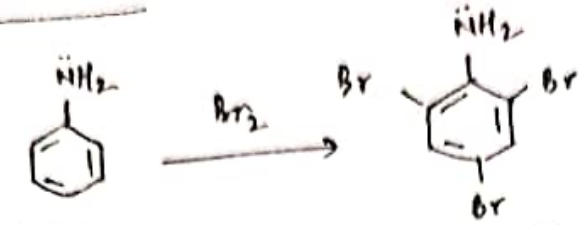
Amines and Diazonium salts

1. The functional group ($-NH_2$) is an "EDG".
2. Amine are o- and p- directing group towards electrophilic substitution rxn.

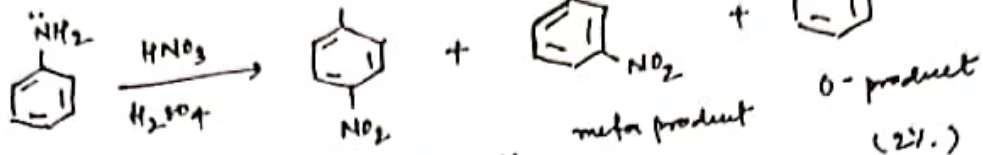
* Halogenation



Aniline

2,4,6 - tribromoaniline.

* Nitration



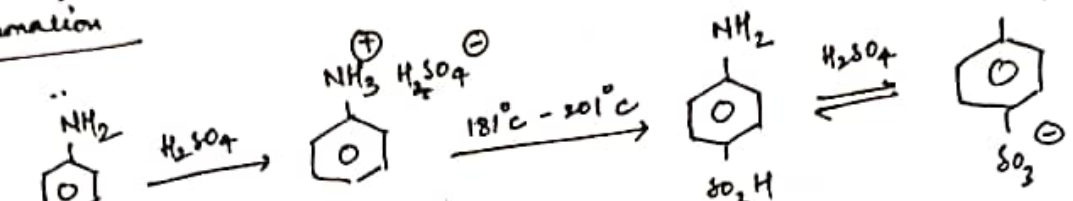
para - product (51%)

meta product (47%)

o - product (2%)

In nitration, meta isomer is also observed. It is because of aniline molecule gets protonated in acidic medium to become anilinium ion which is meta directing.

* Sulphonation

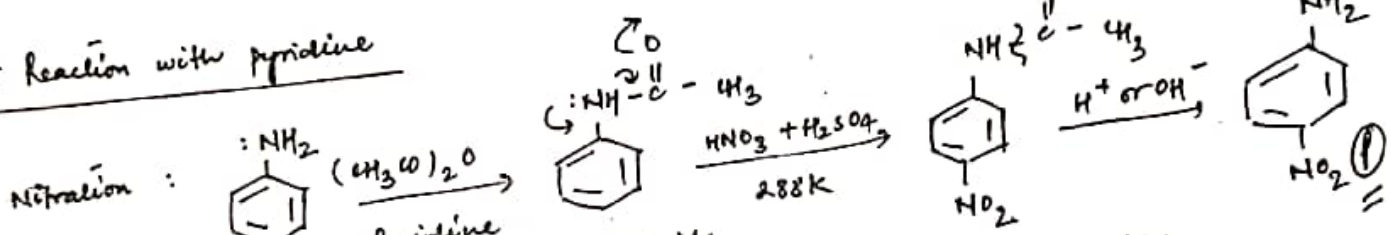


Aniline

Sulphanilic acid

Zwitter ion.

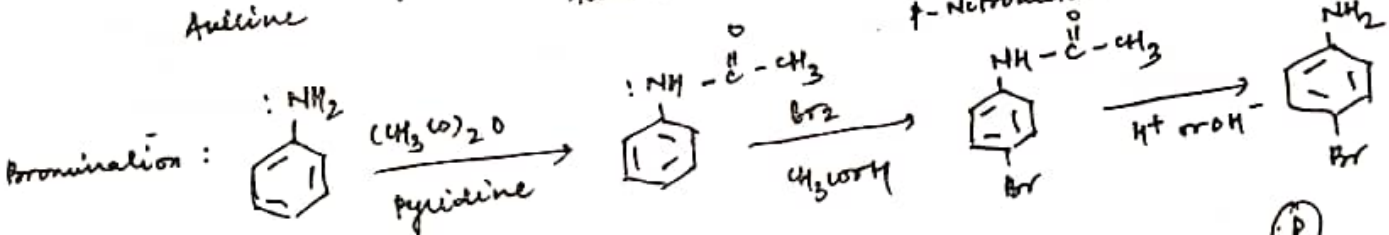
* Reaction with pyridine



Aniline

Acetanilide

p-Nitroacetanilide



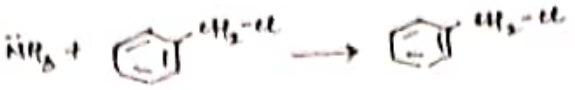
Preparation of Amines from alkylhalides

1. By ammonolysis of alkylhalides : $\ddot{N}H_3 + R\overset{\curvearrowright}{-}X \longrightarrow R-NH_2$ ($X = Cl, Br, I$)

