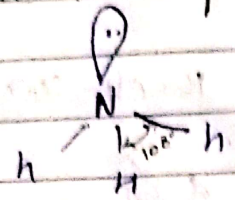
Amines → derivatives of Ammonia

Page No.
Date

- These organic compounds formed by replacing one or more hydrogen of ammonia molecule by alkyl & aryl group

a) Structure of Ammonia

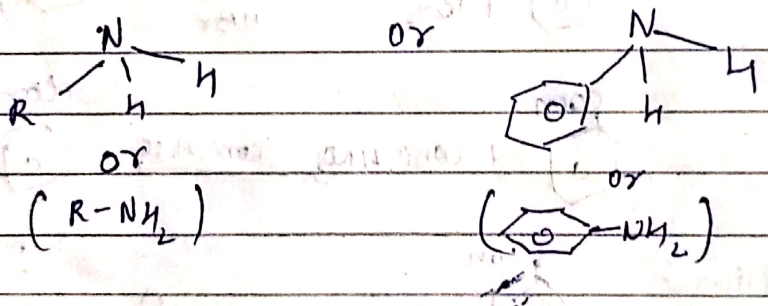


Nitrogen atom in amines is trivalent i.e it forms three covalent bond. The nitrogen atom also has one lone pair of e^-.

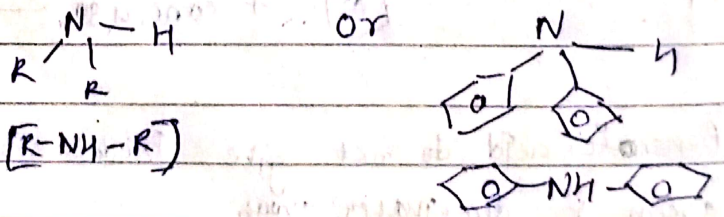
b) 'N' atom in all amines is sp^3 hybridised which has tetrahedral geometry but their shape is 'pyramidal'

* Classification:

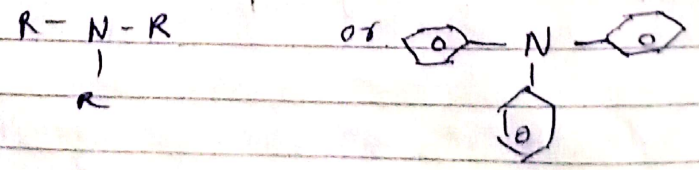
a) 1° Amines: If one hydrogen atom of ammonia is replaced by alkyl or aryl group



b) 2° Amines:



c) 3° Amines:

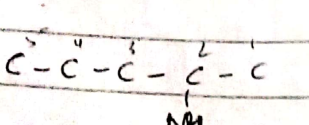


* Nomenclature

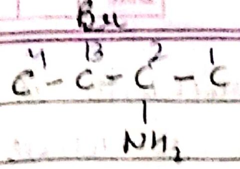
NH_3 | $R-NH_2$ 1° Amine | $R-NH-R$ 2° Amine | $R-\underset{R}{N}-R$ 3° Amine

eg: $C-C-C-C-NH_2$

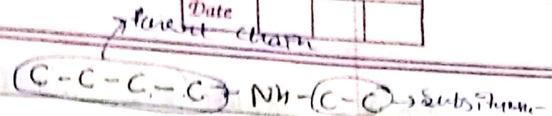
Butan-1-amine



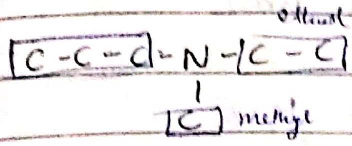
Pentan-2-amine

1. 

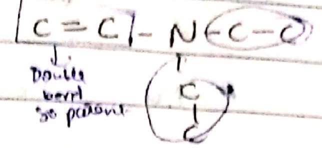
3 - Bromobutan-2-amine.



N - Ethylbutan-1-amine
or
N - Ethyl butanamine



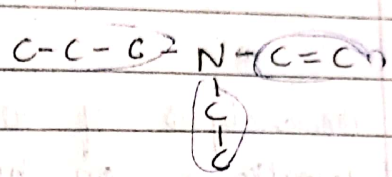
N - Ethyl - N - methyl propan - 1 - amine



N, N - Diethyleth-1-en-1-amine

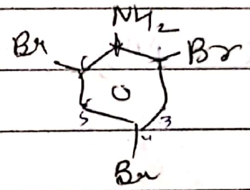
- $NH_2-C-C-C-C-NH_2$

Butane - 1, 2 - diamine.

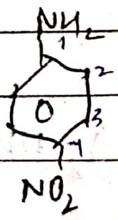


N - Ethyl - N - propyleth-1-ene-1-amine

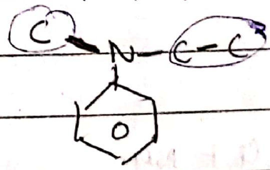
Benzen -1- amine
or
Aniline



2, 4, 6 - Tribromo aniline



4 - Nitroaniline.



N - Ethyl - N - methyl aniline

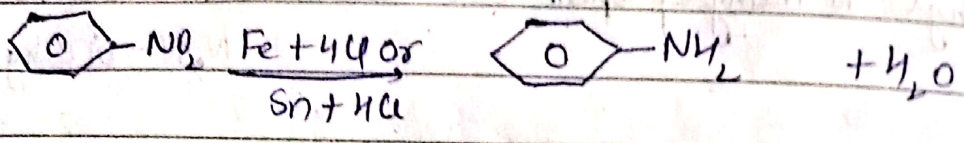
* Method of Preparation of Amine.

① From Reduction of Nitro compounds
Both aliphatic & aromatic amines can be prepared by the reduction of corresponding nitro compounds.

