AMINES

$NH_3 \xrightarrow[-N]{+R} R-NH_2 \xrightarrow[-H]{+R} R_2-NH \xrightarrow[-H]{+R} R_3N$

Primary (1°) Secondary (2°) Tertiary (3°)

⇒ Preparation of Amines

(1) Rxn with Alkyl halide.

(i) Ammonolysis of Alkyl halide

$CH_3Cl + NH_3 \longrightarrow CH_3NH_2 + HCl$

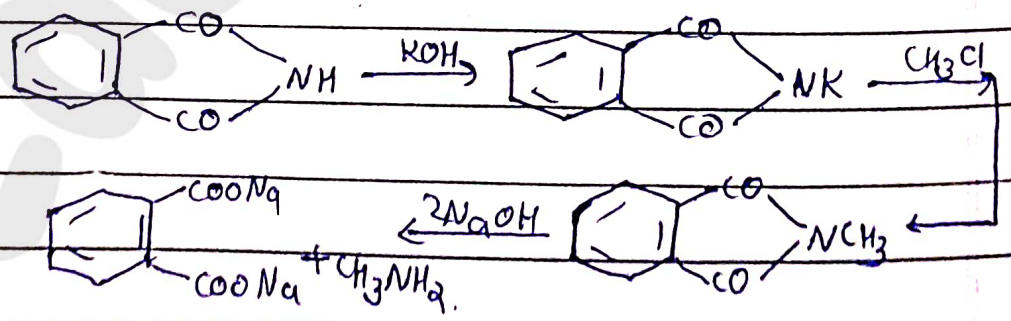
(1° Amine)

if 1° Amine further react with alkyl halide then it form 2°, 3° & quaternary amine.

$CH_3NH_2 \xrightarrow[HCl]{CH_3Cl} (CH_3)_2NH \xrightarrow[HCl]{CH_3Cl} (CH_3)_3N \xrightarrow{CH_3Cl} (CH_3)_4N^+$

(ii) Gabriel phthalimide synthesis

This synthesis is used for pure 1° Alkyl or Aryl Amine.



(iii) Reduction of Nitrocompound

$CH_3CH_2NO_2 \xrightarrow[Fe/Conc.\ HCl]{Sn/Conc.\ HCl\ or} CH_3CH_2NH_2$

$CH_3NO_2 \xrightarrow[Na(Hg)/C_2H_5OH]{LiAlH_4 \text{ or}} CH_3NH_2$

(iv) Reduction of oxime.

$CH_3CH=NOH \xrightarrow{LiAlH_4} CH_3CH_2NH_2$

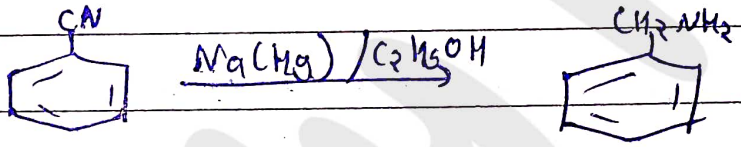
Aldoxime.

$(CH_3)_2C=NOH \xrightarrow{Na(Hg)/C_2H_5OH} (CH_3)_2CHNH_2$

Acetoxime

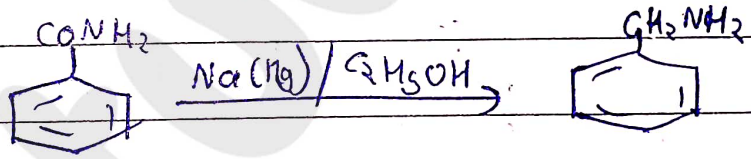
(v) Reduction of Nitrite.

$CH_3CN \xrightarrow{Sn/Conc.HCl} CH_3CH_2NH_2$.



