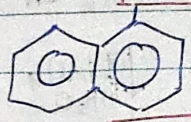
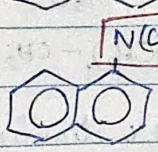
AMINES

1. Classify the following amines as primary, secondary (or) tertiary :-

(i) 

→ only one 'H' replaced. Therefore 1° amine (or) (3-2) H atom ⇒ 1° amine

(ii) 

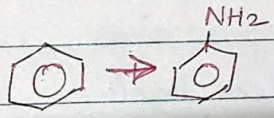
→ all three 'H' atom replaced. Therefore 3° amines (or) (3-0) H atom ⇒ 3° amine

(iii) $(C_2H_5)_2CH\boxed{NH_2}$ → only one 'H' atom replaced.
Therefore 1° (or) 3-2 H atom ⇒ 1° amine

(iv) $(C_2H_5)_2\boxed{NH}$ → Two 'H' atom got replaced. Therefore
2° amines (or) (3-1 'H' atom) ⇒ 2° amines

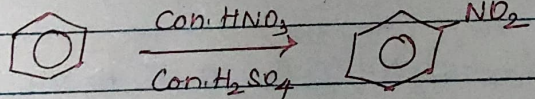
2. How will you convert :

(i) Benzene to aniline



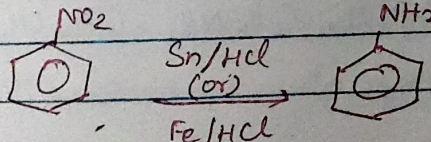
Step : 1

Nitration of Benzene.

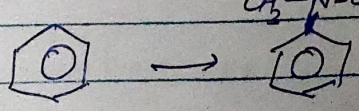


Step : 2

Reduction of Nitro group



(ii) Benzene to N,N-dimethyl aniline



(iii) $Cl-(CH_2)_4-Cl$ into hexan-1,6-diamine?

$Cl-(CH_2)_4-Cl + 2NaCN \xrightarrow[\text{medium}]{\text{alkaline}} NC-(CH_2)_4-CN + 2NaCl$

1,4-dichloro butane

$\xrightarrow[\text{ii) } H_2O]{\text{i) } LiAlH_4}$

$H_2N-H_2C-(CH_2)_4-CH_2-NH_2$

hexa-1,6-diamine

3. Arrange the following in increasing order of their basic strength:

(i) alkyl (1°) aryl (1°) Ammonia Arylalkyl 1° Alkyl 2°
$C_2H_5NH_2$, $C_6H_5NH_2$, NH_3, $C_6H_5CH_2NH_2$ & $(C_2H_5)_2NH$

⇒ If phase is not mentioned, then it is aqueous phase. (-X-)

Alkylamine ← NH_3 ⟵ Aryl amines

more basic less basic

⇒ In aqueous phase, 2° > 3° > 1°

$C_6H_5NH_2 < C_6H_5CH_2-NH_2 < NH_3 < C_2H_5NH_2 < (C_2H_5)_2NH$

(ii) alkyl (1°) alkyl (2°) alkyl (3°) Aryl (1°)
$C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$, $C_6H_5NH_2$

⇒ In aqueous phase, 2° > 3° > 1°

$C_6H_5NH_2 < C_2H_5NH_2 < (C_2H_5)_3N < (C_2H_5)_2NH$

(iii) Methyl (1°) Methyl (2°) Methyl (3°) Aryl (1°) Arylalkyl (1°)
CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$, $C_6H_5NH_2$, $C_6H_5CH_2-NH_2$

⇒ In aqueous (methyl group - exclusive)

2° > 1° > 3°

$C_6H_5NH_2 < C_6H_5CH_2NH_2 < (CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$

4. Among the following which amine is more soluble in water and reason why?

$CH_3-\ddot{N}(H)-CH_3$, $CH_3-CH_2-\ddot{N}H_2$, $\ddot{N}H_3$

(2°) (1°)

Steric hindrance

$CH_3-CH_2-\ddot{N}H_2$ more soluble, due to +I effect & less easily get solvated & protonated.

$$CH_3-CH_2-\ddot{N}H_2 \longrightarrow CH_3-CH_2-\overset{\oplus}{N}H_3.$$

5. Arrange the following in increasing order of boiling point?

(1°) (3°) (2°)

$CH_3-CH_2-CH_2-\ddot{N}H_2$, $CH_3-\ddot{N}(CH_3)-CH_3$, $CH_3-CH_2-\ddot{N}H-CH_3$

All amines having same molecular mass, as we know that,

Increase in carbon number $\propto$ boiling point

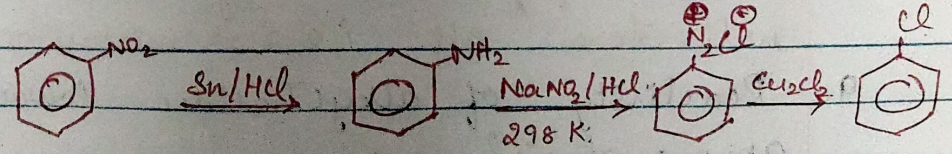
Increase in branching $\propto \frac{1}{\text{boiling point}}$.