→ The reducing agents used are :
(i) catalytic hydrogenation [H_2 - Ni / Pt / Pd]
(ii) Metal in acidic medium [Sn + HCl or Fe + HCl]
(iii) Lithium Aluminium Hydride [$LiAlH_4$]

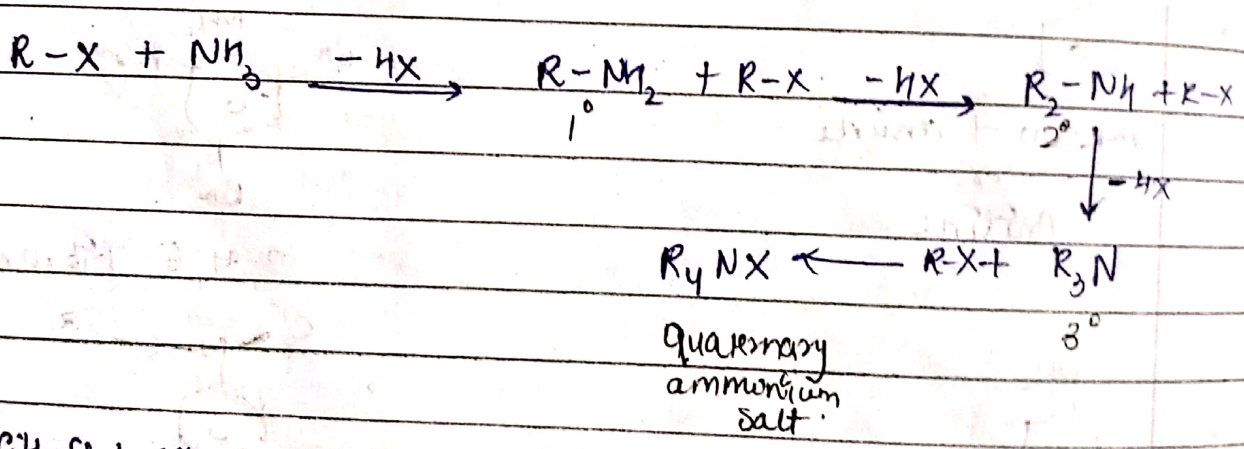
NOTE: Reduction with iron scrap & hydrochloric acid is preferred because $FeCl_2$ formed gets hydrolysed to release hydrochloric acid during the rxn. Thus, only a small amount of HCl is required to initiate the rxn.

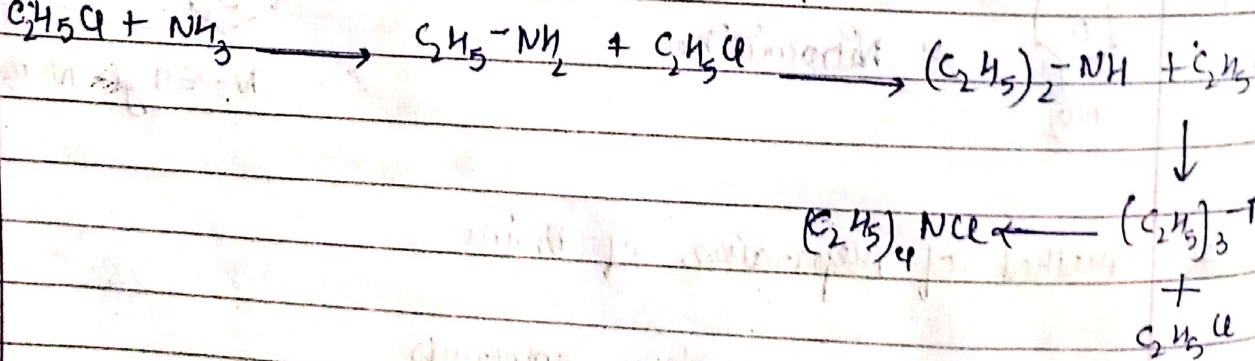
$$R-NO_2 \xrightarrow{Fe+HCl} R-NH_2 + H_2O$$



2) Ammonolysis of alkyl halides. / Hoffman ammonolysis

Haloalkanes on heating with ammonia give mixture of 1°, 2° amines & quaternary ammonium salt.





Note: This method can't be used to prepare arylamines because aryl halides are much less reactive towards nucleophilic substitution rxns than alkyl halides because of Resonance. (C-X) bond of haloarene have partial double bond character.

Reactivity Order: R-I > R-Br > R-Cl.

Disadvantage: It give mixture of amines [1°, 2°, 3°, quarternary]

3) By reduction of Nitriles.

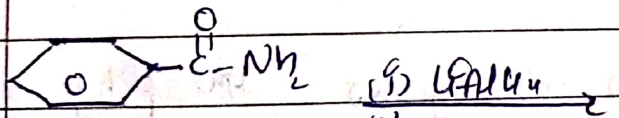
Nitriles can be reduced with $LiAlH_4$ or with catalytic hydrogenation, 1° amines are prepared. This rxn is used in ascent of series.

$$R-C\equiv N \xrightarrow[NaCH_3)/C_2H_5OH]{H_2/Ni} R-CH_2-NH_2$$

$$C_2H_5C\equiv N \xrightarrow{LiAlH_4} C_2H_5CH_2NH_2$$

4) Reduction of Amides.

$$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4} R-CH_2-NH_2$$



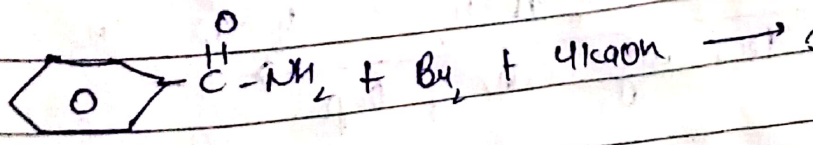
5) Hoffmann Bromamide degradation rxn. (descends of series)

By this method, 1° amines are prepared from acid amides with one carbon less than parent acid amide.