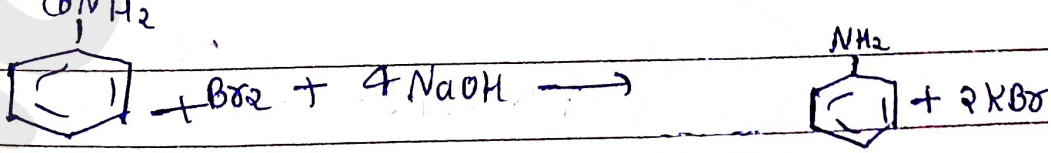
(vi) Reduction of Amides

$CH_3CONH_2 \xrightarrow{LiAlH_4} CH_3CH_2NH_2$



(vii) Hoffmann's Bromoamide degradation Rxn.

$CH_3CONH_2 + Br_2 + 4NaOH \longrightarrow CH_3NH_2 + 2NaBr + Na_2CO_3 + 2H_2O$



$+ K_2CO_3 + 2H_2O$

⇒ Physical properties

① Solubility:- Lower Amines are soluble in water due to formation of H-Bonding.
Aryl Amines are insoluble in water.

(2) Boiling Point

$CH_3CH_2OH > CH_3CH_2NH_2 > CH_3COCH_3 > CH_3OCH_3 > CH_3CH_2CH_3$

Aliphatic Amine have higher B.P.

⇒ Chemical properties

(i) Alkylation

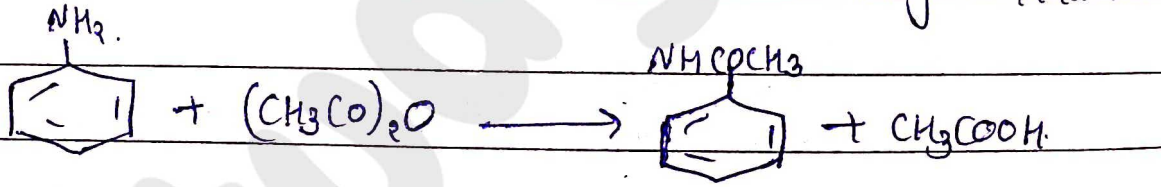
$CH_3CH_2NH_2 + CH_3CH_2Cl \longrightarrow (CH_3CH_2)_2NH \xrightarrow{CH_3CH_2Cl} (CH_3CH_2)_3N \xrightarrow{CH_3CH_2Cl} (CH_3CH_2)_4N^+$

quaternary Amine

(ii) Acylation

$CH_3CH_2NH_2 + (CH_3CO)_2O \longrightarrow CH_3CH_2NHCOCH_3$

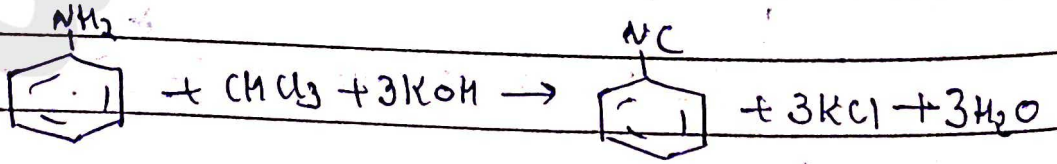
N-ethyl ethanamide



Benzanilide.

