Compounds Containing Nitrogen

Section-I: Nitro Compounds

13.0 DEFINITION

These are nitro derivatives of alkane or arene obtained by replacement of one or more hydrogen atoms from alkanes or arene by same number of nitro (-NO₂) group.

Represented by R–NO $_2$, R $_2$ CH–NO $_2$, R $_3$ C–NO $_2$.

It may be noted that $-NO_2$ group is ambident group, because it can attack on carbon through nitrogen as well as oxygen. When it can attack through nitrogen produces $R-NO_2$ (nitro alkane) while it can attack through oxygen produces R-O-N=O (alkyl nitrite). The chemical properties of nitro alkane and alkyl nitrite are different. Nitro alkanes are more stable than alkyl nitrite.

13.1 PREPARATION METHODS

- From nitration of alkanes: Industrially nitroalkane can be-prepared by two ways.
- a) From vapour phase nitration of alkane: Alkane are heated with cone. nitric acid at 423 K to 698 K to give nitroalkane. Nitration of alkane is substitution reaction in these reactions hydrogen atom from alkanes are replaced by NO₂ group. When alkanes are passed over vapours of nitric acid at 723 K gives nitro alkane. Methane does not undergoes nitration

$$R-H+HO-NO_2 \xrightarrow{721K} R-NO_2+H_2O$$

The alkanes have more than two carbons, there is always a possible that the C–C bond may break at high temperature and mixture of nitroalkanes is formed.

Vapours of nitric acid is passed over propane at 723 K gives 2–nitro propane (33%), 1–nitro propane (32%), nitro ethane (29%) nitro methane (6%).

$$CH_3 - CH_2 - CH_3 + HNO_3 \xrightarrow{723K}$$

$$CH_{3} - CH_{2} - NO_{2} + CH_{3} - NO_{2} + H_{2}O$$

b) Liquid phase nitration: When alkane are heated with conc. HNO₃ under pressure at 413 K gives polynitro compounds.

$$\begin{array}{ccc} \mathrm{CH_3-CH_3+HNO_3} \xrightarrow{413\,\mathrm{K} \\ \mathrm{U.P.}} & \mathrm{CH_2-CH_2+2H_2O} \\ \mathrm{|} & \mathrm{|} \\ \mathrm{NO_2} & \mathrm{NO_2} \end{array}$$

1, 2-dinitro ethane

2) From alkyl halides and AgNO₂: When alkyl halides are heated with silver nitrite gives nitro alkane.

$$R-X + AgNO_2 \xrightarrow{\Delta} R-NO_2 + AgX$$

3) From alkyl halides and NaNO₂ or KNO₂: When alkyl halides are heated with sodium nitrite or potassium nitrite in the presence of dimethyl sulphoxide solvent or N, N-dimethyl formamide gives nitro alkane.

$$R-X + NaNO_2 \xrightarrow{\text{dimethyl sulphoxide}} R-NO_2 + NaX$$

4) From salt of ∞ -halocarboxylic acid:

Cl–CH₂–COONa + NaNO₂
$$\xrightarrow{\text{Boil}}$$
 O₂N–CH₂ – COONa + NaCl 2–nitro sodium ethanoate

$$O_2N-CH_2-COONa \xrightarrow{H_2O}$$

5) From tertiary alkyl amines: Tertiary alkyl amines are oxidised by KMnO₄ give tertiary nitro alkane

$$\begin{array}{c} R \\ | \\ R - \stackrel{|}{C} - NH_2 + 3(O) \xrightarrow{\quad KMnO_4 \quad} R_3C - NO_2 + H_2O \\ | \\ R \end{array}$$

Tertiary alkyl amines Tertiary nitro alkane

2-nitropropane

e.g.
$$CH_3$$

$$CH_3 - C - NH_2 + 3(O) \xrightarrow{KMnO_4} CH_3$$

t-butyl amine

$$\begin{array}{c} \operatorname{CH_3} \\ \operatorname{CH3} - \operatorname{C} \\ -\operatorname{NO_2} + \operatorname{H_2O} \\ \operatorname{CH_3} \end{array}$$

2-methyl 2-nitro propane

6) From acid hydrolysis of α -nitroalkene: When α -nitroalkene on acid hydrolysis gives nitroalkane, aldehyde or ketone.

e.g.
$$CH_3$$

$$CH_3 - C = CH - NO_2 + H_2O \xrightarrow{H^+}$$
2-methyl 1-nitro prop-1-ene

$$\begin{array}{c}
O \\
\parallel \\
CH_3 - NO_2 + CH_3 - C - CH_3
\end{array}$$

- 7) From oxidation of oxime: Aldoxime or ketoxime are oxidised by trifluoroperoxy acetic acid gives primary and secondary nitroalkane repectively.
- a) Oxidation of aldoxime: Aldoximes are oxidised by trifluoroperoxy acetic acid gives primary nitroalkane.

$$\begin{array}{c} H \\ R-C = NOH + (O) \xrightarrow{trifluoroperoxy \\ acetic \ acid} \end{array} \longrightarrow \\ R-CH_2 - NO_2 \\ 1^{\circ} \ nitro \ alkane \end{array}$$

e.g.
$$CH_3 - C = NOH + (O) \xrightarrow{\text{trifluoroperoxy} \atop \text{acetic acid}} CH_3 - CH_2 - NO_2$$

b) Oxidation of ketoxime: Ketoximes are oxidised by trifluoroperoxy acetic acid gives secondary nitroalkane.