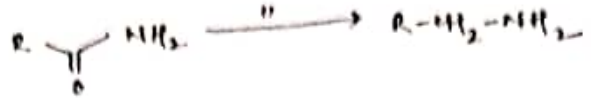
(R carries $+\delta$, X carries $-\delta$)

order of reactivity : $RI > RBr > RCl$

2. Reaction of ethanolic : $NH_3 + C_2H_5Cl \xrightarrow{C_2H_5OH} C_2H_5-NH_2$

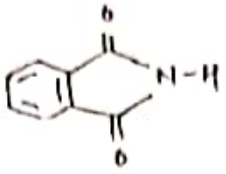


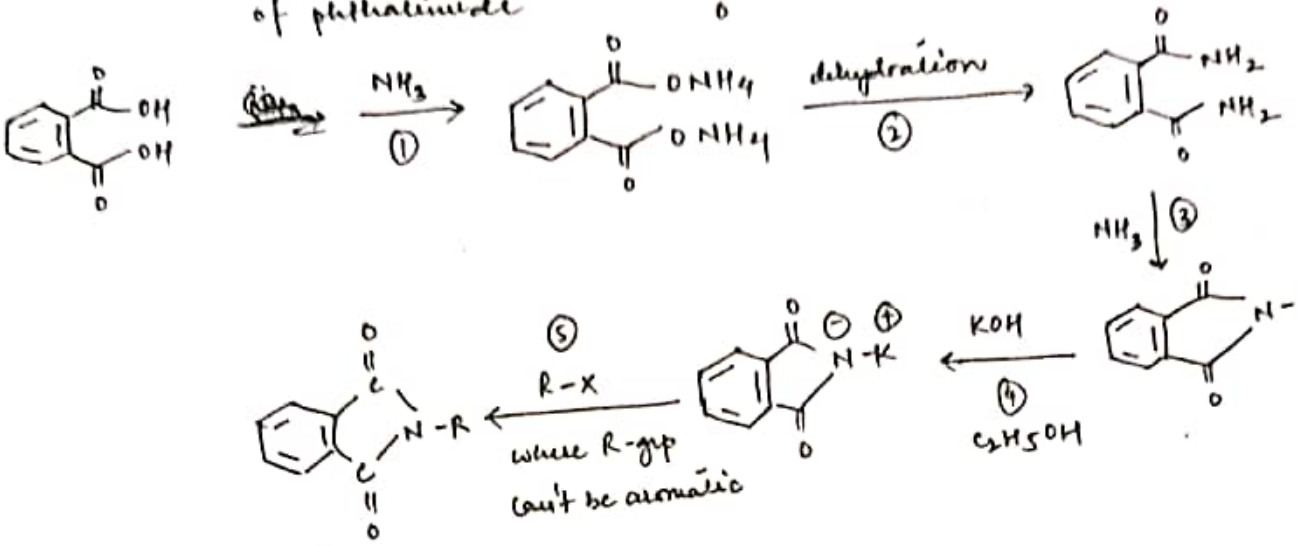
3. Reduction of nitriles : $R-C\equiv N \xrightarrow[H_2/Pd]{LiAlH_4} R-CH_2-NH_2$

Reduction of Amides : 

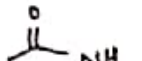
Gabriel phthalimide Synthesis

preparation of phthalimide :





limitation of this reaction is that we can't create aromatic amine . only give 1° aliphatic amines .

- Hoffman Bromoamide reaction :  $+ Br_2 + NaOH \longrightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H$

∴ Turn 1°-amide into 1°-amine with one fewer carbon atom .