(iii) Carbylamine Reaction

$CH_3NH_2 + CHCl_3 + 3KOH \longrightarrow CH_3NC + 3KCl + 3H_2O$



(iv) Rxn with nitrous Acid

$RNH_2 + HNO_2 \xrightarrow{NaNO_2/HCl} R\text{-}OH + N_2 + H_2O$

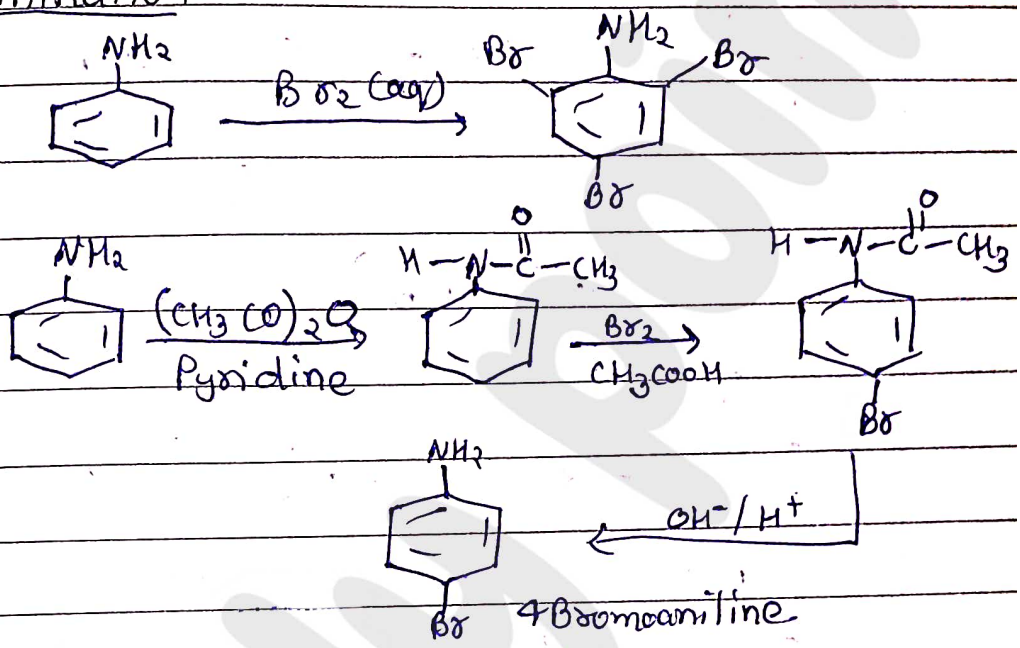
(v) Libermann's nitrous Rxn

$R_2NH + HNO_2 \xrightarrow{NaNO_2/HCl} R_2-N-N=O$

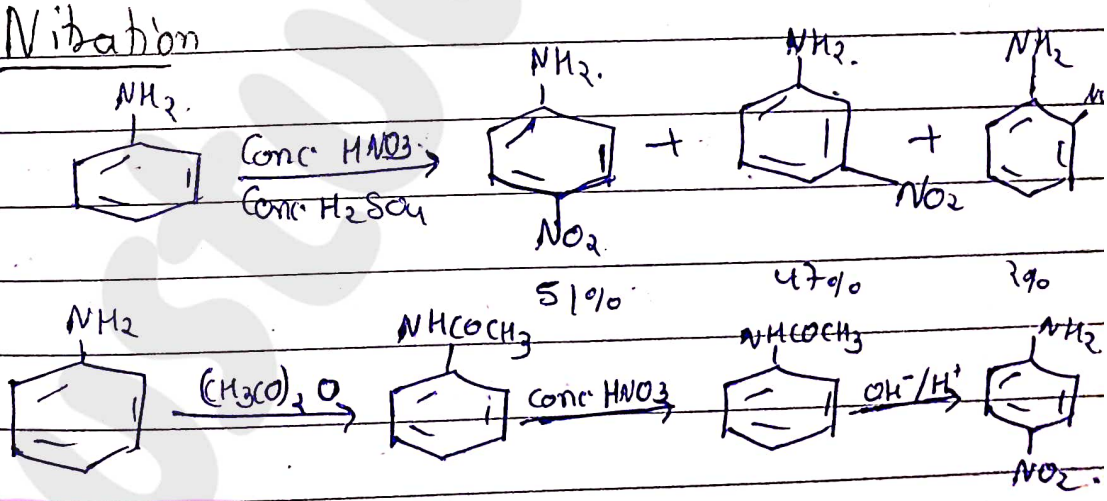
Nitrous Amine

(vi) Electrophilic Substitution Rxn