$$R \xrightarrow{\mid} R - C = NOH + (O) \xrightarrow{\text{trifluoroperoxy} \atop \text{acetic acid}} R - C - NO_{2}$$

$$\downarrow H$$

$$2^{\circ} - \text{nitro alkane}$$

e.g.
$$CH_3$$

$$CH_3 - C = NOH + (O) \xrightarrow{\text{trifluoroperoxy} \atop \text{acetic acid}} CH_3$$

$$CH_3 - CH - NO_2$$

13.2 CHEMICAL PROPERTIES

- 1) Reduction:
- a) Reduction by using Sn + conc.HCl or Fe + cone. HCl or Zn + cone. HCl or LiAIH₄ or catalytic hydrogenation:

$$R-NO_2 + 6 [H] \xrightarrow{Sn + cone. HCl} R-NH_2 + 2H_2O$$

b) Catalytic hydrogenation by using Ni or Pt or Pd at 453K:

$$R-NO_2 + 3H_2 \xrightarrow{Ni 453 K} R-NH_2 + 2H_2O$$

c) Reduction by using Zn + NH₄Cl: Nitroalkanes are reduced by Zn + NH₄Cl gives N-alkyl hydroxylamine.

$$R - NO_2 + 4[H] \xrightarrow{Zn + NH_4Cl} R-NH-OH + H_2O$$

N-alkyl hydroxyl amine

e.g.
$$CH_3 - NO_2 + 4(H) \xrightarrow{Zn + NH_4Cl} \rightarrow$$

$$CH_3 - NH - OH + H_2O$$
N-methyl hydroxyl amine

c) Reduction by using SnCl₂ + HCl (stannous chloride and HCl):

$$R - CH_2 - NO_2 + 4 [H] \xrightarrow{SnCl_2 + HCl}$$

$$R - CH_2 - NH - OH + R - CH = NOH$$

$$N-alkyl hydroxyl amine aldoxime$$

e.g.
$$CH_3 - CH_2 + NO_2 + 4H \xrightarrow{SnCl_2 + HCl} \rightarrow$$

 $CH_3 - CH_2 - NH - OH + CH_3 - CH = N - OH$
 $N - ethyl hydroxyl amine$ acetaldoxime

- 2) Acid hydrolysis or Distinction test between 1°, 2°, 3° nitro alkane or reaction with dil. HCl or dil. H,SO₄
 - a) Primary nitro alkane: Primary nitroalkane on acid hydrolysis gives carboxylic acid and hydroxyl amine.

$$\begin{array}{c} R-CH_{2}-NO_{2}+H_{2}O \xrightarrow{\text{dil.HCl}} \\ \\ R-COOH+NH_{2}OH \\ \\ \text{e.g.} \ CH_{3}-CH_{2}-NO_{2}+H_{2}O \xrightarrow{\text{dil.HCl}} \\ \end{array} \\ \rightarrow \end{array}$$

b) Secondary nitroalkane: These on acid hydrolysis gives ketones.

$$2 R_{2}CH - NO_{2} + H_{2}O \xrightarrow{\text{dil.HCl}} \Delta$$

$$2R_{2}C = O + N_{2}O + 2H_{2}O$$
e.g.
$$2(CH_{3})2 CH - NO2 + H_{2}O \xrightarrow{\text{dil.HCl}} \Delta$$
acetone

c) Tertiary nitroalkane: They do not undergoes acid hydrolysis

$$R_3C - NO_2 \xrightarrow{\text{dil.HCl}} No \text{ reaction}$$

- 3) Halogenation: Primary and secondary nitroalkane are readily halogenated in alkaline medium. The α –H atom is replaced by chlorine or bromine atom.
- a) Primary nitro alkane: When 1° –nitroalkane reacts with chlorine in alkaline medium. The α H atom of 1° –nitro alkane is / are replaced by chlorine to give di or trihalo derivatives.

e.g. i)
$$CH_3-NO_2 + 3 Cl_2 + NaOH \longrightarrow$$

$$Cl_3C-NO_2 + 3NaCl + 3H_2O$$
chloropicrin (insecticide)
ii) $CH_3 - CH_2-NO_2 + 2Br_2 + 2 NaOH$

$$\longrightarrow CH_3 - CBr_2 - NO_2 + 2 NaBr + 2H_2O$$

dibromo nitro ethane

b) Secondary nitroalkane:

They gives only monohaloderivatives

$$\begin{array}{c} \text{R-CH-NO}_2 + \text{Br}_2 + \text{NaOH} & \longrightarrow \\ \mid \\ \text{R} \end{array}$$

$$\begin{array}{c} \operatorname{Br} \\ | \\ \operatorname{R-C} \\ | \\ \operatorname{R} \end{array} - \operatorname{NO}_2 + \operatorname{NaBr} + \operatorname{H}_2\operatorname{O}$$

e.g.
$$CH_3$$

$$CH_3 - CH - NO_2 + Br_2 + NaOH \longrightarrow$$

$$Br$$

$$CH_3 - C - NO_2 + NaBr + H_2O$$

$$CH_3$$

2-bromo 2-nitropropropane

c) Tertiary nitro alkane:

They do not react with halogens

$$R_3C-NO_2 + Cl_2 + NaOH \longrightarrow No reaction$$

4) Reaction with nitrous acid (Victor Meyers's test):

Primary, secondary and tertiary nitro alkane reacts differently with nitrous acid.

a) Primary nitroalkane: They react with nitrous acid gives nitrolic acid, which is then treated with NaOH gives red colour sodium salt.

$$\begin{array}{c} H \\ | \\ R-C \\ | \\ NO_2 \end{array} - H + HO-N = O \longrightarrow$$

$$\begin{array}{c} \mathbf{H} \\ | \\ \mathbf{R} - \mathbf{C} \\ | \\ \mathbf{NO}_2 \end{array} - \mathbf{N} = \mathbf{0} + \mathbf{H}_2 \mathbf{O}$$

nitrolic acid (nitro form)

