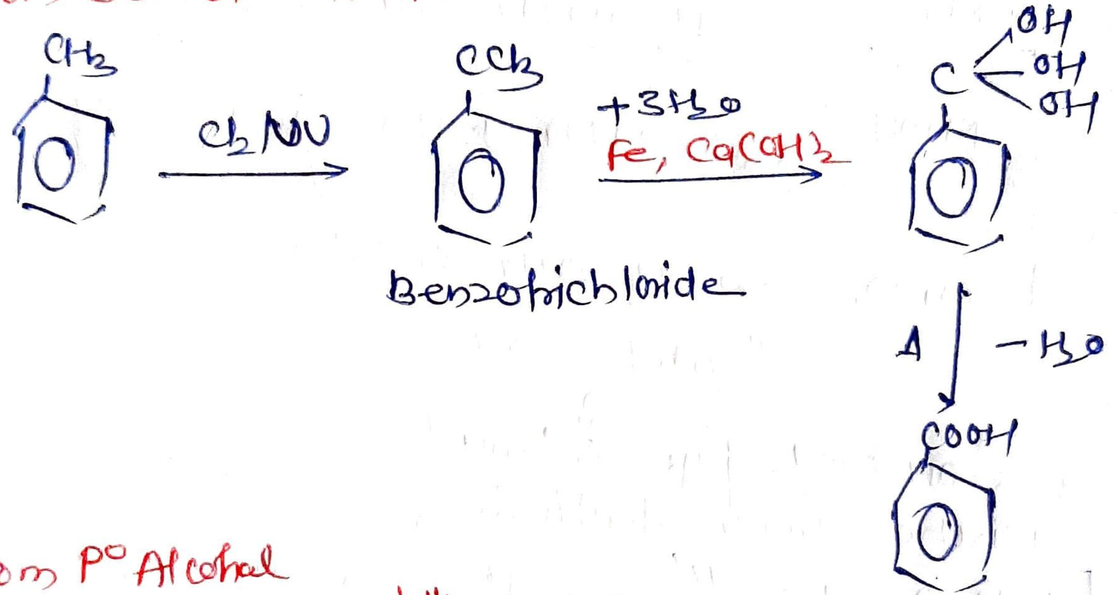
③ Oxidation of alkyl benzene



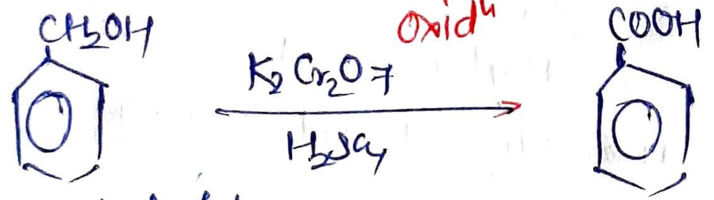
④ From Phthalic acid – by Decarboxylation (partial)



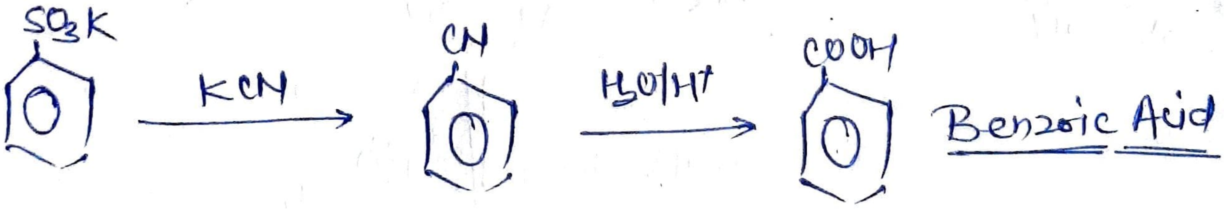
⑤ From Benzotrichloride



⑥ From P° Alcohol

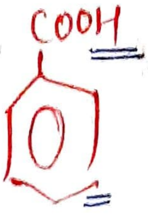


⑦ From Sulphonic Acid (Pot Salt of benzene Sulphonic acid)



⑧

CHEMICAL REACTION



Ⓘ Reactions Involving –COOH group :→

Ⓐ cleavaging of –OH bond $[Ar-\overset{O}{\overset{||}{C}}-O+H]$

①

$\xrightarrow{2Na} 2.C_6H_5COONa + H_2$ Forming Salt.