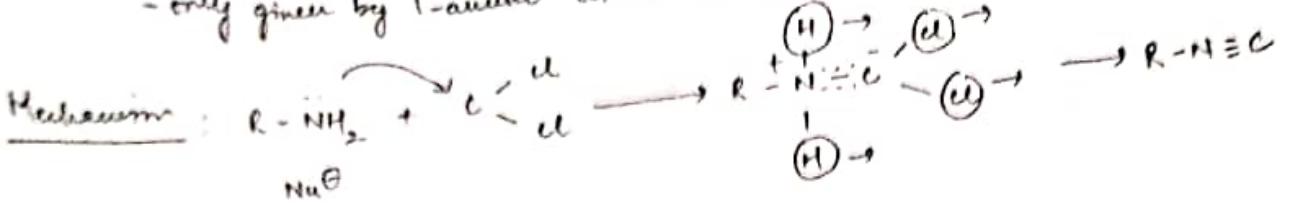
• Carbylamine Reaction (Isocyanide Test)

$R-NH_2 \xrightarrow[\text{High } \Delta]{CHCl_3 + KOH} R-NC \;/\; R-\overset{\oplus}{N}\equiv C^{\ominus}$ (foul smelling) - observation

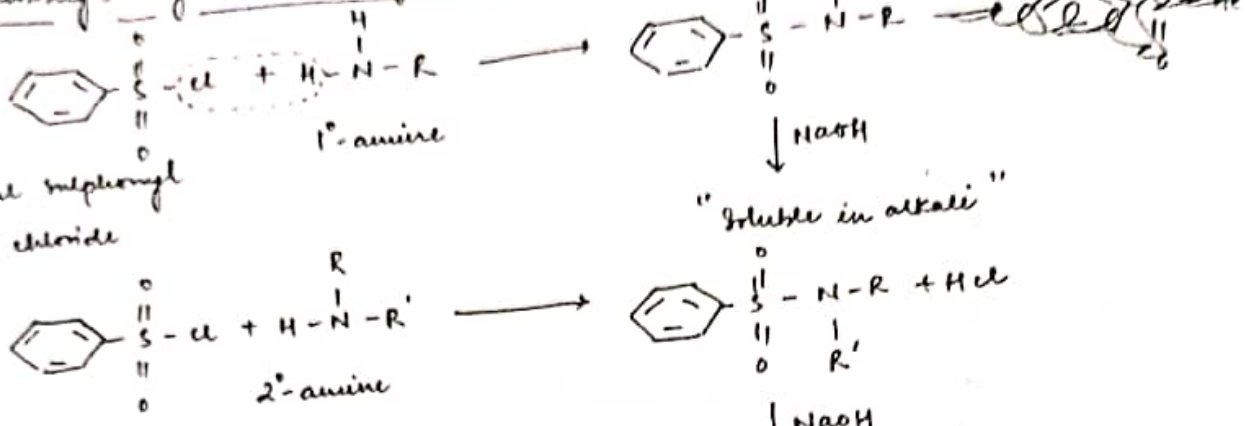
Isocyanide

- only given by 1°-amine either aromatic or aliphatic amines.

Mechanism:



• Hinsberg's reagent & Hinsberg's Test



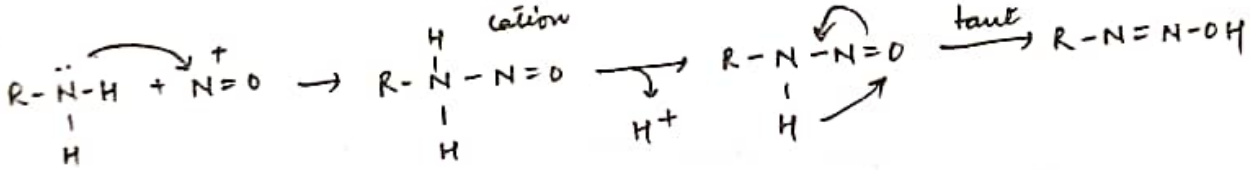
∵ Note: 3°-amine does not give hinsberg's test because in 3°-amine does not have any H-atom. hence, no reaction.

• Reaction of Nitrous acid ($\equiv HNO_2$)

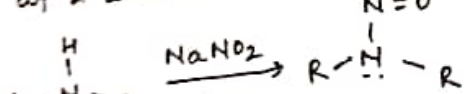
Mechanism: HNO_2 → weak acid

$HO-N=O + H^+ \longrightarrow \overset{+}{N}=O + H_2O$

Nitrosonium cation

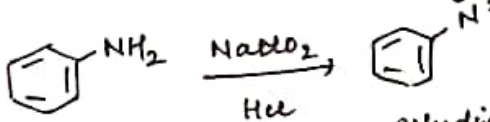


1. NO^+ of 2° amine



(N-nitrosamine)