Nitrolic acid tautomerise to form blue coloured aci form of nitrolic acid.

$$\begin{array}{ccc}
H \\
R - C - N = O
\end{array}$$
tautomerise
$$\begin{array}{ccc}
R - C - N = O \\
\downarrow N \\
N \\
O & HO
\end{array}$$

$$\begin{array}{cccc}
O \oplus \\
O \oplus \\
O \oplus
\end{array}$$

nitroform of nitrolic acid Aci form (Blue colour) Aci form of nitrolic acid react with NaOH gives red colour sodium salt of nitrolic acid.

$$R-C-N=O$$
 + NaOH \longrightarrow $R-C-N=O$
 NaO
 NaO
 O^{\oplus}

Red colour sodium salt of nitrolic acid

b) Secondary nitroalkane: They react with nitrous acid gives blue coloured nitrosonitroalkane or pseudonitrol, which no more contain α –H atom hence do not dissolve in NaOH and blue colour is retained.

$$\begin{array}{c}
R \\
R-C \\
NO,
\end{array}$$

$$\begin{array}{c} R \\ R-C \\ NO_2 \end{array} - N = O \xrightarrow{NaOH} Bluecolour$$

Blue colour

(Pseudonitrol or nitroso nitro alkane)

Tertiary nitroalkane: They do not react with nitrous acid because of absence of α –H atom.

$$R_3C - NO_2 + HNO_2 \longrightarrow No reaction.$$

5) Acidic nature of α –H atom (Action of alkali).

The α -H atom in aliphatic primary and secondary nitro alkane is acidic due to electron withdrawing nature of nitro group.

In strong alkaline medium they behave as acid and form salt.

The acidic nature is explain on the basis of tautomerism. primary and secondary nitro alkane tautomerise to form nitronic acid. Tertiary nitro alkane do not have α –H atom and therefore they do not exhibit tautomerism.

$$R-CH_2-N \xrightarrow{\oplus} O$$
 tautomerise $R-CH=N \xrightarrow{O} OH$

Nitroform

nitronic acid

(isonitroform or aci form)

The equilibrium is entirly shifted towards nitroform due to resonance stabilization of nitro group.

The aci form or isonitro form is weak acid iv) dissolve in aqueous NaOH to form salt.

$$R-CH = NOH$$
 + NaOH $-H_2O$

Aci form

$$R-CH=N$$
 O^{Θ}

Sodium salt of nitronic acid

Application: When sodium salt of primary and v) secondary aci form of nitronic acid is treated with 50% H₂SO₄ at room temperature gives aldehydes and ketones respectively. This reaction is known as Nef - Carbonyl synthesis.

$$2R-CH=N ONa + 2H_2SO_4 R.T.$$

1° sodium salt of aci form of nitronic acid $2R-CHO+N_2O+2NaHSO_4+H_2O$

$$2R - \overset{R}{\overset{\mid}{C}} = \overset{\oplus}{\overset{\mid}{N}} \overset{ONa}{\overset{}{O}} + 2H_2SO_4 \xrightarrow{\qquad R.T.}$$

2° sodium salt of aci form of nitronic acid $2R-CO-R + N_2O + 2NaHSO_4 + H_2O$ Ketone

e.g.

i)
$$2CH_3-CH=N$$
 $O\Theta + 2H_2SO_4$ $R.T.$

sodium salt of aci form of methyl nitronic acid $2CH_3 - CHO + N_2O + 2 NaHSO_4 + H_2O$ acetaldehyde

ii)
$$2CH_3 - C = N$$
 ONa
 OOO
 OOO
 OOO
 OOO
 OOO
 OOO

sodium salt of aci form of dimethyl nitronic acid $2CH_{3} - CO-CH_{3} + N_{2}O + 2NaHSO_{4} + H_{2}O$

- Condensation with aldehydes and ketones:
- It is characteristic reaction of nitroalkane 1) containing α –H atom.
- 2) Primary and secondary nitroalkane containing α –H atom condense with aldehyde or ketone in the phesence of ethanolic KOH gives hydroxy nitro derivatives.
- The reaction is quite similar to aldol condensation 3) reaction and proceeds the formation of carbanion.

$$\begin{array}{ccc} & OH \\ H-C & -CH_2-NO_2 & \xrightarrow{-H_2O} CH_2 = CH-NO_2 \\ & & H \end{array}$$

2-nitro ethanol

1– ni tro ethene

Section-II: Amines

13.0 Definition:

These are alkyl or aryl derivatives of ammonia obtained by replacement of one or more hydrogen atoms from ammonia by alkyl or aryl groups. These are represented as R-NH₂, R₂NH, R₃N. All amines are represented by general formula C_nH2_{n+3}.

13.1 ISOMERISM

Primary amines: They shows chain, position, optical isomerism themselves and functional isomerism with 2° and 3° amines. Total number of primary amines $I = 2^{n-2}$.

Secondary amines: They shows optical, metamerism, themselves and functional isomerism with 1° and 3° amines.

Tertiary amines: They shows optical, metamerism, themselves and functional isomerism with 1° and 2° amines. Total number of primary, secondary and tertiary amines $I = 2^{n-1}$.