$\xrightarrow{NaOH} C_6H_5COONa + H_2O$ Neutralizing aromatic ā Δ forming Salt

$Na_2CO_3 \rightarrow 2C_6H_5COONa + CO_2 + H_2O$

"Sod. Benzoate"

Ⓑ cleavage of C–OH bond – $[AR-\overset{O}{\overset{||}{C}}+OH]$

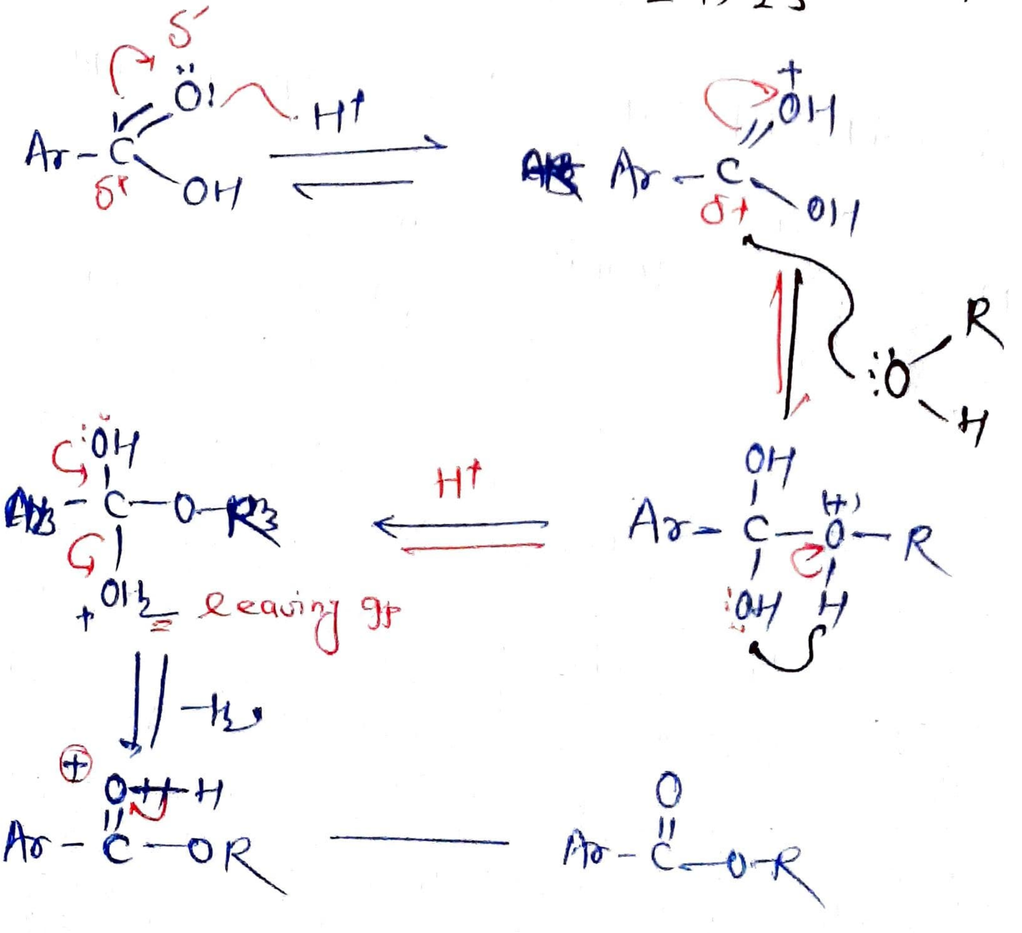
Fischer Speier Esterification

②

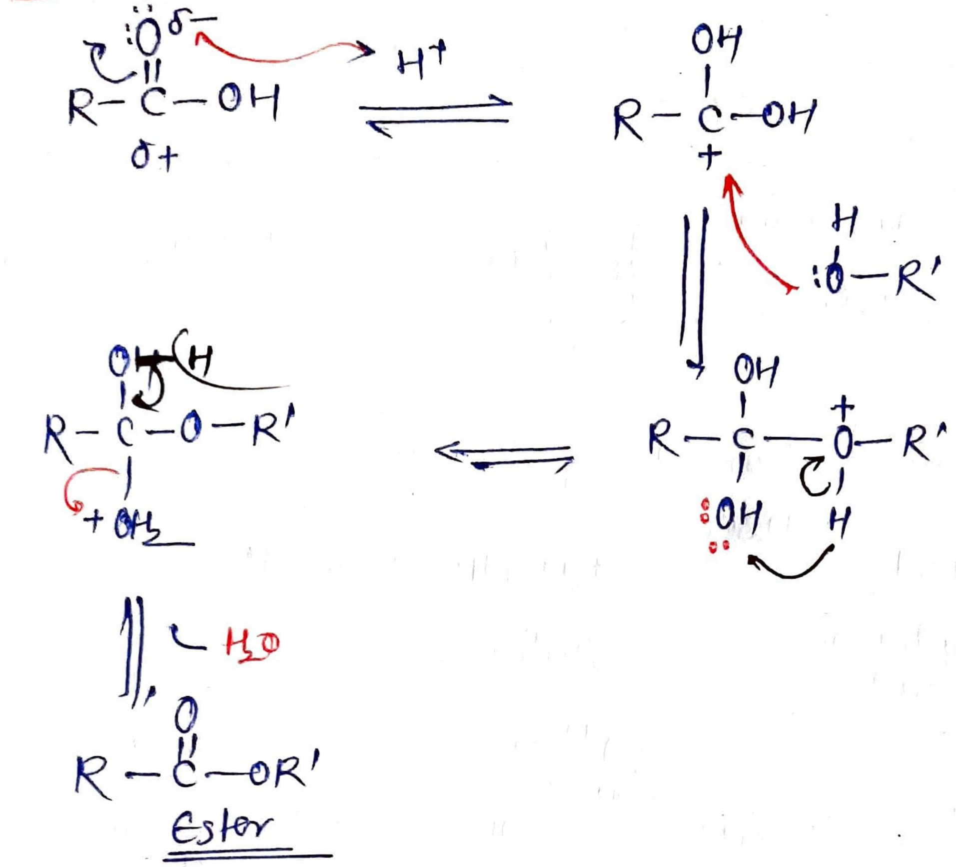
$+ H-O-C_2H_5 \xrightarrow{H^+} C_6H_5-\overset{O}{\overset{||}{C}}-O-C_2H_5$