Acid amide on treatment with Br_2 & aqueous or alcoholic alkali [NaOH & KOH] gives 1° amines

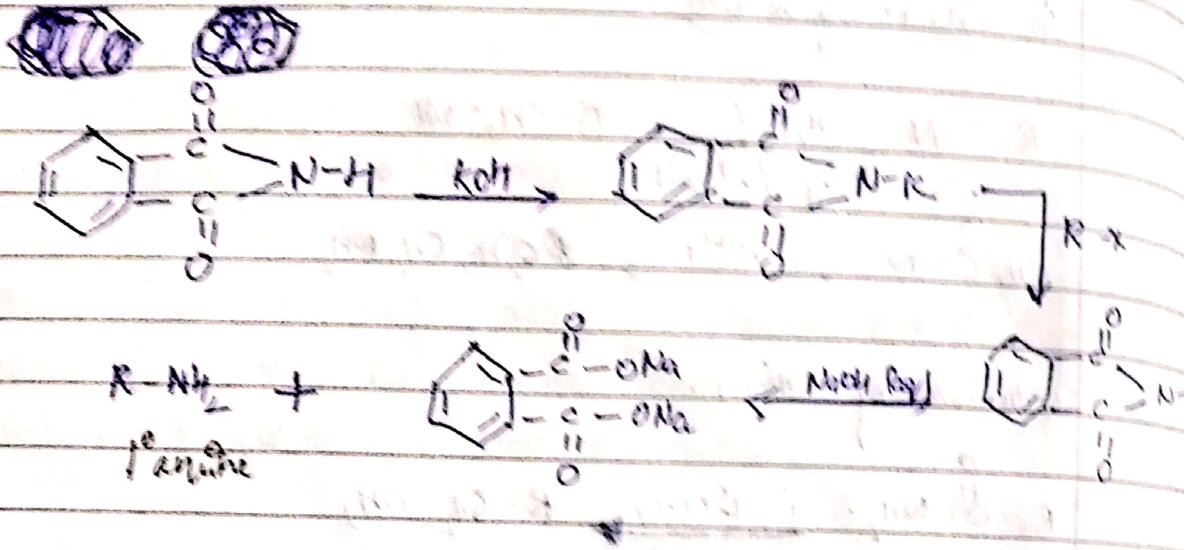
$$R-\overset{O}{\overset{\|}{C}}-NH_2 + Br_2 + 4NaOH \longrightarrow \underset{\text{amine}}{R-NH_2} + Na_2CO_3 + NaBr + H_2O$$

amide



c) Gabriel Phthalimide synthesis. [only for aliphatic over 1° amines]

It is used when phthalimide is treated with alcoholic solution of potassium hydroxide, potassium salt of phthalimide is formed which on heating with alkyl halide followed by alkaline hydrolysis produces a primary amine.



* Physical properties.

- The lower aliphatic amines are gases with fishy smell, 1° amines with three or more carbon atoms are liquid & still higher ones are solid. Among arylamines the lower members are liquids while higher members are solid.

* Boiling point :-

- Amines can form intermolecular hydrogen bonding. So they have higher b.pt than alkanes of comparable molecular mass.
- Among isomeric amines, 1° amines have higher b.pt than 2° amines & 2° amines have higher b.pt than 3° amines.

$$CH_3(CH_2)_3NH_2 > CH_3CH_2NHCH_3 > CH_3-\overset{CH_3}{\underset{|}{N}}-CH_3$$

decreasing order of b.p

This is because 1° amines have two hydrogen atoms in amino group. So these have more hydrogen bonding

whereas 2° amines has only one hydrogen atoms & 3° amine has no hydrogen

CH_3-NH_2 CH_3NHCH_3 $(CH_3)_3N$

- Carboxylic acids & alcohols have higher b.p than amines because " acids & alcohols are more polar than amines so, they have stronger hydrogen bonding & have higher b.p

$HCOOH > CH_3CH_2OH > CH_3CH_2NH_2 > CH_3CH_2CH_3$

- Solubility:
- lower aliphatic amines are soluble in water due to formation of intermolecular H-bonding with water molecules.
- As the size of alkyl group increases, the hydrophobic character also increases. So, tendency to form hydrogen bond decreases & solubility also decreases. That is why amines with six or more carbons are insoluble in water.
- All aromatic amines like aniline & toluidine are insoluble in water but are soluble in organic solvent.

Chemical Properties of Amines:

1) Carbylamine Rxn or Isocyanide Test

Aliphatic & aromatic 1° amines form isocyanides on warming with chloroform & alcoholic KOH. These isocyanides have foul smell. So this rxn is used as a (test for 1° amines)

$$R-NH_2 + CHCl_3 + KOH \xrightarrow{heat} R-NC + KCl + H_2O$$

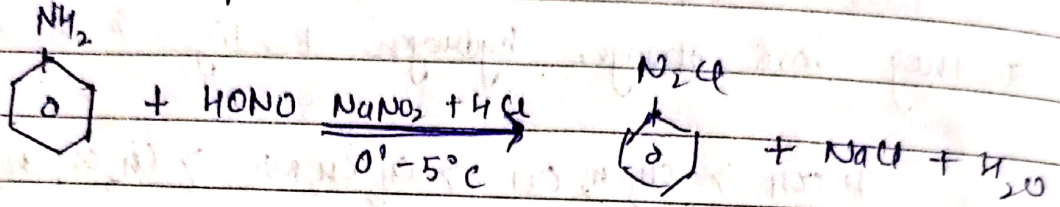
$$C_2H_5 + CHCl_3 + KOH \xrightarrow{heat} \underset{\text{carbylamine}}{C_2H_5-NC} + KCl + H_2O$$

(2) Rxn with nitrous acid / Diazotization Rxn.

