Amine

Assignment - solution

Q1. IUPAC Name

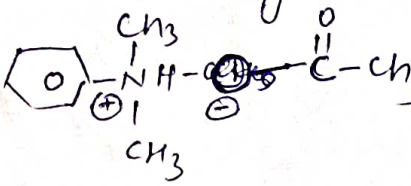
(i) Butan-2-amine

(ii) $CH_3-NH-\underset{\underset{CH_3}{|}}{CH}-CH_3$ (N-Methyl propan-2-amine)

(iii) $CH_3-\underset{\underset{CH_3}{|}}{N}-CH_3$ (N,N-Dimethylmethanamine)

(iv) N-Methyl aniline (v) N-Phenyl ethanamide

(vi) N,N,N-Trimethyl anilinium bromide

(vii)  [(N,N-Dimethyl-N-phenyl amino) ethanoate]

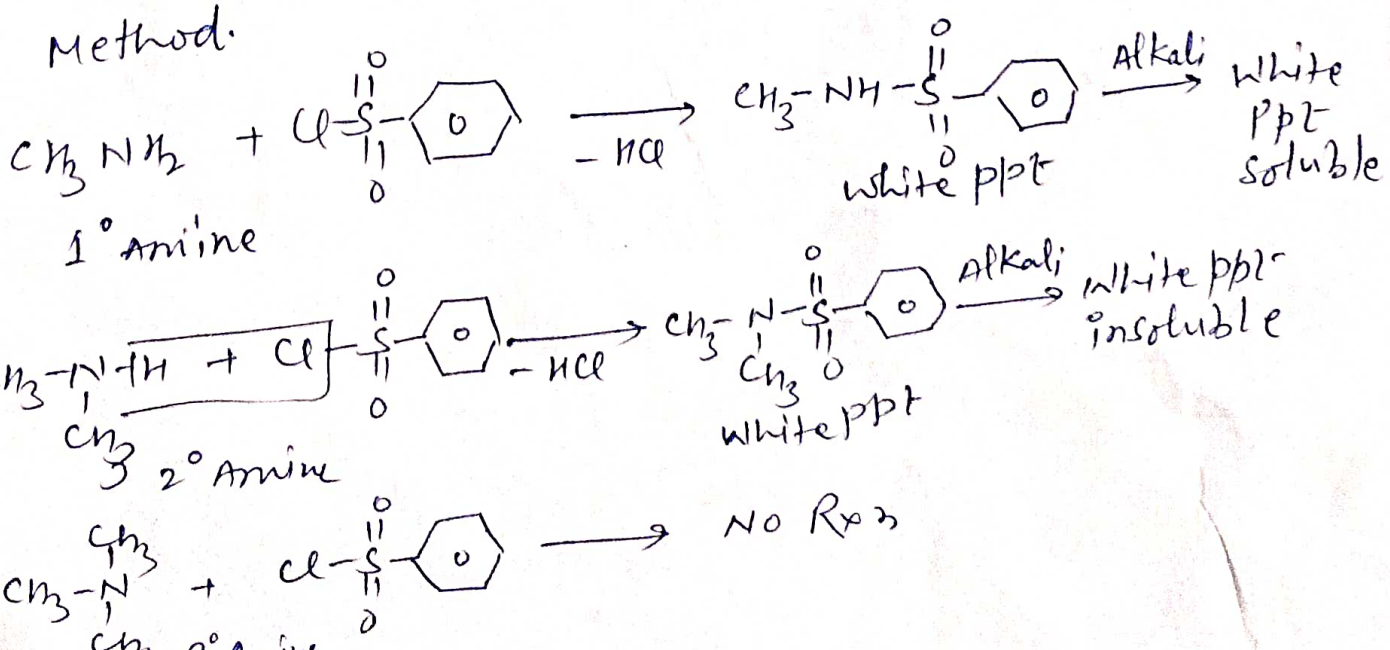
(viii) p-Methoxy aniline

(ix) Hexamethylenediamine (x) N-phenyl aniline

(xi) Phenyl hydroxyl amine

Q2. Name Rxn (Do this from class notes)

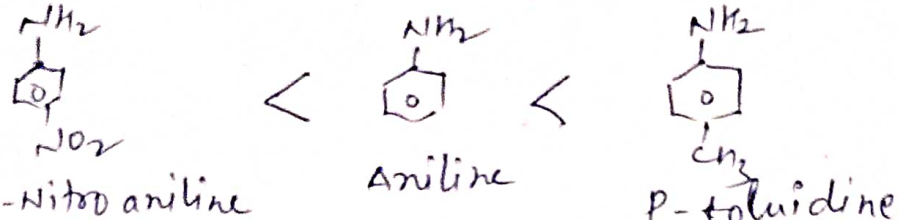
Q3 1°, 2° & 3° Amine can be identify by Heinsberg's Method.