Ethyl Benzoate

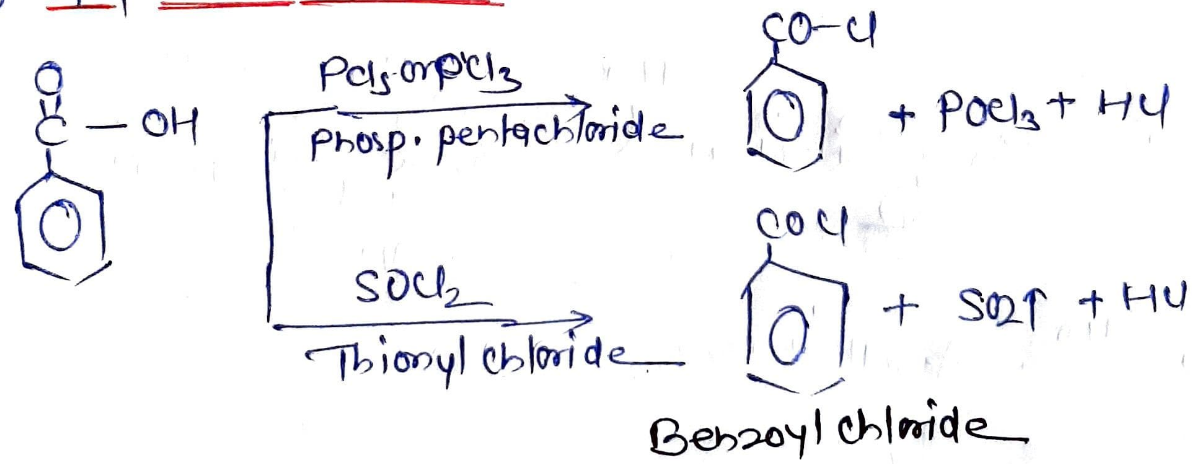
H_2SO_4, P_2O_5 - dehydrating Agent

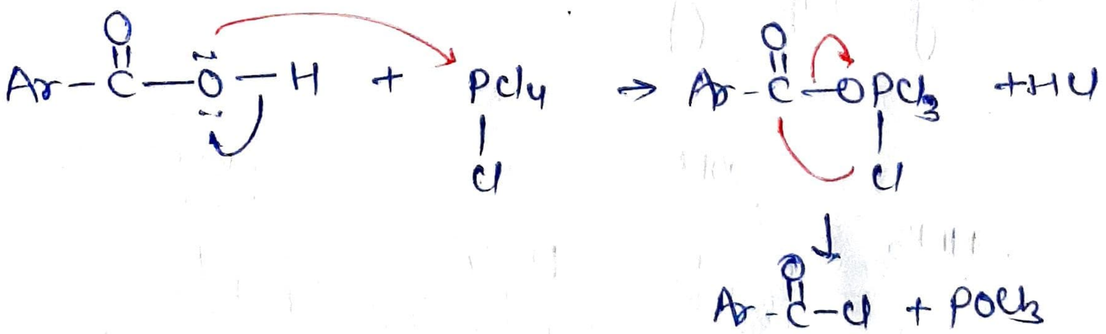


Esterification



③ Acyl Halide Formation





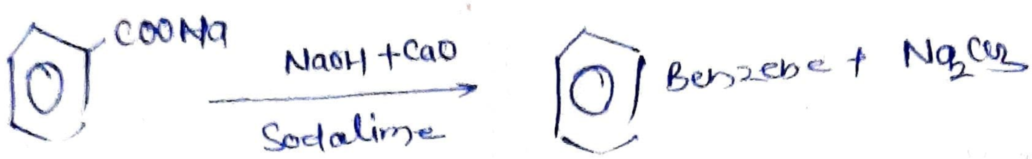
④ Reaction with Amonia

$C_6H_5COOH + NH_3 \longrightarrow C_6H_5COONH_4 \longrightarrow C_6H_5CONH_2 + H_2O$