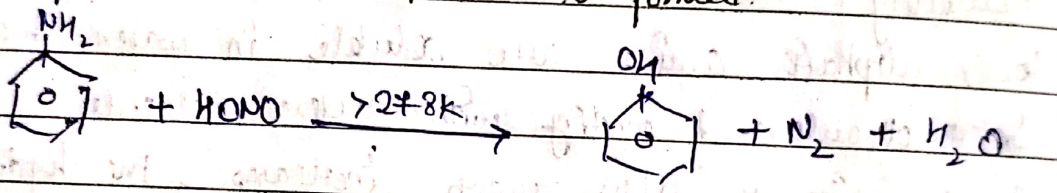
Nitrous acid is unstable. So, it is prepared in situ by the action of $NaNO_2$ with ice-cold dilute HCl or H_2SO_4

$$NaNO_2 + HCl \longrightarrow HNO_2 + NaCl$$

⇒ at low temp. 273-278K



⇒ at temp. above 278K phenol is formed.



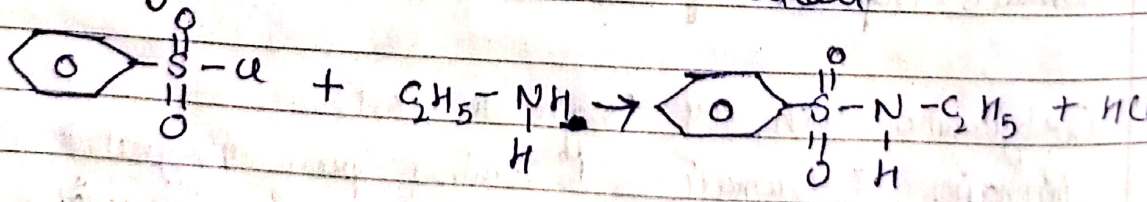
⇒ with 1° aliphatic amines.

$$C_2H_5-NH_2 + HONO \longrightarrow C_2H_5OH + N_2 + H_2O$$

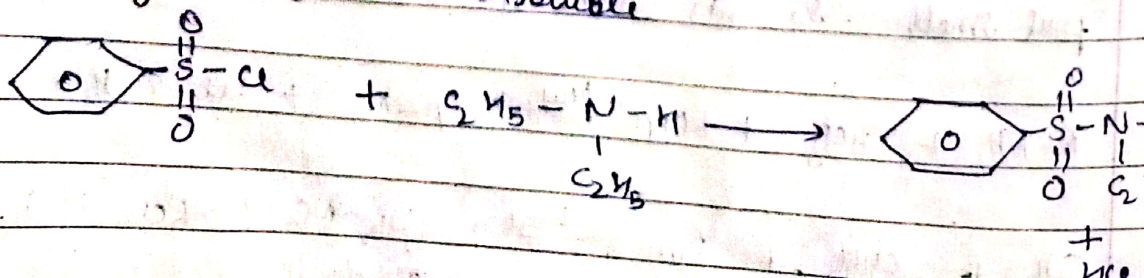
(3) Rxn with arylsulphonyl chloride / Identification of 1°, 2° & 3° amines

Hinsberg reagent [Benzene sulphonyl chloride] → 

- Primary amines → soluble in alkali



- Secondary amines → Insoluble



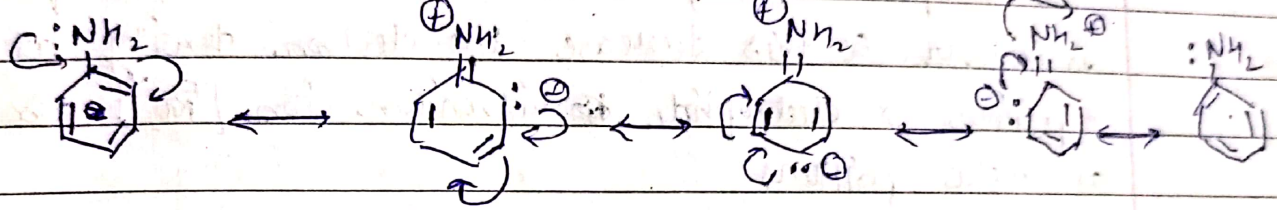
- Tertiary amines.

⇒ 3° amines do not react with benzenesulphonyl chloride. because it does not have any hydrogen $\left[R-\underset{R}{\overset{R}{N}}-R\right]$

(4) Electrophilic substitution Rxn.

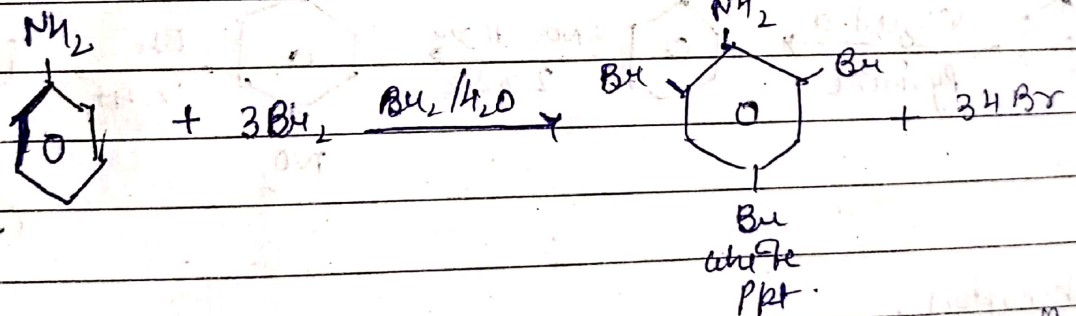
NH_2 is highly activating group so aniline is more reactive than benzene ring.