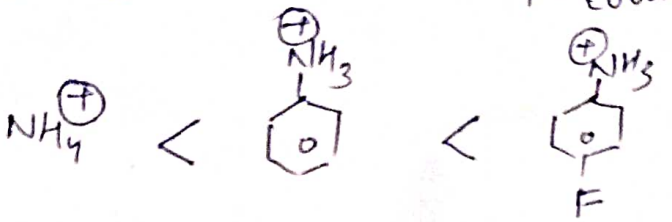
Q4. (i) $NH_3 < C_2H_5NH_2 < (C_2H_5)_3N < (C_2H_5)_2NH$

(ii)

$$C_2H_5NH_2 < CH_3NH_2 < (C_2H_5)_2NH < (C_2H_5)_3N$$

(iii) 

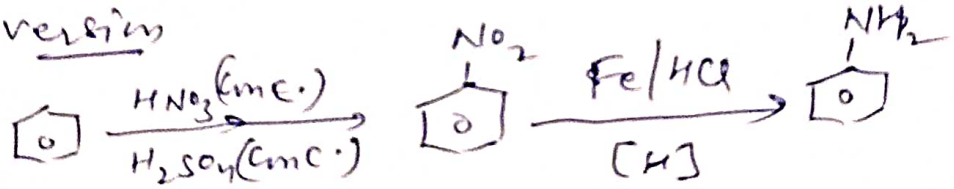
p-Nitro aniline < Aniline < p-toluidine

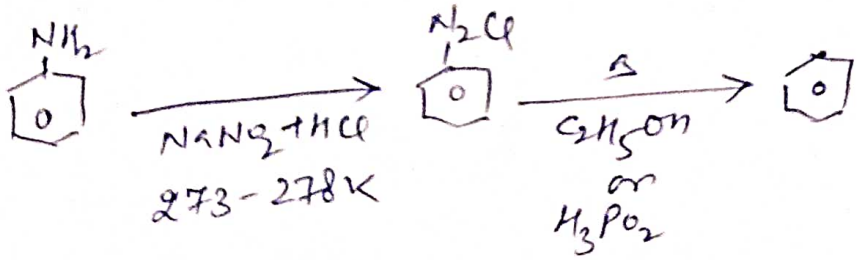
(iv) 

Q5 (i) $CH_3CH_2Cl + NH_3(excess) \longrightarrow CH_3-CH_2NH_2$

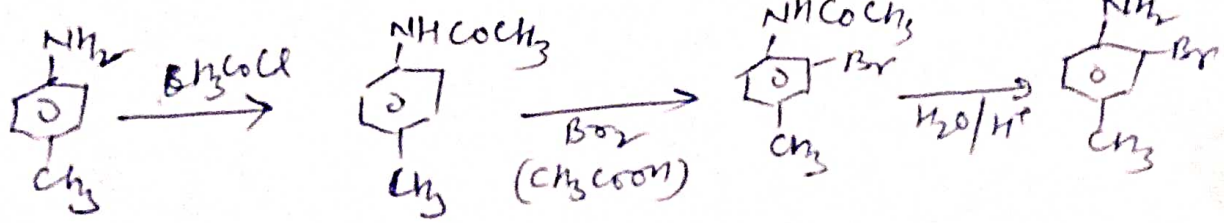
(ii) $CH_3CH_2Cl(excess) + NH_3 \longrightarrow CH_3CH_2NH_2$ (1° amine) $\xrightarrow{CH_3CH_2Cl} (CH_3CH_2)_2NH$ (2° amine) $\xrightarrow{CH_3CH_2Cl} (CH_3CH_2)_3N$ (3° amine) $\xrightarrow{CH_3CH_2Cl} [(CH_3CH_2)_4N^+]Cl^-$ (4° amine salt)