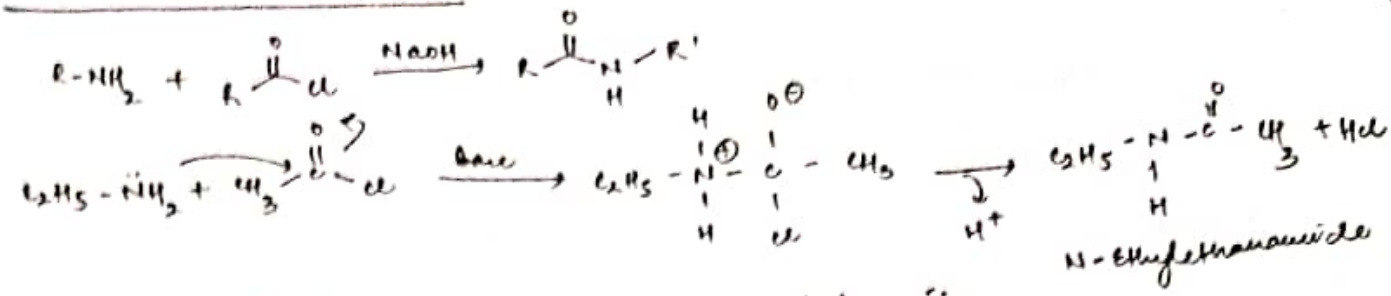
2. NO^+ of 1° amine :



aryldiazonium.

∵ Any other 1°-amine will decompose too quickly.

• Schotten - Baumann Reaction



∵ Note : only 1°, 2°-amines show this reaction.

• Basicity of Amines

$$R-NH_2 + H_2O \longrightarrow R-NH_3^+ + OH^-$$

conjugate acid

$$K = \frac{[R-NH_3^+][OH^-]}{[R-NH_2][H_2O]} \quad ; \quad [H_2O] = 1 \quad K_b = \frac{[R-NH_3^+][OH^-]}{[R-NH_2]}$$

∵ Basic strength (K_b) $\propto \frac{1}{pK_b}$

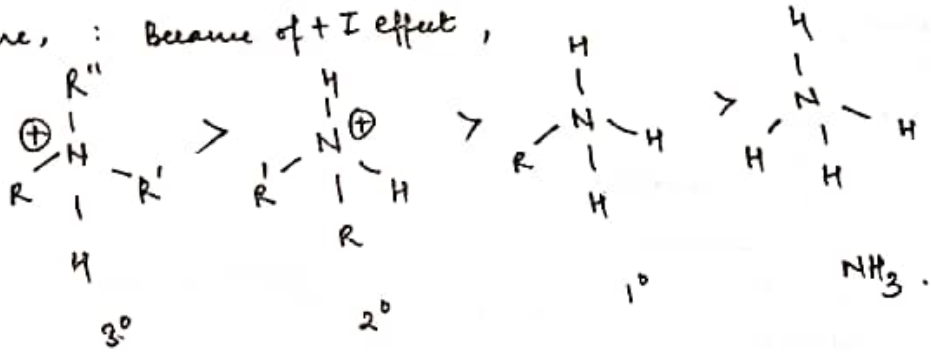
$K_b \uparrow$ = Basic strength ↑

$pK_b = -\log[K_b]$

$pK_b \downarrow$ • Basic strength ↑

∵ Higher the CA more good base in amines.

(Gas phase, : Because of +I effect,



3° 2° 1° NH_3.

Solvent phase, : Solvation effect & Steric hindrance ;

R = $-CH_3$ (more basic)

R = $-C_2H_5$.

w/o methyl

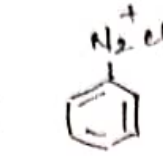
wt methyl

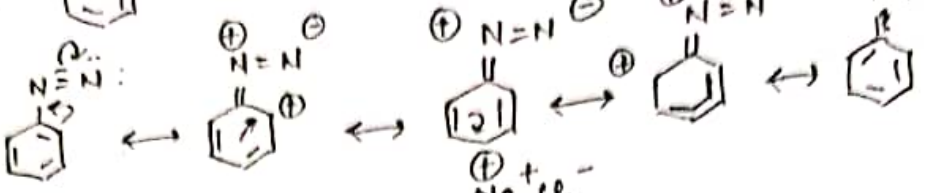
$(C_2H_5)NH > (C_2H_5)_3N > (C_2H_5)NH_2 > NH_3 \quad (CH_3)_2NH > CH_3NH_2 > (CH_3)N > NH_3$

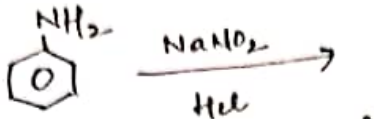
2° 3° 1° 2° 1° 3°.