Ammonium Benzoate Benzamide

© Reaction on -COOH group

⑤ Decarboxylation

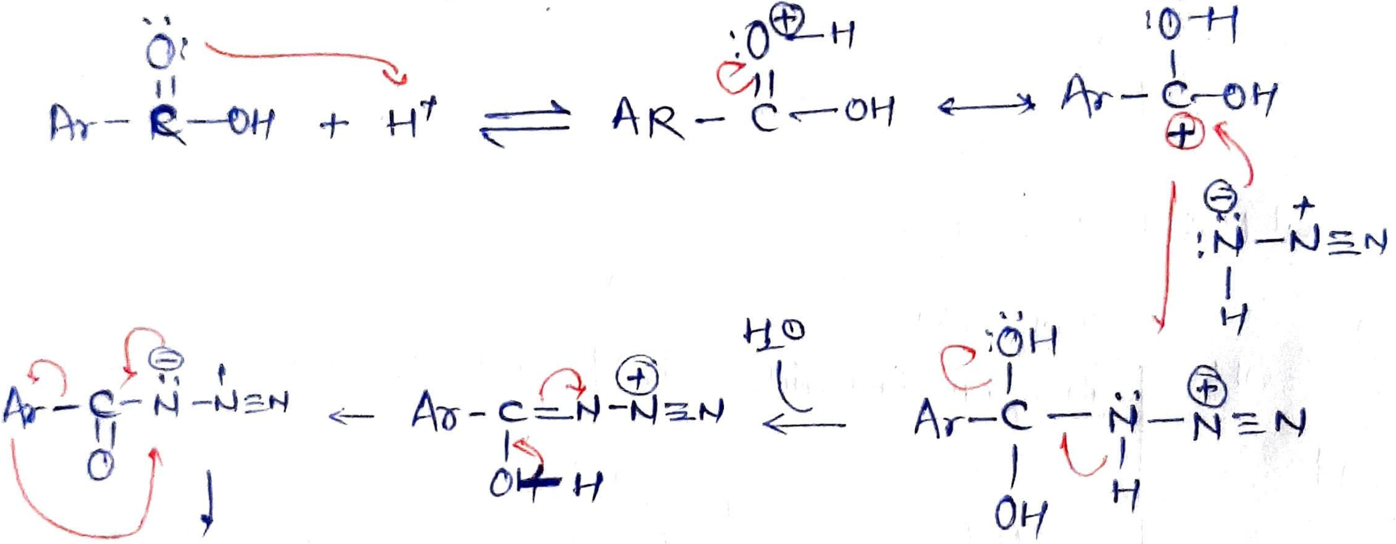


⑥ Schmidt Reaction - Formation of p° amine

$$C_6H_5COOH + HN_3 \xrightarrow{H_2SO_4} C_6H_5NH_2 + CO_2 + N_2$$

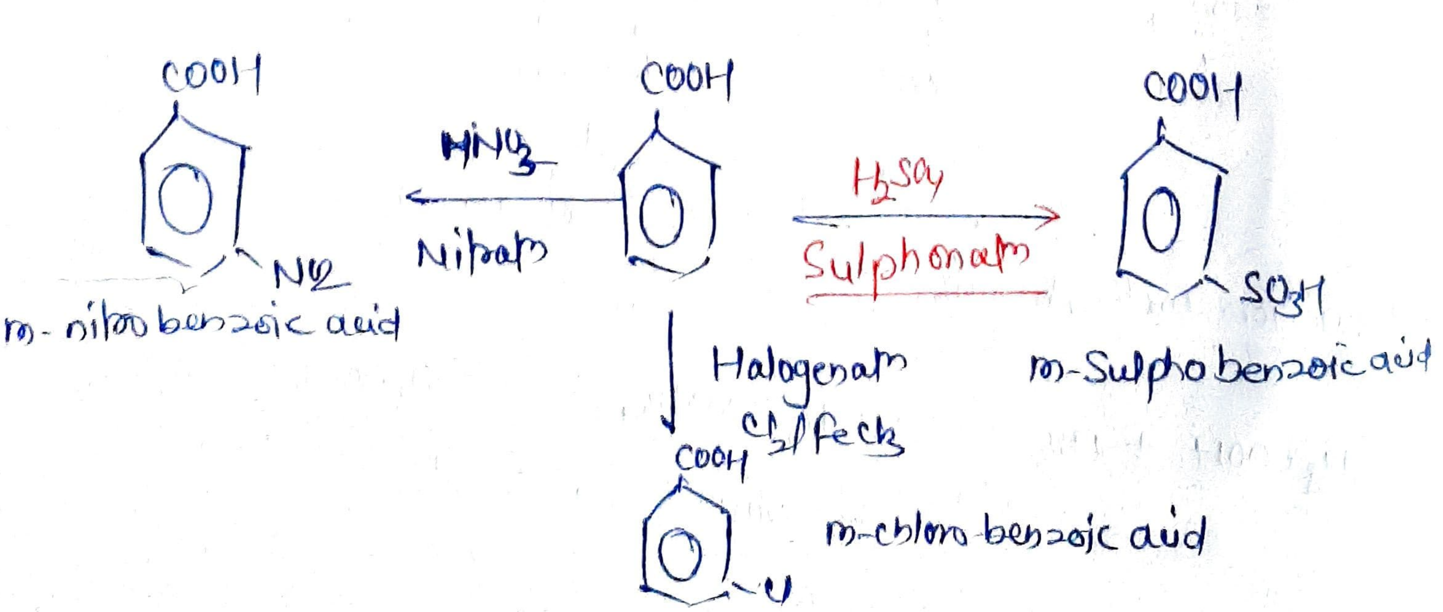
Hydrazoic acid

Aniline



$$Ar-\ddot{N}=C=O \xrightarrow{H_2O} Ar-NH_2 + CO_2\uparrow$$

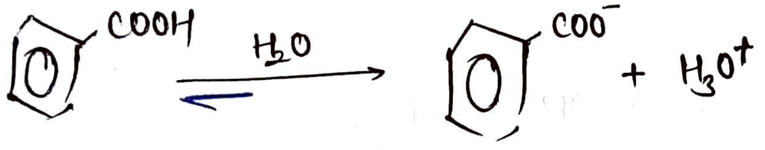
II Reaction Involving - ring - ESR - meta director