- e.g. 1) C_1H_2N (2-isomers)
 - a) CH₂CH₂NH₂ ethyl amine
 - b) (CH₂),NH dimethyl amine
 - 2) C_3H_9N (4-isomers. 2 primary, 1 secondary, 1 tertiary)
 - a) CH₂CH₂CH₂NH₂ n-propyl amine
 - b) (CH₂)₂CHNH₂ isopropyl amine
 - c) CH₂NHC₂H₅ ethyl methyl amine
 - d) (CH₂)₂N tri methyl amine
 - 3) $C_4H_{11}N$ (8-isomers. 4 primary, 3 secondary, 1 tertiary)

1° aminesa -

- a) CH₂CH₂CH₂CH₂NH₃ n-butyl amine
- b) (CH₃)₂CHCH₂NH₂ isobutyl amine
- c) CH₃CH₂CHNH₂CH₃ secondary butyl amine (optically active)
- d) (CH₂)₂CNH₂ t-butyl amine

2° amines -

- a) $CH_3NHCH_2CH_2CH_3$ methyl n–propyl amine
- b) CH₃NHCH(CH₃)₂ methyl iso-propyl amine
- c) CH₃CH₂NHCH₂CH₃ diethyl amine **3° amines**
- a) $(CH_3)_2NC_2H_5$ ethyl dimethyl amine

13.2 STRUCTURE OF AMINES

In all amines nitrogen atom is sp³ hybridised state and molecule has pyramidal structure. Each three sp³ hybrid orbital of nitrogen overlap with orbitals of hydrogen or carbon depending upon types of amine (1°, 2°, 3°). The fourth orbital of nitrogen in all amines containing lone pair of electrons. Due to presence of lone pair of electrons the bond angle is less than 109° 5'. Trimethyl amine has bond angle 108°.

13.3 PREPARATION METHODS

1. Hoffmann ammonolysis of alkyl halides orbenzyl halide:

When excess of alkyl halide is heated with alcoholic solution of ammonia in sealed tube at 373K, gives mixture of primary amines, secondary amines, tertiary amines and quaternary ammonium salt.

e.g. When excess of methyl iodide is heated with alcoholic solution of ammonia in sealed tube at 373K, gives methyl amine, dimethyl amine, trimethyl amine and tetramethyl ammonium iodide.

$$R-I + NH_3 \xrightarrow{373K} R-NH2 + HI$$

$$R-NH_2 + R-I \xrightarrow{373K} R_2NH + HI$$

$$R_2NH + R-I \xrightarrow{373K} R3N + HI$$

$$R_3N + R-I \xrightarrow{373K} R_4 N^+I^-$$

When methyl iodide is heated with excess of alcoholic ammonia, gives methyl amine.

$$CH_3-I + NH_3 \xrightarrow{373K} CH_3-NH_2 + HI$$
excess methyl amine

Limitations:

- i) In this method 1°, 2°, 3° amines are formed along with quaternary ammonium salt. Hence, separation of these is difficult.
- ii) This method is not good for the preparation of aryl amines, as aryl halides are less reactive than alkyl halides in nucleophilic substitution reaction.
- iii) If excess of alkyl halide is used, quaternary ammonium salt is main product.
- iv) If excess of ammonia is used, formation of 2° and 3° amines is suppressed but only upto certain extent.

- v) The purity of amines obtained in this method is very low.
- vi) Hofmann's fails ammonolysis of 3° alkyl halide because 3° alkyl halides undergo dehydrohalogenation.

Thus the reactivity of R-X is R-I > R-Br > R-Cl.

Tertiary butyl amine can not be prepared by this method.

$$\begin{array}{c} \operatorname{CH_3} \\ | \\ \operatorname{CH_3} - \operatorname{C} - \operatorname{X} \\ | \\ \operatorname{CH_3} \end{array} + \operatorname{NH_3} \xrightarrow{373 \operatorname{K} \atop \text{alcoholic}} \rightarrow$$

$$CH_3 \\ CH_3 - C = CH_2 + NH_4X$$

2. From reduction of oximes:

When aldo or keto oximes are reduced by Na + ethanol or LiAlH₄ or Zn + CH₃COOH or Na. Hg + H₂O gives primary amine.ln which oxime group (=NOH) is converted into $-NH_2$ group.

= N-OH + 4 [H]
$$\xrightarrow{\text{Na+ethanol}}$$
 -NH₂ + H₂O

- 3. By reduction of cyanides or nitriles (Mendius reduction): Cyanides are reduced by
- i) Ni or Pt or Pd at 453K
- ii) Na + ethanol or LiAlH₄ gives primary amines.
 In which -C

 N group is converted into -CH₂ -NH₂ group

a) Reduction by using Na + ethanol:

e.g. When nitrile is reduced by Na + ethanol, gives amine.

$$R-C \equiv N + 4 [H] \xrightarrow{Na + ethanol} R-CH_2-NH_2$$
 alkyl cyanide amine

b) Catalytic hydrogenation by using Ni or Pt or Pd at 453K

$$R-C \equiv N + 2H2 \xrightarrow{Ni \cdot 453K} R-CH_2-NH_2$$

cyanide primary amine

Note:

i) Sn + conc. HCl, Na.Hg + H₂O, Fe + cone. HCl, Zn + cone. HCl, does not reduces >C = C< or -C = C- bond.

- ii) H_2 + Ni reduces > C = C<, -C = C-, $-NO_2$, = NOH, -C=N
- 4. Reduction of nitroparaffins:

When nitroparaffins are reduced by Sn or Fe or Zn + conc. HCl or Zn + conc. H₂SO₄ or LiAlH₄ or H₂ and Ni at 453K, gives primary amines. In which –NO₂ group is converted into –NH₂ group.

$$R-NO_2 + 6 [H] \xrightarrow{Sn + conc. HCl} R-NH_2 + 2H_2O$$

Catalytic hydrogenation by using Ni or Pt or Pd at 453K:

$$R-NO_2 + 3H_2 \xrightarrow{Ni 453K} R-NH_2 + 2H_2O$$

Note: Reduction with Fe + cone. HCl is preferred because FeCl₂ formed gets hydrolysed to release HCl during reaction. Thus only small amount of HCl is required to initiate the reaction.