⇒ Resonance in Aniline

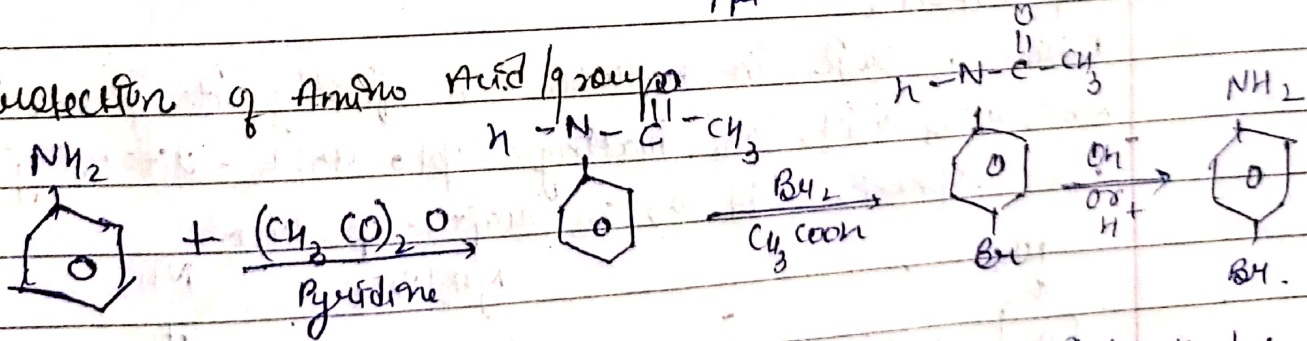


It is o- & p- directing.

⇒ Bromination → This rxn can be used to distinguish aliphatic & aromatic 1° amine



- Protection of Amino Acid group

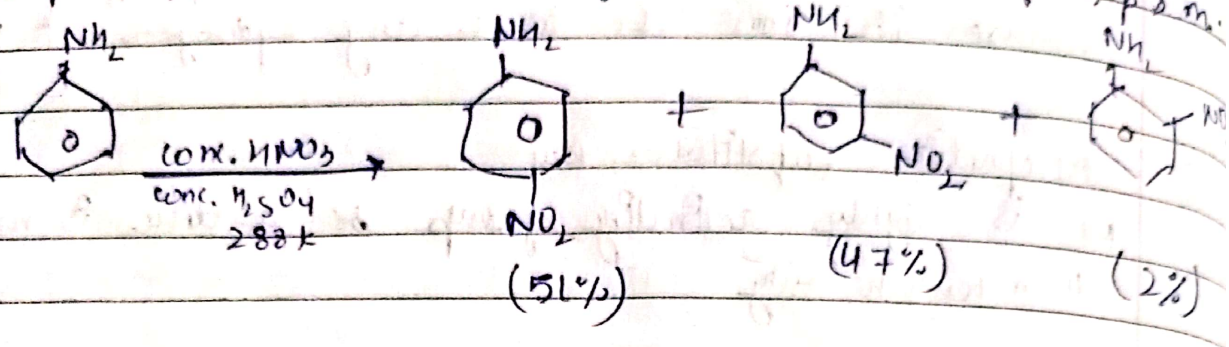


⇒ Due to activation of benzene ring, a disubstituted product is formed so aniline is protected by acylation to get mono substituted product.

Page No.
Date

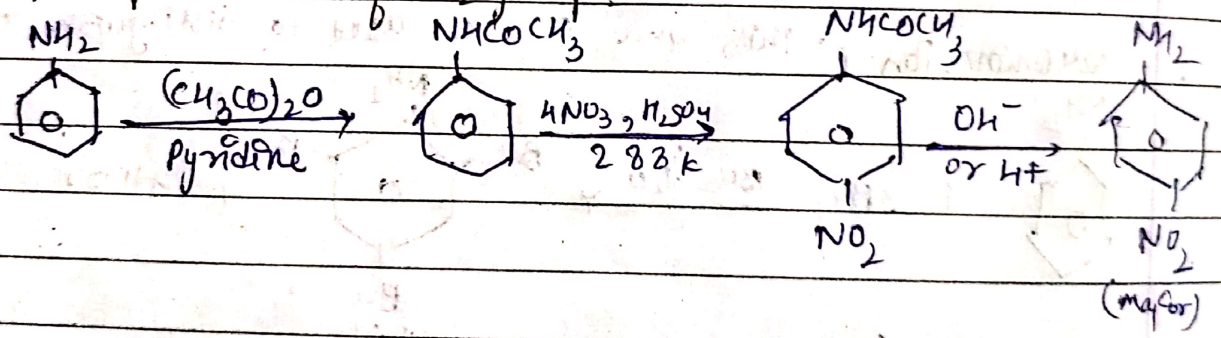
⇒ Nitration

Before protection, aniline gives a mixture of o, p & m.



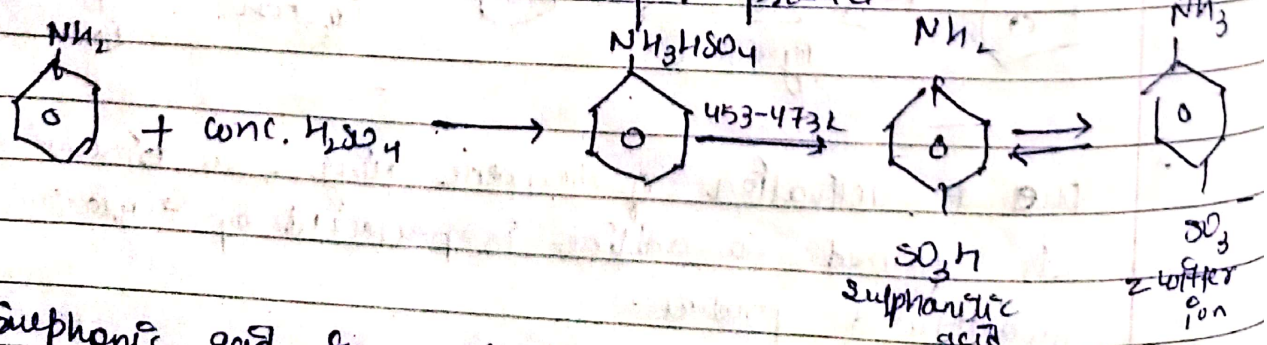
- Due to protonation, anilinium ion is formed which is E.W.G. So this decrease the electron density at o & p - position & electrophile nitronium ion [NO_2^+] also attacks at meta positions.