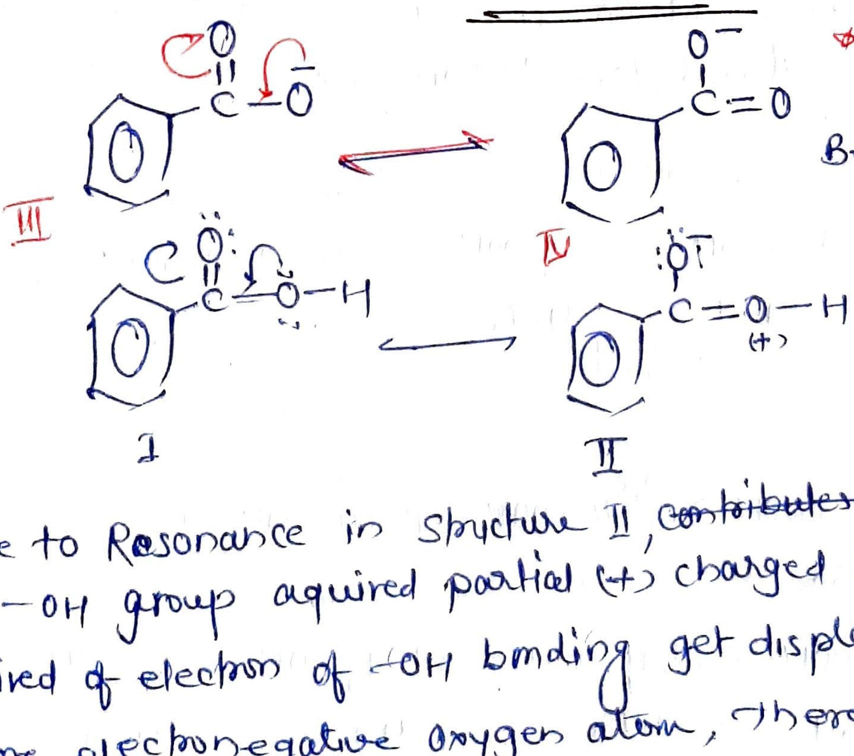
USES – ① various synthetic applicatn
② As Germicide – in medicine for urinary infection & in vapour form for disinfecting bronchial tube
③ As food preservative – Sod. benzoate

ACIDITY OF BENZOIC ACID

H+ releasing comp. in aq. media are Acid. The Aromatic acid ionize in their aq. solutn to give H_3^+O & carboxylate ion



Benzoate ion



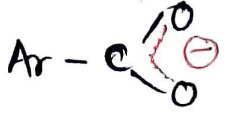
* e⁻ Not delocalized in benzene ring

Benzoate Resonance

aromatic acid Resonance

Due to Resonance in structure II, ~~contributes~~ the oxygen atom of –OH group aquired partial (+) charged hence the shared paired of electron of –OH bonding get displaced towards the more electronegative oxygen atom, therefore the release of H+ proton from the acid & forms carboxylate ion

* The carboxylate ion is much more resonance stabilize than aromatic acid, this is due fact of that structure III & IV are equivelent. Hence greater stability of $C_6H_5COO^-$ ion the equilibrium shift towards forward direction and H_3O^+ ion is released



Ionization of Aromatic Acid

$$Ar-COOH + H_2O \rightleftharpoons Ar-COO^- + H_3O^+$$

hydronium ion

$$Ka = \frac{(ArCOO^-)(H_3O^+)}{(Ar-COOH)}$$

Ka : Dissociation Constant

\# $Ka \propto [H_3O^+]$ Conc - Acidity or pka = -log ka $\propto \frac{1}{acidity}$

\# lower pka value Stronger acid.