Q6 Conversion

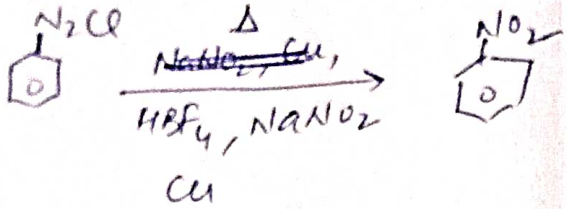
(i) 

(ii) 

(iii) $CH_3COOH \xrightarrow{LiAlH_4} CH_3CH_2OH \xrightarrow{NH_3} CH_3CH_2NH_2$

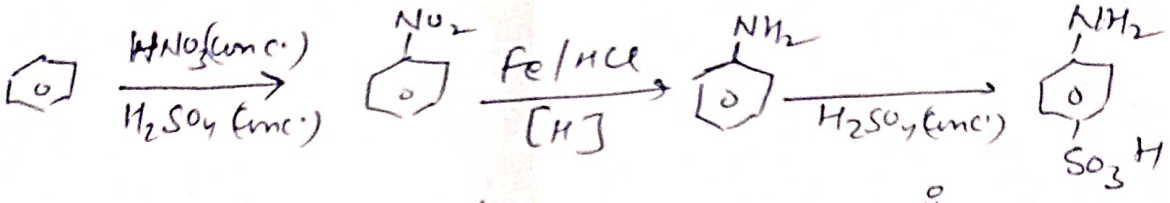
(iv) 

(v) $CH_3Br \xrightarrow{KCN} CH_3CN \xrightarrow{LiAlH_4} CH_3CH_2NH_2$

(vi) 

(vii) $CH_3CH_2NH_2 \xrightarrow{HONO} CH_3CH_2OH \xrightarrow{KMnO_4/H^+} CH_3COOH$

$CH_3COOH \xrightarrow{\Delta,\ NH_3} CH_3-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[KOH]{Br_2} CH_3NH_2$

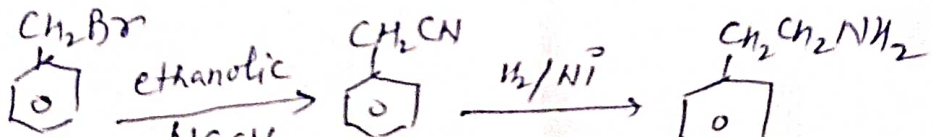
(viii) 

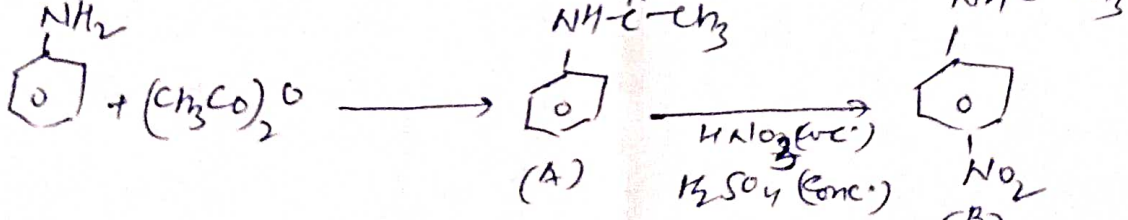
(ix) $CH_3CH_2CH_2CH_2CH_2CN \xrightarrow{OH^-/H_2O_2} CH_3CH_2CH_2CH_2CH_2-\overset{O}{\overset{\|}{C}}-NH_2$

$CH_3CH_2CH_2CH_2CH_2NH_2 \xleftarrow[Br_2]{KOH}$

Q7 $CH_3CH_2I \xrightarrow{NaCN} CH_3CH_2CN$ (A) $\xrightarrow[\text{Partial Hydrolysis}]{OH^-} CH_3CH_2-\overset{O}{\overset{\|}{C}}-NH_2$ (B)

$CH_3CH_2NH_2$ (C) $\xleftarrow[Br_2]{NaOH}$

Q8 (i) 

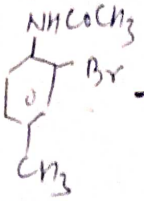
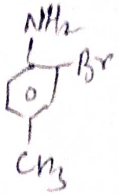
(ii) 

(iii) $C_6H_5N_2Cl \xrightarrow{CuCN} C_6H_5CN \xrightarrow{H_2O/H^+} C_6H_5COOH$

(A) (B)

(iv) $C_6H_5NO_2 \xrightarrow{Fe/HCl}$  $\xrightarrow{H_2SO_4}$ 

(A) (B)