- After protection of NH_2 group.

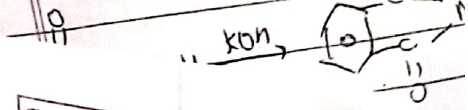


⇒ Sulphonation.

Aniline is basic in nature. So, firstly it forms salt with conc. H_2SO_4 which on heating upto 453k - 473k gives p-isomer i.e sulphonic acid as a major product.



Sulphonic acid is used as the starting material for the manufacturing of antibiotics called sulphadrugs.



Page No.
Date

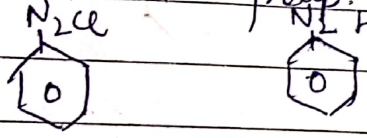
Zwitter ion: It is a dipolar ion which is formed due to internal salt formation b/w basic group [NH_2] & acidic group [$-SO_3H$]

NOTE: Aniline does not give Friedal craft Alkylation & Acylation due to the salt formation with lewis acid

* Diazonium salts:

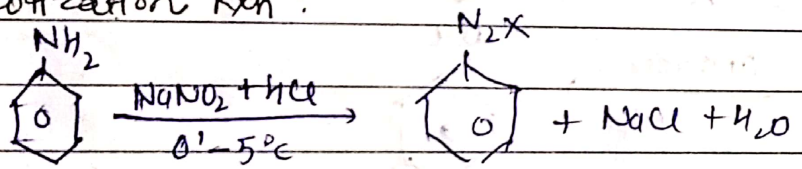
The Diazonium salts have the general formula ArN_2X where Ar is an aryl group X may be Cl, BH_4, HSO_4, BF etc. The N_2 called diazonium group.

eg:



* Methods of Preparation

Diazotization Rxn:



$$C_6H_5NH_2 \xrightarrow[0'-5^\circ C]{NaNO_2 + HCl} C_6H_5N_2X + NaCl + H_2O$$

* Stability: 1° aliphatic amines form highly unstable alkyl diazonium salt. 1° aromatic amines form arene diazonium salt which are stable for a short time in solution at low temp 0°-5°C

* Physical properties:

- It is colourless crystalline solid, soluble in water, stable in cold water but react with warm water
- It decomposes in dry state
- Benzene diazonium fluoroborate is water insoluble & stable at room temp.

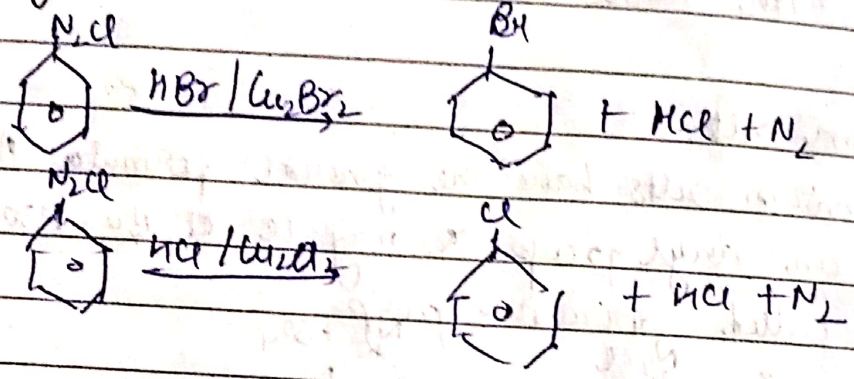
→ Chemical properties.

Rxn are divided into two groups

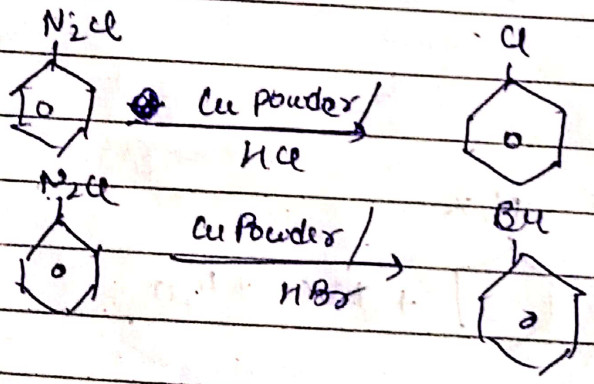
Rxn involving displacement of Nitrogen

Rxn involving retention of Diazo group.

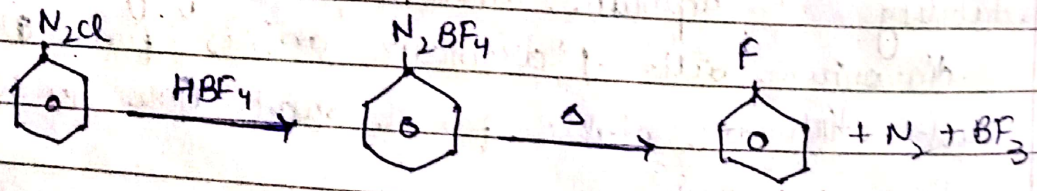
* Sandmeyer's Rxn.