- Acidity order

$$Ar-COOH > Ar-OH > ROH$$

pka : 4.19 = 10 17

- (-)charged at phenoxide(O^-) ion is less effectively delocalized over one Oxygen atom & less electronegative carbon atom. hence Carboxylate ion has

$$Ar-COOH > CH_3COOH$$

pka 4.19 4.75

\# (-)charged at $-COO^-$

\# ↓ Strength - ↑ Acidity

- Alephetic acid -

-I Effect

↑ Acidity

$FCH_2-COOH > ClCH_2-COOH > BrCH_2-COOH > ICH_2-COOH > CH_3COOH$

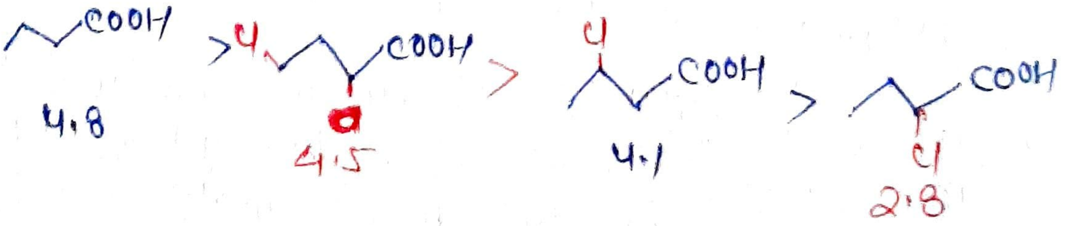
2.66 2.81 2.86 3.15 4.8

$Cl_3C\,COOH > Cl_2CH\,COOH > ClCH_2COOH > CH_3COOH$

0.64 1.48 4.1 4.75

+I effect

↓ Acidity



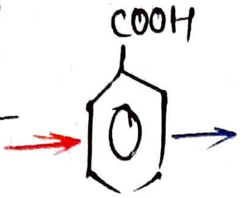
Effects of Substituents

El^- releasing group

$-CH_3, -OH, -NH_2$

$-OCH_3$

↓ Acidity



El^- withdrawing group

$-CN, -NO_2, -CHO, -Cl$

↑ Acidity

Electron Releasing group - decrease the acidity of Aromatic acid, due to destabilize the carboxylate ion relatively to undissociated aromatic acid by intensify (↑) the -ve charged on the carboxylate ion.

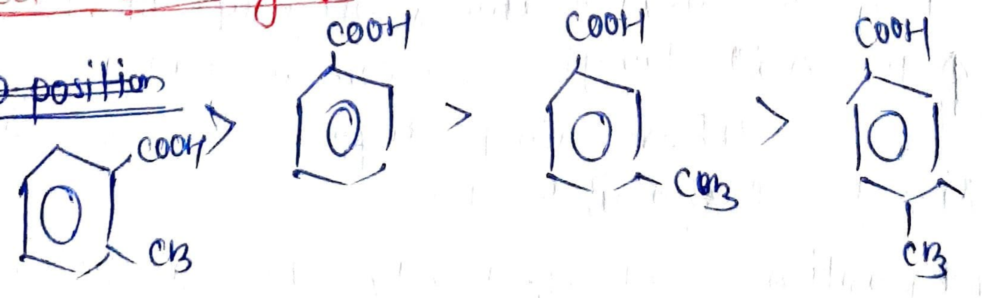
Electron withdrawing group - increase the acidic strength of aromatic acid, due to stabilize the carboxylate ion by dispersing the -ve charged on carboxylate ion.

① **+I Effect** - el^- releasing & inductive effect such as $-R$ $(-CH_3, -CH_2CH_3)$ groups tend to increase the el^- density on the Oxygen atom of $-OH$ group, As result decrease its polarity & make the release of H^+ difficult & ↓ Acid strength.

Such groups have acid weakening effect when present in para & meta position but effect relatively more in meta position

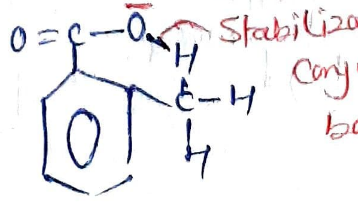
~~Electron Donating group~~ +I

* ~~o-position~~



pKa 3.9 4.2 4.25 4.4

* Ortho position almost always increase the acidity of benzoic acid due to steric inhibition of resonance stability of acid as compared to carboxylate ion