(v)  $\xrightarrow{CH_3COCl}$  $\xrightarrow{Br_2/Fe}$  $\xrightarrow{H_2O/H^+}$ 

(A) (B) (C)

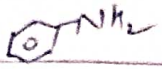
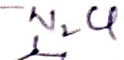
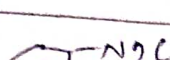
Q9 Distinguish Test

(i)

Test	Methylamine 1° amine	Dimethylamine 2° amine
Hinsberg's Test	Methylamine + Benzene Sulphonyl Chloride → White ppt which is Soluble in Alkali	Dimethylamine + Benzene Sulphonyl Chloride → White ppt insoluble in alkali

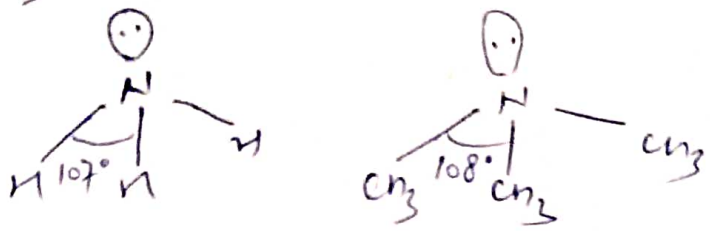
(ii)

Test	Secondary Amine	Tertiary amine
Hinsberg's Test	Secondary amine + Benzene Sulphonyl chloride ↓ White ppt insoluble in alkali	Tertiary amine + Benzene sulphonyl chloride ↓ No Reaction

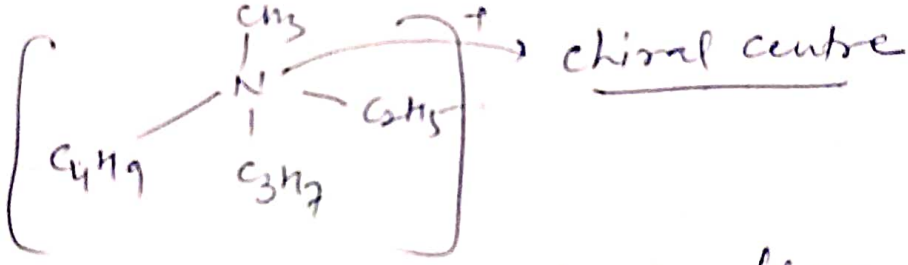
(iii) Test	Ethylamine $C_2H_5NH_2$	Aniline 
Azo dye Test	Ethylamine + Benzene diazonium Chloride ↓ No Rxn	Aniline + Benzene diazonium Chloride $\xrightarrow[\text{Ice Bath}]{}$ Yellow dye
(iv) Test	Aniline 	Benzylamine 
Azo dye Test	Aniline +  ↓ Ice Bath Yellow dye	Benzylamine +  ↓ Ice Bath No Rxn
(v) Test	Methylamine	Methanol
Isocyanide Test	Methylamine + $CHCl_3$ + KOH ↓ Offensive Smell	Methanol + $CHCl_3$ + KOH ↓ No change
(vi) Test	Methylamine 1° Amine	N,N-Dimethylamine 2° Amine
Hinsberg's Test	Methylamine + Benzenesulphonyl Chloride ↓ White ppt Soluble in alkali	N,N-Dimethylamine + Benzene Sulphonyl Chloride ↓ White ppt insoluble in alkali

(vii) Same distinguish test as part (V)

Q10 (i) The C-N-C bond angle in trimetayl amine is 108° as trimetayl amine has same structure as NH_3 acc. to VSEPR i.e. pyramidal shape



(ii) Quaternary ammonium salt having four different alkyl group are optically active as Nitrogen of Quaternary ammonium salt act as chiral centre.



(iii) Alkyl amine are more basic than NH_3 as alkyl group has +I - inductive effect which increases the electron density over the nitrogen in alkyl amine.

(iv) Aniline can't be prepared by Gabriel phthalimide synthesis, as this reaction is carried out acc. to Nucleophilic substitution Rxn which aryl halide can't carried out due to Resonance.

(v) Gabriel phthalimide synthesis takes place according to S_N2 mechanism that's why primary amine can be prepared by this method.

(vi) Ethyl amine is soluble in water as it can form hydrogen bond with water but aniline can't because phenyl group is bulky group which hinder the formation H-bond with water.