3° ⇒ More branching, less surface, less vandenwaal's force

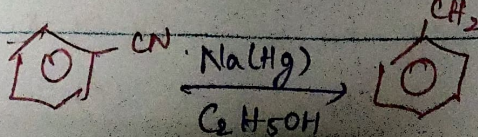
⇒ $3° < 2° < 1°$

6. How will you convert the following:-

(i) Nitrobenzene to Chlorobenzene.



(ii) Cyanobenzene to benzyl amine



(OR) $LiAlH_4$ (OR) H_2/Ni

7. Write complete equation for ammonol

Case: 1

$$R-X + NH_3 \xrightarrow[\text{Pressure}]{473K} R-NH_2 + HX$$

$$\downarrow NH_3 \text{ (excess)}$$

$R-NH_2$ (1° amine)
Major

Case: 2

$$R-X + NH_3 \xrightarrow[\text{Pressure}]{473K} \underset{(1^\circ)}{R-NH_2} + HX$$

$$\downarrow R-X \text{ (excess)}$$

$$R_4\overset{\oplus}{N} \xleftarrow[\text{(excess)}]{R-X} R_3\ddot{N}: \xleftarrow[\text{excess}]{R-X} \underset{(2^\circ)}{R_2-NH}$$

(4°) (3°)

	R-X	NH_3	Product
⟹	equimolar & 1 mole	equimolar 1 mole	All 4 ($1^\circ, 2^\circ, 3^\circ, 4^\circ$) amines will form.
⟹	Excess ext 10 mole	less 1 mole	$1^\circ, 2^\circ, 3^\circ, 4^\circ$ mixture will form
⟹	less ext 1 mole	excess 10 mole.	1° amine will be major

8. Reason why ammonolysis is not best method to prepare primary amine?

⟹ Presence of equimolar (or) excess alkyl halide (R-X) will form all $1^\circ, 2^\circ, 3^\circ, 4^\circ$ mixture of amin

9. Reactivity of alkyl halides towards ammonolysis?

⟹ $R-I > R-Br > R-Cl > R-F$

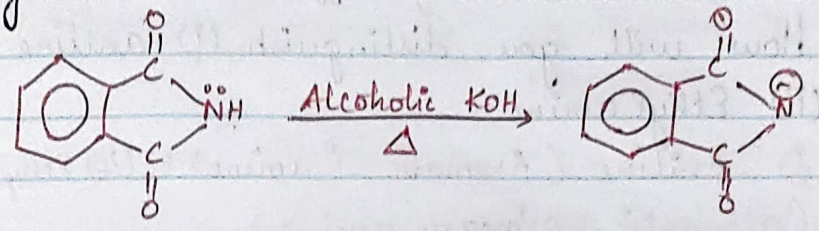
⟹ $CH_3-\underset{\underset{CH_3}{|}}{\overset{CH_3}{|}}{C}-X > CH_3-\underset{CH_3}{\underset{|}{CH}}-X > CH_3-CH_2-X$

(3°) (2°) (1°)

10. Which among the method is best for preparation of primary amine?

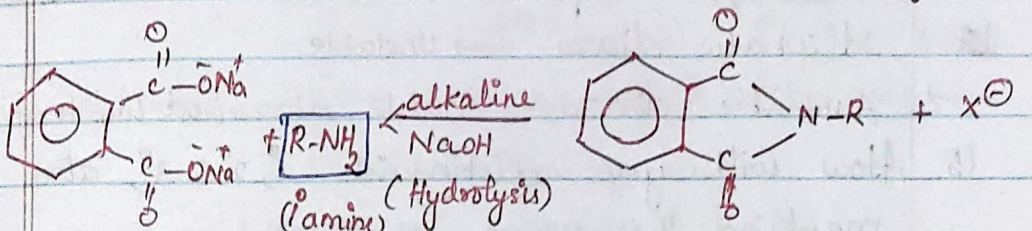
⇒ Gabriel- Pthalimide Synthesis.

11. Write complete Equation of Gabriel- Pthalimide Synthesis?



pthalimide

↓ R–X. Alkyl halide



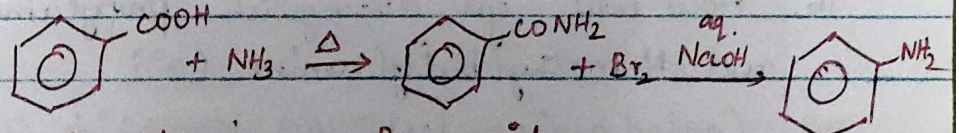
⇒ Exclusive method for preparation of primary amine.