5) Reduction of amide: Amides are reduced by LiAIH₄ or Na + C₂H₅OH to get primary amine.

$$\begin{array}{c} O \\ \parallel \\ R- \stackrel{\text{i) LiAlH}_4}{C-NH_2} + 4[H] \stackrel{\text{i) LiAlH}_4}{\longrightarrow} \\ R-CH_2-NH_2 + H_2O \end{array}$$

$$Ph - C - NH_2 + 4[H] \xrightarrow{Na + C_2H_3OH} Ph - CH_2 - NH_2 + H_2O$$

6. Hofmann's bromide degradation reaction:

By this method the amide (-CONH₂) group is converted in to primary amine (-NH₂).

When amides are heated with bromine and aqueous or alcoholic KOH or NaOH Or KOBr or NaOBr give pure primary amine.

In the degradation method migration of alkyl or aryl group takes place from carbonyl carbon of the amide to nitrogen atom. The amine so formed containing one carbon atom less than amide.

$$R-CONH_{2} + Br_{2} + 4KOH \xrightarrow{\text{alcohol}} \Lambda$$

$$R-NH_{2} + 2 KBr + K_{2}CO_{3} + 2H_{2}O$$
e.g.
$$CH_{3}-CONH_{2} + Br_{2} + 4KOH \xrightarrow{\text{alcohol}} \Lambda$$

$$CH_{3}-NH_{2} + 2KBr + K_{2}CO_{3} + 2H_{2}O$$

7) Gabriel phthalimide synthesis:

This method involves the following three steps.

- i) Phthalimide is reacted with ethanolic KOH to give potassium phthalimide.
- ii) Potassium phthalimide is reacted with R-X to

give N-alkyl phthalimide.

The N-alkyl phthalimide is hydrolysed by dil. HCl to give pure primary amine.

$$\begin{array}{c}
\begin{array}{c}
CO\\ CO
\end{array}
\end{array}$$

$$\begin{array}{c}
NK+H_2CO\\ CO
\end{array}$$

Step – (ii)

potassium phthalimide

N-alkyl phthalimide

$$\begin{array}{c}
\begin{array}{c}
CO\\
CO
\end{array}
N-R + 2H-OH \xrightarrow{\text{dil.HCl}} \\
COOH \\
COOH
\end{array}
+ R-NH_2$$

phthalic acid primary amine

Advantages: Only pure 1º aliphatic amine can be prepared from alkyl halides by Gabriel synthesis, because alkyl halides undergoes nucleophilic substitution reaction. The reactivity of R-X is $1^0 > 2^0 > 3^0$.

Limitation: Aromatic primary amine i.e (aniline cannot be prepared by this method because Ar-X do not undergoes nucleophilic substitution reaction (i.e. the breaking of C-X bond in haloarene is quite difficult). Potassium phthalimide at ordinary condition do not give Nphenyl phthalimide with halo arene.

13.4 BASIC NATURE OF AMINES

Basic nature of amines can be explained on the basis of Arrhenius theory, Lewis theory, Lowry – Bronsted theory.

Arrhenius theory: Primary, secondary and tertiary amines dissolved in water forming alkyl ammonium hydroxide, which dissociate to produce hydroxide ion. Therefore, aqueous solution of amines contains free OH- ion. The OH- ion is stronger base, and it has greater attraction for proton than amines. Therefore, equilibrium is shifted towards left side. Thus, aqueous solution of amines contains more undissociated alkyl ammonium hydroxide molecule. Hence, amines are weak basic in nature.

e.g.
$$R-NH_2 + H_2O \Longrightarrow R-NH_3 + OH^-$$

amine alkyl ammonium
hydroxide $\Longrightarrow R-NH_3^+ + OH^-$

Lewis theory: Amines containing lone pair of electron on nitrogen atom. These lone pair can donate or share easily to electron deficient species to form coordinate bond. Thus, amines are Lewis base.

e.g.

i)
$$R-NH_2 + H_2O \Longrightarrow R-NH_3^+ OH^- \Longrightarrow$$
 amine alkyl ammonium hydroxide
$$R-NH^{3+} + OH^-$$

ii)
$$R-NH_2 + HC1 \longrightarrow R-NH_3^+ Cl^-$$
 alkylammonium chloride

iii)
$$2R-NH_2 + H_2SO_4 \longrightarrow (R-NH_3)_2^+ SO_4^{--}$$
 alkyl ammonium sulphate

Lowrry - Bronsted theory: According to Lowrry Bronsted theory, the substance which accept proton are base. Amines accept proton from water and acids, hence amines are basic nature.

e.g.
$$R-NH_2 + HC1 \longrightarrow R-NH_3^+ Cl^-$$

alkylammonium chloride

13.4.1 Comparison of basic character of aliphatic amines and ammonia:

The basic nature of amines can be better understood by Kb or pKb value. Larger the value of Kb or smaller the value of pKb stronger is the base.

The lone pair of electron on nitrogen is available for coordination with a proton, determining the relative strength of amines. The relative basicity of amines depends upon availability of lone pair of electrons for protonation. Easier the protonation stronger will be the base. This can be explain on the basis of +I effect and -I effect.

$$R-NH_2 + H^+ \longrightarrow R-NH_3^+$$

+ I effect: Electron donating +I effect of alkyl i) group increase the basicity of amines. The alkyl group increase the electron density on nitrogen atom, thereby increasing the availability of the lone pair of electrons on nitrogen atom to proton.