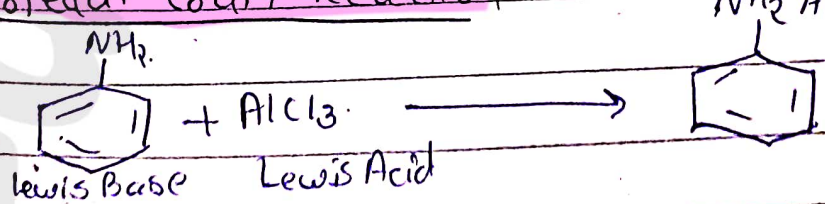
Bromination



Nitration

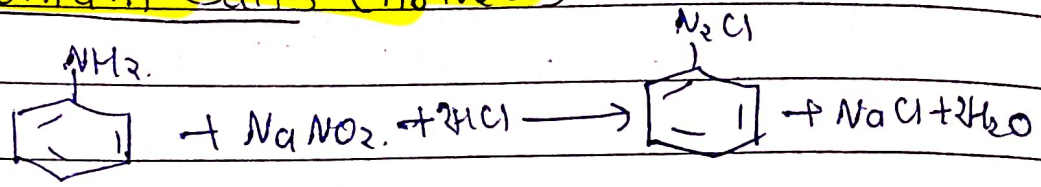


(vii) Friedal Craft Reaction

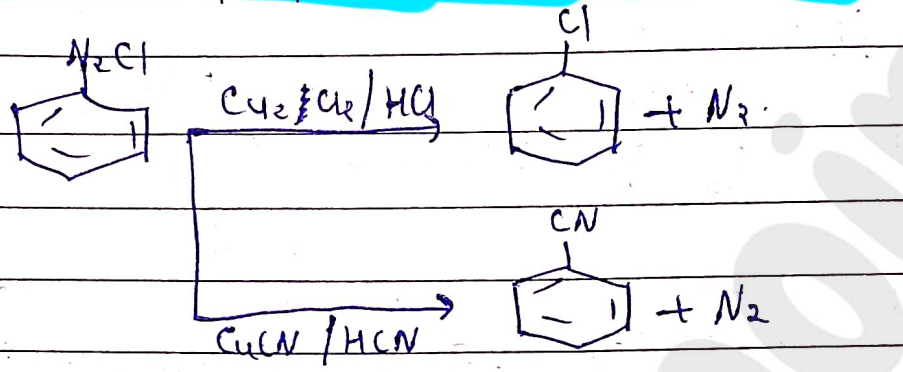


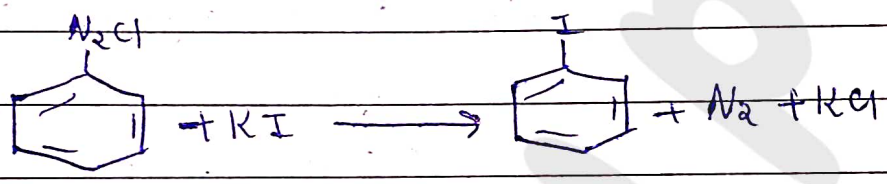
Aniline does not perform freedal craft reaction due to nitrogen of anilinium acquires +ve charge thus it acts as strong deactivating group.

⇒ Diazonium Salts (ArN_2Cl)