(vii) Aniline is soluble in HCl as aniline is base + HCl is acid both reacts to form salt.

(viii) Amines have lower boiling point as compared to alcohol having comparable molecular mass because strength of intermolecular Hydrogen bond in alcohol is more than that of amine as oxygen is more electronegative than Nitrogen.

(ix) Because 1° Amine form extensive inter-molecular H-bonding than 2° & 3° Amines

(x) As Aniline is less basic than Ammonia because in Aniline lone pair of Nitrogen get delocalised due to resonance.

(xi) Aniline doesn't undergo Friedel craft reaction because Aniline is basic in nature while friedel craft reagent anhyd. $AlCl_3$ is acid which reacts together to form salt.

(xii) Aniline readily form 2,4,6-Tribromoaniline on reaction with bromine water because $-NH_2$ group in aniline is highly activating group.

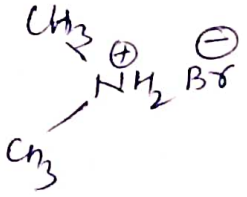
(xiii) Sulphanilic acid is soluble in water because it is ionic in nature due to the formation of zwitter ion.

(xiv) Methyl amine being basic in nature which reacts with water to form hydroxide ion which upon reacts with $FeCl_3$ to form $Fe(OH)_3$ ppt.

(xv) Diazonium salt of aromatic amines are more stable due to resonance.

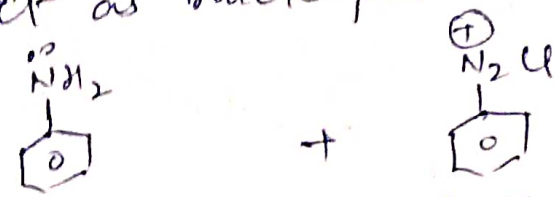
(xvi) Do this Ques from class notes.

Q11 Amines act as Nucleophile because in amine, Nitrogen contain lone pair of electrons which makes amine electron rich.

example $CH_3\ddot{N}H_2 + CH_3Cl \longrightarrow$ 

Q12 Diazonium ion act as electrophile because in Diazonium ion, Nitrogen has +ve charge so, it is electron deficient.

example which shows that diazonium salt act as nucleophile is azo dye test

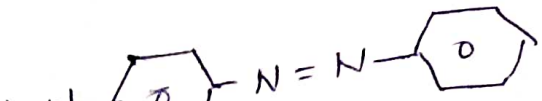


Aniline
Nucleophile

Benzene diazonium chloride (electrophile)

↓ Ice bath

(coupling Rxn)



Yellow Dye

Q13

A, B, C

C_3H_9N

Isomeric amine

Benzene Sulphonyl Chloride

Product which is soluble in NaOH

1° Amine

Benzene Sulphonyl Chloride

Product which is insoluble in NaOH

2° Amine

Benzene Sulphonyl Chloride

No Rxn

3° Amine

∴ A = $CH_3CH_2CH_2NH_2$

B = $CH_3-\underset{\underset{C_2H_5}{|}}{NH}$

C = $CH_3-\underset{\underset{CH_3}{|}}{N}-CH_3$

Q14 (A) C_2H_3N $\xrightarrow{Ni/H_2}$ (B) $\xrightarrow[\text{(Nitrous Acid)}]{HONO}$ C_2H_5OH

(B) $\xrightarrow{CHCl_3 + NaOH}$ Foul smelling (C)

CH_3CN (A) $\xrightarrow{H_2/Ni}$ $CH_3CH_2NH_2$ (B) $\xrightarrow{HONO}$ CH_3CH_2OH

(B) $\xrightarrow{CHCl_3 + NaOH}$ CH_3CH_2NC (Ethyl isocyanide) foul smell (C)

Q15 (A) $C_3H_6O_2$ $\xrightarrow[\Delta]{NH_3}$ (B) $\xrightarrow[NaOH]{Br_2}$ C C_2H_7N $\xrightarrow[NaOH]{CHCl_3}$ D (foul smell)

CH_3CH_2COOH (A) $\xrightarrow[\Delta]{NH_3}$ $CH_3CH_2CONH_2$ (B) $\xrightarrow[NaOH]{Br_2}$ $CH_3CH_2NH_2$ (C)

(C) $\xrightarrow{CHCl_3 + NaOH}$ CH_3CH_2NC foul smell (D)