For example, the methyl group are electron donating and they will increase the electron density on nitrogen from 1° to 3° amines and therefore its basic nature will increases. Thus, the basicity of amines in aqueous medium follows the order,

$$3^{0}$$
 amines $> 2^{0}$ amines $> 1^{\circ}$ amines $> NH_{3}$ (CH₃)₂N $> (CH_{3})_{2}NH > CH_{3}NH_{2} > NH_{3}$ However, in aqueous medium it has been observed that trimethyl amines is less basic than dimethyl amine and methyl amines.

This may be explain on the basis of steric effect. (It is a repulsion between two or more groups or atoms in a molecule.) and solvation effect.

Steric effect: In trimethyl amine, the three methyl group cover nitrogen from all sides and thus makes the protonation difficult resulting the reduced in its basicity.

Solvation effect: When amines are dissolved in water they under goes hydration through hydrogen bonding. The protonated amines form hydrogen bonding with water and release energy known hydration energy. Now greater the extent of hydrogen bonding in protonated amines more will be it's stabilisation and greater will be the tendency to change in to cation and more will be the basic nature of amines.

a)
$$R-NH_2 + H-OH \Longrightarrow R-NH_3^+ + OH^-$$
 alkyl ammo. ion

$$H.....OH_2$$

 $R - N + -H.....OH_2$ Maximum hydration
 $H.....OH_2$

b)
$$R_2NH + H-OH \Longrightarrow R_2NH_2^+ + OH^-$$
 dialkyl ammo. ion

$$\begin{array}{ccc} \mathbf{R_2} \overset{\oplus}{\mathbf{N}}\mathbf{-H.....OH_2} \\ | & \mathbf{Moderate\ hydration} \\ \mathbf{H.....OH_2} \end{array}$$

c)
$$R_3N + H-OH \rightleftharpoons R_3NH^+ + OH^-$$

trialkyl ammo. ion

$$R_3 \overset{\oplus}{N} - H \dots OH_2 \quad Minimum \, hydration$$

Thus primary amines are more hydrated than secondary and tertiary amines. Hence basicity of amines on hydration is $1^{\circ} > 2^{\circ} > 3^{\circ}$ amines.

The combined effect i.e inductive and solvation the dimethyl amine is stronger base than methyl amine.

It may be noted that in gases state, where solvent effect is missing the basicity of amine is

$$R_3N > R_2NH > R - NH_2 > NH_3$$

The relative basic character of amines in water is

Alkyl groups Relative basicity

$$CH_3$$
 R_2 $NH > R-NH_2 > R_3N > NH_3$
 C_2H_5 $R_2NH > R_3N > R-NH_2 > NH_3$
Thus, relative basicity of aliphatic amine is
 $(C_2H_5)_2$ NH $>$ $(C_2H5)_3N$ $>$ $(CH_3h)_2H$ $>$
 $C_2H_5NH_2$ $>$ CH_3NH_2 $>$ $(CH_3)_2N$ $>$ NH_3

ii) -I effect: Electron withdrawing inductive effect (-I) decreases the strength of amines.

e.g. i)
$$CH_3 - NH_2 > CH_2Cl - NH_2 > CHCl_2 - NH_2$$

> $CCl_3 - NH_2$

ii)
$$CH_3 - CH - NH_2 > CH_3 - CH - NH_2 > CH$$
 Cl F

11.4.2 Comparison of basic character of aryl amines, alkyl amine and ammonia:

Aryl amines are less basic than alkyl amines, arakyl amines and ammonia because of lone pair of electron on nitrogen in conjugation with benzene ring and thus making less available for protonation.

$$\overset{\uparrow}{\longleftrightarrow} \overset{\downarrow}{\longleftrightarrow} \overset{\downarrow}$$

a) Electron donating group i.e. NH₂, OCH₃, CH₃ stabilize the cation and increase the basic strength of amines.

Note:

- 1. More the electron donating power of the group, more the basicity of substituted aniline
- 2. More the number of electron donating groups, more the basicity of substituted aniline.
- 3. Electron donating power of group or atom is NH₂ > OCH₃ > CH₃

e.g.
$$\bigvee_{NH_2}^{NH_2}$$
 \rightarrow $\bigvee_{O CH_3}^{NH_2}$ \rightarrow $\bigvee_{CH_3}^{NH_2}$

Note that –NH₂ group has more electron donating power than –OCH₃ and –CH₃ hence p–amino aniline is more basic.

b) Electron withdrawing groups (W) like -NO₂, C₆H₅-, SO₃, -5O₃H, -COOH, -CN, X etc. destabilize the cation and decrease the basic strength.

Note:

- 1. More the electron withdrawing power of the group, less the basicity of substituted aniline
- 2. More the number of electron withdrawing groups, less the basicity of substituted aniline.
- 3. Following electron withdrawing group decrease the basicity of aromatic amines in the order of $SO_3H > SO_3 > COOH > OH > NO_2 > CN > F > Cl > Br > I > C_6H_5$

It may be noted that, when SO₃H, COOH, OH groups are attached to benzene nucleus. These compounds are benzene sulphonic acid, benzoic acid and phenol. These are acidic in nature. Hence, these are least basic.

$$NH_2$$
 NH_2 NH_2

Note that -NO₂ has more electron withdrawing power or ring deactivating power than Ci, Br, CN hence p-nitro aniline is less basic.

11.4.3 Comparison of basic character of aralkyl amine and aryl amine

In aryl amine NH₂ group is directly attached to benzene nucleus, the lone pair of electron on nitrogen is conjugate with benzene ring. Hence lone pair of electron not readily available for protonation.