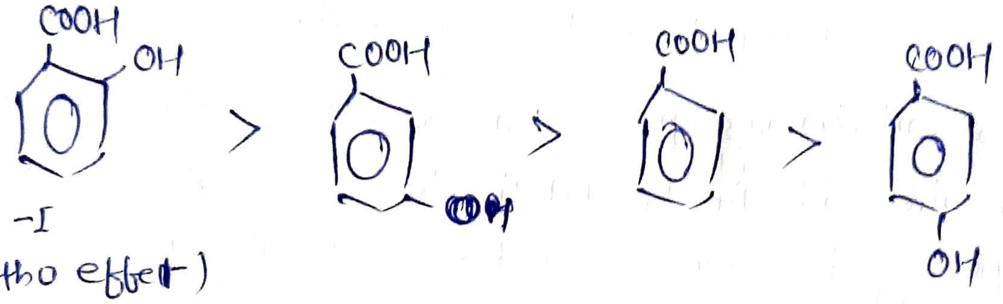
Stabilization of Conjugated base

② +M & -I effect - The group like $-OH$, $-NH_2$, $-OCH_3$, $-Cl$ have e^- releasing mesomeric (+M) effect & e^- withdrawing (-I) effect show different behaviour at o, m, p-position.

At - o & p → e^- releasing mesomeric +M effect is dominant
→ ↓ Acidic strength

o → ortho effect - ↑ Acidity

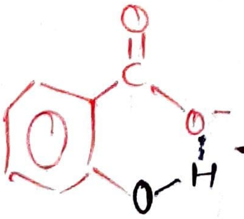
m - -I effect - ↑ Acidity



+M, -I
(ortho effect)

+M

pKa 3. 4.08 4.2 4.6

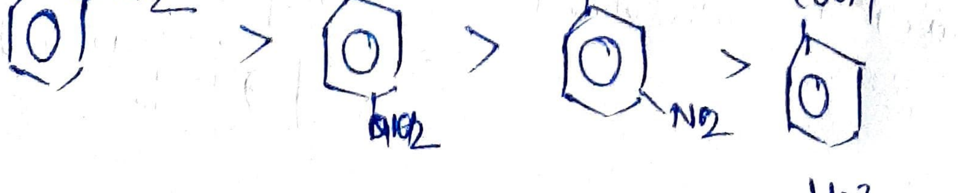


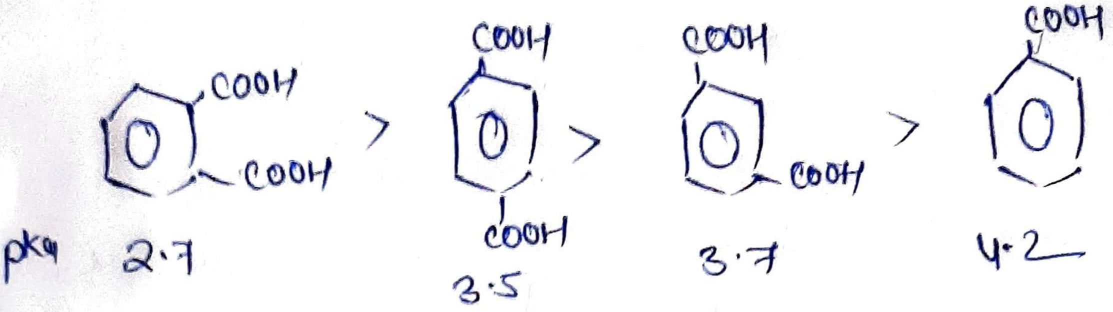
— Stabilize the conjugated carboxylate base
(H-bonding)

③ **-I & -M effect** :- The groups like $-NO_2$, $-CHO$, $-CN$, $-SO_3H$) having polar multiple bonds & withdraw the e^- of the oxygen atm of -OH group due to -M / -I and ↑ the Acid strength of aromatic acid.

These group disperse the -ve charged & stabilize the carboxylate ion.

- M position - -I effect only - less stabilized
- p-position - -M & -I effect - more stabilize
- o-positn - ortho effect





conclusion

#O-position > benzoic acid & other ∵ Strongest

#P-position => withdrawing > BA > Releasing

#m.position = withdrawing > BA

+I (CH_3) < BA

-I (-OH, -Cl) > BA