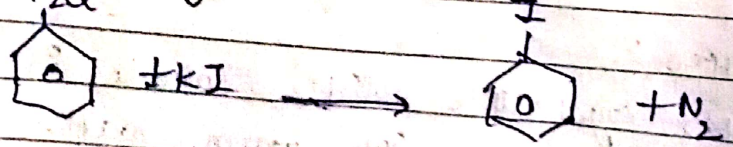
* Gattermann Rxn



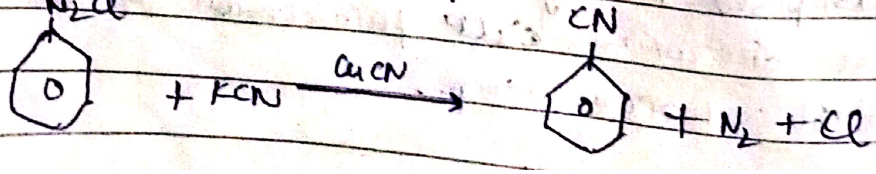
* Balz schiemann Rxn



* Replacement by Iodide ion



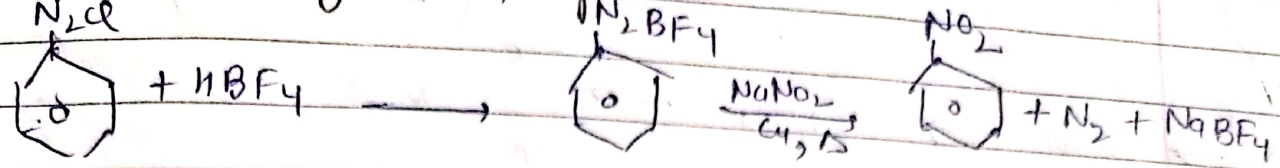
* Replacement by cyano group



forms ... with H_2O molecules ... because ...

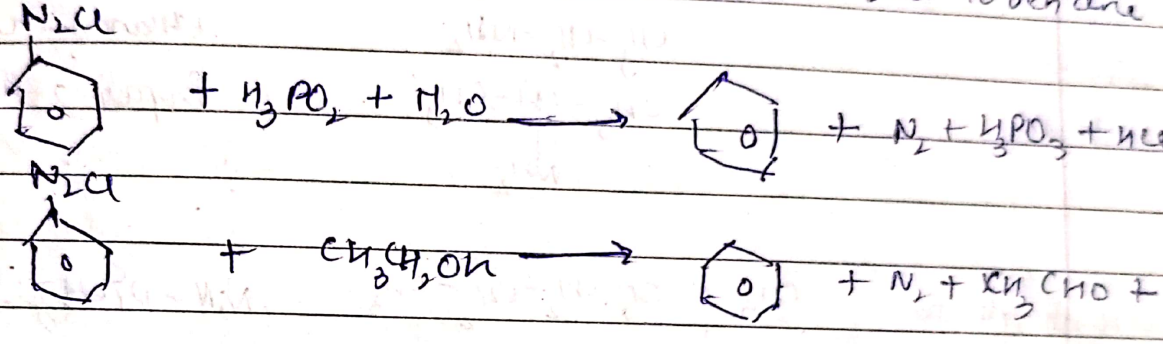
Solubility ✗

* Replacement by NO_2 group

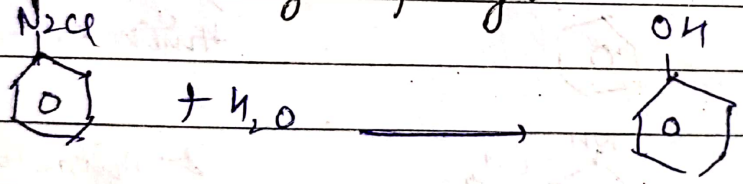


* Replacement by H

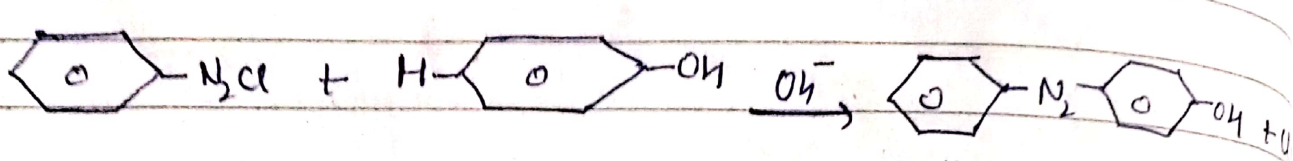
Benzene is formed. Mild reducing agent like phosphinic acid $[H_3PO_2]$ or ethanol reduce diazonium salt to benzene



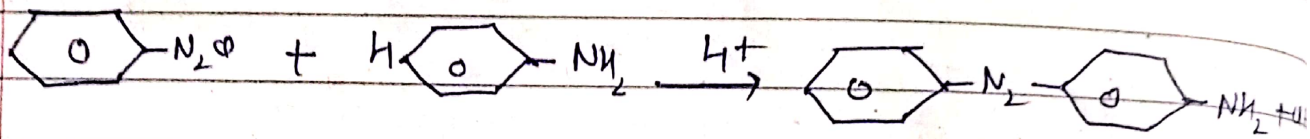
* Replacement by hydroxyl.



* Coupling Rxn :- when benzene diazonium chloride couples with with aromatic compound like phenol & aniline at their para positions & give azodyes.



p-Hydroxyazobenzene
(orange dye)



p-Aminoazobenzene
(yellow dye)

It's a dye test & also test for aliphatic & Aromatic amine

* Chemical properties of Amines

Amines have lone pair of e- on nitrogen atom which they are capable of donating due to which they behave as lewis base

$$R-NH_2 + H_2O \underset{\text{concentration} = 1}{\rightleftharpoons} R-NH_3^{\oplus} + OH^-$$

$$K_b = \frac{[R-NH_3^{\oplus}][OH^{\ominus}]}{[R-NH_2]}$$

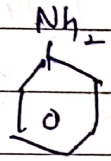
- $K_b \propto$ Basic strength
- $pK_b = -\log K_b$
- $pK_b \propto \frac{1}{\text{Basic strength}}$
- Larger the value of K_b is more is basic strength of amine
- smaller the value of pK_b is more is basic strength of amine.