In aralkyl amine the NH₂ group is attached to side chain, the lone pair of electron on nitrogen atom is not conjugate with benzene ring. Hence lone pair of electrons are readily available for protonation. Thus all aralkyl amine are more basic than aryl amines.

$$CH_2NH_2$$
 NH_2 OH_2 OH_2 OH_3 OH_4 OH_4 OH_5 $OH_$

e.g.

$$CH_2NH_2 \qquad NH_2 \qquad NH_2$$
 $CH_3 \qquad CH_2-NH_2 \qquad N(CH_3)_2$

ii) $CH_3 \qquad NHCH_2 \qquad NHCH_3$



Effect of substituents on nitrogen atom:

When hydrogen atoms in NH₂ group of aniline are replaced by electron donating groups then basicity of amine increases.

When hydrogen atom in NH₂ group of aniline are replaced by electron withdrawing group then basicity of amine decreases.

$$NH_2$$
 NHC_6H_5 $N(C_6H_5)_2$

Thus comparative basic nature of all amines is, Aliphatic amines > Aralkyl amines > Aryl amines Some K, and pK, value of amines in aqueous medium.

Amines	K _b value	pK _b value
Primary alkanamines:		
Methanamine	4.5×10^{-4}	3.38
Ethanamine	5.1×10^{-4}	3.29
Propan-2-amine	4.0×10^{-4}	3.40
Phenylmethanamine	2.0×10^{-5}	4.70
Secondary alkanamine	s :	
N-Methylmethanamine	5.4×10^{-4}	3.27
N-Ethylethanamine	10×10^{-4}	3.00
Tertiary alanamines:		
N, N-Dimethylmethanamine	0.6×10^{-4}	4.22
N, N-Diethylethanamine	5.6×10^{-4}	3.25
Ammonia		
Arylamines:	1.8×10^{-5}	4.75
Benzenamine	4.2×10^{-10}	9.38
N–Methylaniline	7.1×10^{-10}	9.30
N, N–Dimethylaniline	11.7×10^{-10}	8.92

13.5 CHEMICAL PROPERTIS

- I) Reactions show the basic nature of amines.
- 1. **Reaction with water:**
- **Primary amine:** a)

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

Secondary amine: b)

$$R_2NH + H_2O \Longrightarrow R_2NH_2^+ + OH^-$$

dialkyl amine dialkyl ammonium ion

Tertiary amine: c)

$$R_3N + H_2O \Longrightarrow R_3NH^+ + OH^-$$

tertiary amine trio alkyl ammo. ion

2. Reaction with dilute or cone, HCl (mineral acid):

When amines are reacted with cone. HCl, gives alkyl ammonium chloride.

Primary amine: a)

$$R-NH_{2} + HCl \longrightarrow R-NH_{3}^{+} Cl^{-}$$
alkylamine alkylammonium chloride
$$R-NH_{3} + Cl^{-} + NaOH \longrightarrow R-NH_{2}$$

$$+ NaX + H_{2}O$$

alkylammonium chloride

Secondary amine: b)

$$R_1NH + HC1 \longrightarrow R_2NH_1 + C1$$

dialkyl amine dialkyl ammonium chloride

- Reaction with dil. H₂SO₄ (mineral acid): When amines are reacted with dil H₂SO₄ gives corresponding ammonium sulphate.
- **Primary amines:** When primary amines are reacted with dil H₂SO₄ gives alkyl ammonium sulphate.

$$2R-NH_2 + H_2SO_4 \longrightarrow [R-NH_3]_2^+ SO_4^{--}$$

Secondary amines: When secondary amines are reacted with dil H2SO4 gives dialkyl ammonium sulphate.

$$2R_2NH + H_2SO_4 \longrightarrow [R_2NH_2]^+_2 SO_4^{-1}$$

Tertiary amines: When tertiary amines are reacted with dil H₂SO₄ gives trialkyl ammonium sulphate.

$$2R_3N + H_2SO_4 \longrightarrow [R_3NH]^+, SO_4^{--}$$

- II) Distinction test between 1°, 2° and 3° amines:
- A) Acylation of aliphatic and aromatic amines : Reaction with acetyl chloride (CH₃-COCl):
- Primary amines: a)

$$R-NH_2 + CH_3-COC1 \xrightarrow{\text{Pyridine}}$$

primary amine

$$R-NH-COCH_3 + CH_3-COC1 \xrightarrow{Pyridine}$$

$$R-N(COCH_3)_2 + HCl$$
 diacetyl alkyl amine

b) Secondary amines: Secondary amine contains one replaceable hydrogen atom. Hence, they forms monoacetyl derivative or N, Ndisubstituted amide.

$$R_2NH + CH_3-COC1 \xrightarrow{Pyridine}$$

sec. amine

$$R_2N-COCH_3 + HC1$$

mono acetyl dialkyl amine

Tertiary amines: Tertiary amine (Aliphatic and aromatic) does not react with acetyl chloride due to absence of replaceable hydrogen atoms.

$$R_3N + CH_3-COC1 \longrightarrow No reaction$$

Note:

These are nucleophilic substitution reactions. 1^o and 20 amines can not be ditinguished by acetylation.

Benzoylation of amines : Benzoyl chloride is used as benzolyting agent.