12. How will you convert the following:-

(i) Benzoic acid to Aniline

(ii) Methanamine to ethanamine

⇒ (i)



Benzoic acid — Benzamide — Aniline

⇒ (ii) CH_3NH_2 $\xrightarrow{NaNO_2+HCl}$ CH_3OH $\xrightarrow{PCl_5}$ CH_3Cl

Methanamine

↓ Alk. NaCN

$CH_3CH_2NH_2$ $\xleftarrow[ii)\ H_3^+O]{Di\text{-}isobutyl\ AlH}$ CH_3-CN

Ethanamine

13. Reason why Aromatic primary amines cannot be prepared by Gabriel-Pthalimide Synthesis?

⇒ C-Cl bond in aromatic system involves in resonance & obtained partial double bond, it is very difficult to break.

14. How will you distinguish (i) aniline (ii) Ethyl amine

⇒ (i) Aniline (Aromatic 1° amine) & (ii) Ethylamine (aliphatic primary amine)

⇒ azo dye test with nitrous acid (HNO_2) ⇒ aliphatic will not form stable diazo

15. ⇒ Aliphatic diazo → unstable

⇒ Aromatic diazo → Stable diazo (at low temp)

15. How will you distinguish 1°, 2° & 3°, also mention the name of reagent:

⇒ Hinsberg reagent → Benzene sulphonyl chloride

⇒ 1° & 2° will form salt with benzene sulphonyl chloride (Hinsberg reagent)

⇒ 3° will not form

⇒ Salt of 1° amine will dissolve in dilute NaOH but not the salt of 2° amine

16. How will you distinguish propylamine (1°) and N-methylbutylamine (2°)

⇒ Carbylamine test (or) isocyanide test

it will answer only for 1° amines

17. Give structures of A, B, C in the following:

(i) $CH_3CH_2I \xrightarrow{NaCN} A \xrightarrow[\text{Partial hydrolysis}]{OH^-} B \xrightarrow{NaOH+Br_2} C.$

(i) $CH_3CH_2I \xrightarrow{NaCN} CH_3CH_2CN$ (A) (Ethyl cyanide)

Nucleophilic substitution of $-CN$.

$CH_3CH_2CN \xrightarrow[\text{Partial hydrolysis}]{OH^-} CH_3CH_2CONH_2$ (B)

propanamide.

$CH_3CH_2CONH_2 \xrightarrow{NaOH+Br_2} CH_3CH_2-NH_2$ (C) (Ethyl amine)

(Hoffmann bromamide degradation)

(ii) $CH_3CH_2NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273\,k]{NaNO_2+HCl} B \xrightarrow[\Delta]{H_2O/H^+} C.$

$CH_3CH_2NO_2 \xrightarrow[(Or)\ Sn/HCl]{Fe/HCl} CH_3CH_2NH_2$ (A) Ethyl amine.

(reduction of nitro)

$CH_3CH_2NH_2 \xrightarrow[273\,k]{NaNO_2+HCl} CH_3-CH_2\overset{+}{N_2}Cl^-$ (B)

(Diazotisation)

$CH_3CH_2-\overset{+}{N_2}Cl^- \xrightarrow[\Delta]{H_2O/H^+} CH_3CH_2-OH$ (C) Ethanol.

(iii) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{NaOBr} B \xrightarrow{NaNO_2/HCl} C.$

$CH_3COOH \xrightarrow[\Delta]{NH_3} \underset{(A)}{CH_3CONH_2} + H_2O$

Ethanamide.

$CH_3CONH_2 \xrightarrow{NaOBr} CH_3-NH_2$ (B) Methanamine.

$(NaOH+Br_2) \rightarrow$ Hoffmann Bromamide degradation

$CH_3-NH_2 \xrightarrow{NaNO_2/HCl} CH_3-\overset{+}{N_2}Cl^- \rightarrow CH_3OH$ (C)

(decomposes immediately)

(iv) $C_6H_5-NH_2 + (CH_3CO)_2O \longrightarrow C_6H_5NH-\overset{O}{\overset{\|}{C}}-CH_3$

(Amino group protection by acetyl)

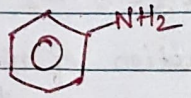
(v) $C_6H_5-\overset{+}{N_2}Cl^- \xrightarrow[(ii)\ NaNO_2/Cu,\Delta]{(i)\ HBF_4} C_6H_5\overset{+}{N_2}BF_4^- \xrightarrow[Cu,\Delta]{NaNO_2} C_6H_5NO_2$

18. An aromatic compound 'A' on treatment with aqueous ammonia and heating forms compound 'B' which on heating with Br_2 & KOH forms compound 'C' of molecular formula C_6H_7N. Write structure & Name of A, B & C.

⇒ Aromatic compound + $NH_3 \xrightarrow{\Delta}$ (B)
(A)

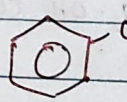
⇒ B + $\underset{\text{Hoffmann}}{NaOH + Br_2}$ C (C_6H_7N) degradation gives product with one carbon less. Therefore B having '7' carbon.

⇒ Product 'C' must be aromatic amine

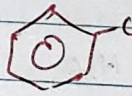

(C_6H_7N)

C ⇒ Aniline.

'B' must be amide, $C_6H_7N \leftarrow C_7H_7NO$


B ⇒ benzamide.

'A' must be benzoic acid



⇒