* Comparison of basic strength of Ammonia & Aliphatic Amines.

NH_3 is a weaker base than aliphatic amines. In amines, alkyl group has +I effect & it increases e⁻ density on nitrogen. So, nitrogen easily donates its pair of e⁻ whereas in ammonia, no such +I effect is present.

- $NH_3 < R-NH_2$

  ↳ Alkyl/aliphatic amine is more basic than ammonia since, Alkyl grp increase basic strength ↑ due to +I effect [e⁻ donating nature of alkyl group].

- $NH_3 >$ 

Ammonia is more basic than aromatic amine due to resonance

* Comparison of basic strength of 1°, 2° & 3° Amines [Gaseous Phase]

In gaseous phase, order of basic strength is

3° amine > 2° amine > 1° amine.

as no. of alkyl groups increases, +I effect increases hence basic strength also increases.

* Basic strength of Amines in aqueous soln:

- Solution given by 3 factors:

① +I effect ② Steric hinderance ③ Solvation of ions

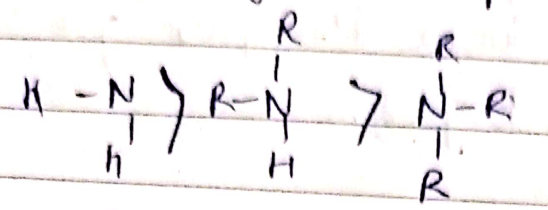
+I-effect

⇒ As alkyl group increases, +I effect increase hence base strength increases.

3° > 2° > 1°

Steric Hinderance

As alkyl grp increases, steric hinderance increases & it get difficult to give lone pair of e⁻



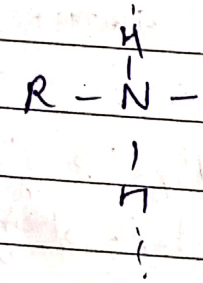
$1^\circ > 2^\circ > 3^\circ$

Solvation of ions.

$$R\text{-}NH_2 + H_2O \longrightarrow R\text{-}NH_3^+ + OH^-$$

$1^\circ > 2^\circ > 3^\circ$

Because 1° has



3 hydrogen so it can form

3 sides.

It means the energy released due to attraction of water molecule with +ve ammonia ion of amines. Larger the hydrogen bonding, more is solvation & more is stability of cation. So more is basic strength.

Basic strength of ethyl amine (except methyl)

$2^\circ > 3^\circ > 1^\circ$

$(C_2H_5)NH > (C_2H_5)_3N > C_2H_5NH_2$

Basic strength of methyl amine

$2^\circ > 1^\circ > 3^\circ$

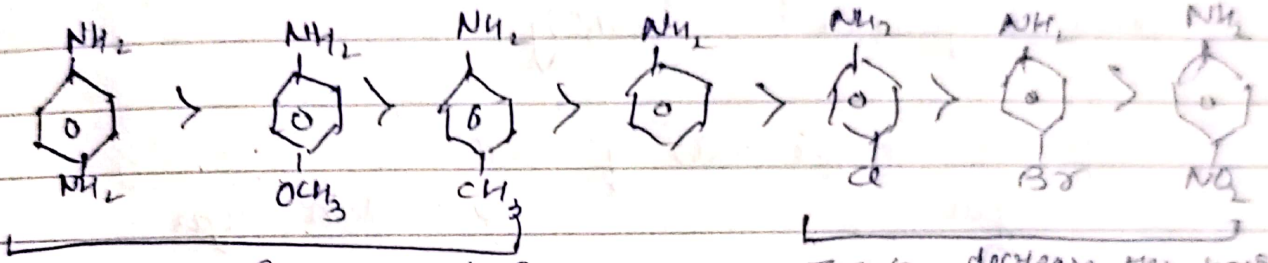
$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N$

* NOR :

- Electron withdrawing grp like $COOH$, $COCl$, $CONH_2$, COR, CN, SO_3H, NO_2, $-X$, decrease the electron density on nitrogen of aniline. Hence decrease the basic strength of amines.

- Electron donating groups like CH_3, OCH_3, OH, NH_2 etc increase the e^- density on nitrogen hence increase the basic strength of amines.

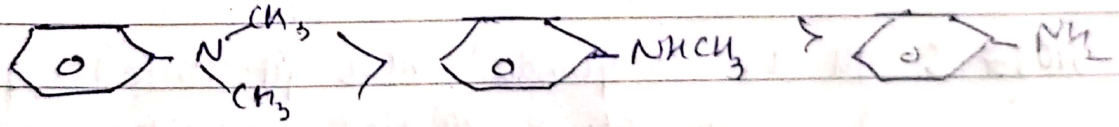
- Ortho effect includes steric hinderance as well as some electronic factors.



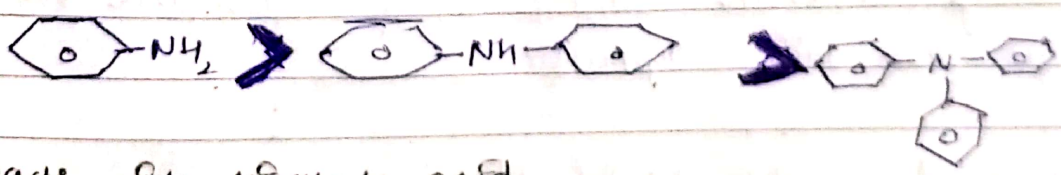
E.W.G increase the basic strength of aniline

E.W.G decrease the basic strength of aniline

- Longer the no. of e^- releasing alkyl grp is, more is the basic strength



- E.W.G like phenyl grp, the basic strength of aryl amine decreased



* Reacts with mineral acid

Amines react with acids & form salt

$CH_3NH_2 + HCl \longrightarrow CH_3NH_3Cl$