Diazonium salts

$R-N_2^+X^-$: X = F^-, Cl^-, Br^-, I^-, HSO_4^-, BF_4^-, etc.

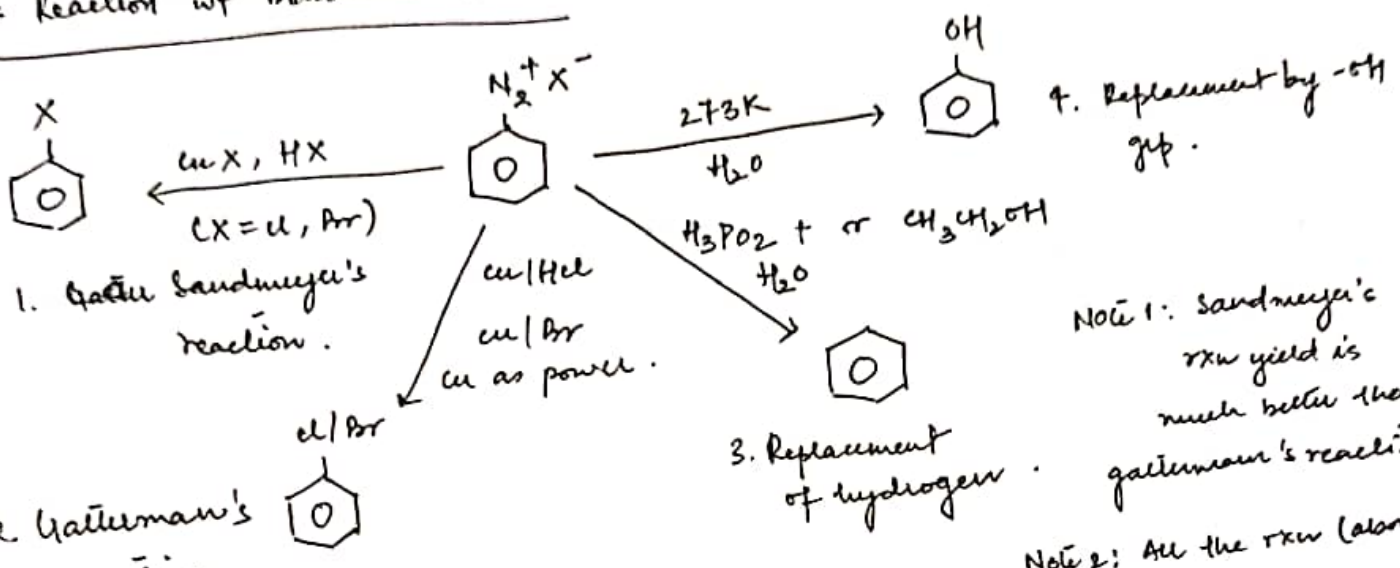
- Aliphatic Diazonium ⇒ $CH_3-N_2^+Cl^-$: less stable than aromatic diazonium salts because of resonance.
- Aromatic Diazonium ⇒  Benzene diazonium chloride.



- Preparation ⇒ 

Aniline → Benzene diazonium chloride. + HCl + $2H_2O$.

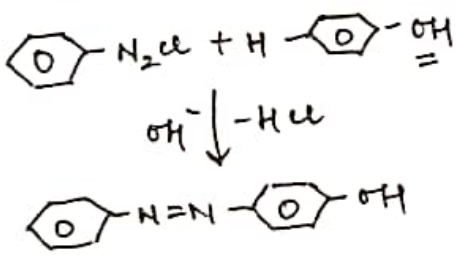
Reaction of Diazonium salts



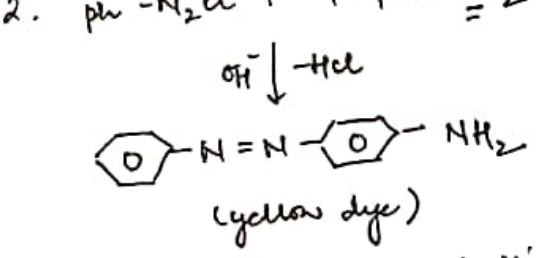
Note 1: Sandmeyer's rxn yield is much better than gattermann's reaction.

Note 2: All the rxn (above) are based upon displacement of nitrogen.

Dyes : Retention of nitrogen (coupling rxn) : -

1. 

(organe dye).

2. 

(yellow dye)

Diazonium salts are colourless crystalline solid which are soluble in water and stable in cold water.