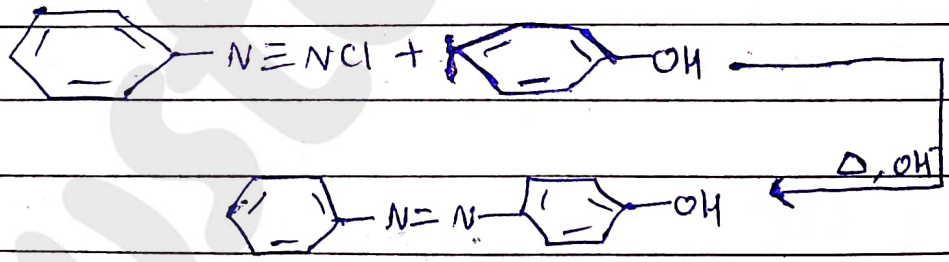


Chemical properties of diazonium

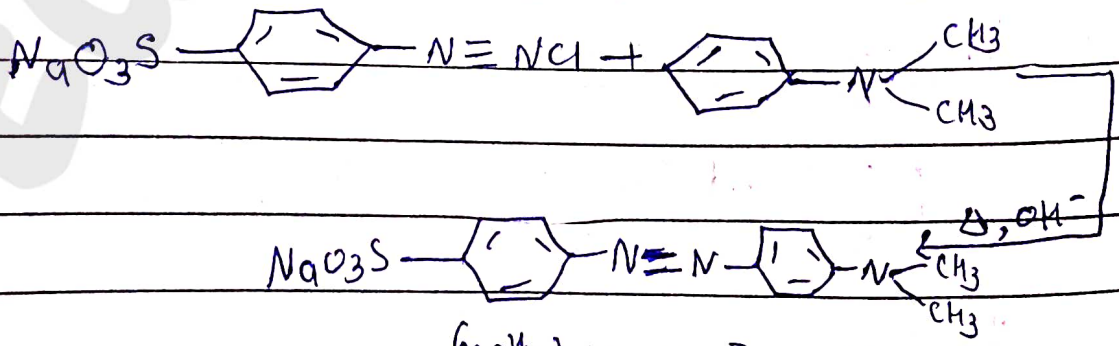




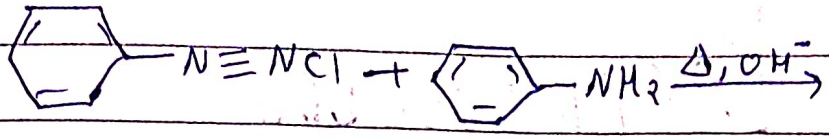
Coupling Rxn

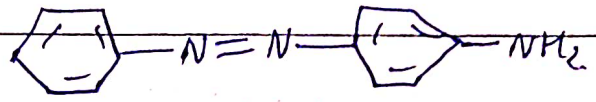


p-hydroxyazobenzene
(orangedyl)



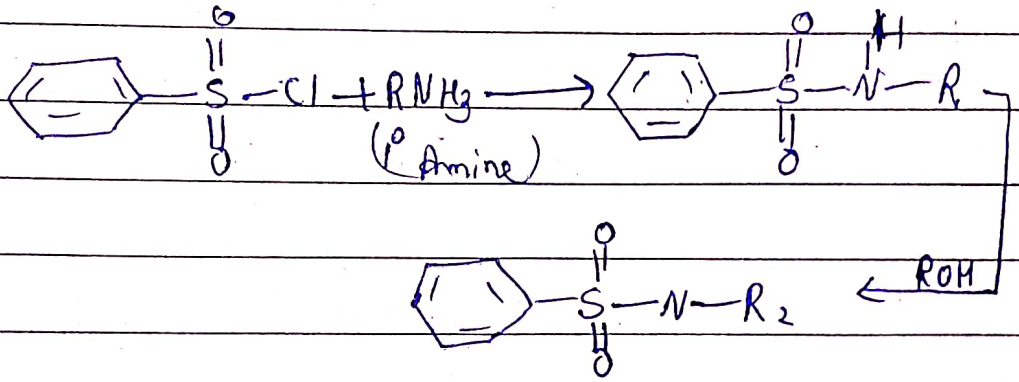
(methyl) orange

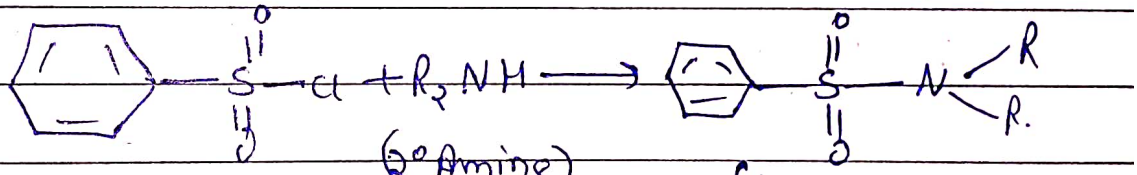




P-aminoazibenze (Yellow dye)

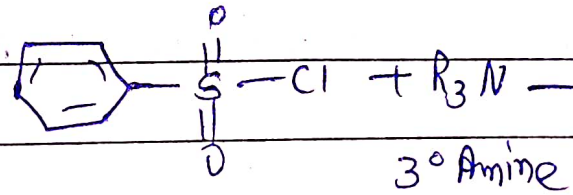
⇒ **Chemical test of Amine.**





(2° Amine)

(Insoluble in Alkali)



3° Amine