1) 1° amines

$$CH_3NH_2 + C_6H_5COC1 \xrightarrow{C_5H_5N}$$
 $CH_3NHCOC_6H_5 + HC1$
 N —methyl benzamide

$$C_6H_5NH_2 + C_6H_5COC1 \xrightarrow{C_5H_5N}$$

$$C_6H_5NHCOC_6H_5 + HC1$$

N-Phenyl benzamide or benzanilide

 2° – amines

$$(CH_3)_2$$
 NH + C_6H_5COCl $\xrightarrow{C_5H_5N}$ $(CH_3)_2$ NCOC $_6H_5$ + HCl N,N-dimethyl benzamide

$$(C_6H_5)_2NH + C_6H_5COC1 \xrightarrow{C_5H_5N}$$

$$(C_6H_5)_2$$
 NCOC $_6H_5$ + HCl
N,N–diphenyl benzamide

- Tertiary amines does not undergoes benzoylation reaction.
- B) Reaction with nitrous acid:
- 1. **Primary amines:** All primary amines are reacted with nitrous acid in cold, gives alcohol with evolution of nitrogen gas (except methyl amine).

$$\begin{aligned} \text{R-NH}_2 + \text{HNO}_2 + \text{HCl} & \xrightarrow{-2\text{H}_2\text{O}} \\ & [\text{R-N}_2^+ \text{Cl-}] & \xrightarrow{\text{H}_2\text{O}} & \text{R-OH} + \text{N}_2 + \text{HCl} \\ & \text{unstable} \end{aligned}$$

Note: These are nucleophilic substitution reactions.

e.g.

 When ethyl amine is reacted with nitrous acid or NaNO₂ + dil. HCl in cold, gives ethyl alcohol with evolution nitrogen gas.

$$\begin{array}{c} {\rm C_2H_5-NH_2\,+\,HNO_2} \ \xrightarrow{\quad NaNO_2+HCl} \\ \\ {\rm C_2H_5-OH\,+\,H_2O\,+\,N_2} \ \uparrow \\ \\ {\rm ethyl\,amine\,ethyl\,alcohol} \end{array}$$

ii)
$$NH_2$$

$$NH_2$$

$$NH_2$$

$$NH_2$$

$$N_2 \stackrel{\Theta}{C}$$

$$+NaCI + 2H_2C$$

iii) According to Whitmore methyl amine reacts with nitrous acid in cold gives dimethyl ether and

methyl nitrite.

$$2\text{CH}_{3}-\text{NH}_{2} + 2\text{HNO}_{2} \xrightarrow{\text{NaNO}_{2}+\text{HCl} \atop \text{cold}} \rightarrow \\ \text{CH}_{3}-\text{O}-\text{CH}_{3} + 2\text{N}_{2} + 3\text{H}_{2}\text{O} \\ \text{dimethyl ether}$$

$$CH_{3}-NH_{2}+2\ HNO_{2}\xrightarrow{NaNO_{2}+HCl}$$

$$CH_{3}-O-N=O+N_{2}+2H_{2}O$$

$$methyl\ nitrite$$

Note: Pore 2⁰ and 3⁰ alcohol does not prepared by this method.

2. Secondary amines: When secondary amine is reacted with HNO₂ or NaNO₂ + dil. HCl in cold, gives water insoluble yellow oily nitrosoamine compound'.

$$R_2NH + HNO_2 \xrightarrow{NaNO_2 + HCl} R_2N - N = O + H_2O$$

dialkyl amine dialkyl nitrosoamine

e.g.

$$\begin{array}{c}
\text{NHCH}_{3} \\
\text{N-N=O} \\
+\text{HNO}_{2} \xrightarrow{\text{NaNO}_{2} + \text{HCl}} \\
\text{cold}
\end{array}
+\text{H}_{2}\text{O}$$

Note:

- i) These are electrophilic substitution reactions.
- ii) The nitrosoamine on warming with little phenol and conc. H₂SO₄ produce red colouration, which turn blue on treatment with NaOH. This colour change provide excellent test for 2° amines. This test is known as Libermann's nitrosoamine test.
- **3. Tertiary amines :** Tertiary amine does not contain replaceable hydrogen atom hence it seems does not react with HNO₂, as it gives unstable water soluble product i.e. R₃N⁺HNO₂⁻ trialkyl ammonium nitrite.

$$R_3N + HNO_2 \longrightarrow R_3N^+HNO_2^-$$

trialkyl ammonium nitrite.

Aromatic tertiary amines undergoes electriphilic substitution reaction at para position to give 4–nitroso N,N–dimethyl aniline

$$\begin{array}{c}
N(CH_3)_2 \\
+ HNO_2 \xrightarrow{\text{NaNO}_2 + HCl} \\
\text{cold}
\end{array}$$

$$\begin{array}{c}
N(CH_3)_2 \\
+ H_2O$$

C) Hinsberg's test:

1. **Primary amines:** These are reacted with benzene sulphonyl chloride (Hinsberg's reagent) gives N-alkyl benzene sulphonamide which contain acidic hydrogen atom attached to nitrogen atom, which is soluble in KOH to give clear solution, which on acidification give insoluble compound.

$$R-NH_2 + C_6H_5SO_2C1 \longrightarrow$$

$$R-NHSO_2C_6H_5 + HC1$$

N-alkyl benzene sulphonamide

2. Secondary amines: These are reacted with benzene sulphonyl chloride gives ppt of N, N—dialkyl benzene sulphonamide which is insoluble in KOH or acid.

$$R_2NH + C_6H_5SO_2C1 \longrightarrow R_2NSO_2C_6H_5 + HC1$$

N, N-dialkyl benzene sulphonamide

3. Tertiary amines : These are not react with benzene sulphonyl chloride.

$$R_3N + C_6H_5SO_3Cl \longrightarrow No reaction$$

D) Hofmann's carbyl amine reaction:

When haloform (CHX₃) is heated with primary amine and alcoholic KOH gives carbyl amine (alkyl isocyanide or alkyl isonitrile). Which has very bad nectar odour or disagreeable or obnoxious smell and toxic in nature. This is known as carbyl amine reaction.

Use: This reaction is useful for detection of primary amine and haloform.

$$R-NH_2 + CHX_3 + 3KOH \xrightarrow{\Delta}$$

$$R-NC + 3 KX + 3H_2O$$

ale. alkyl isocyanide

III) Alkylation amines:

$$R-NH_2 + R-X \xrightarrow{\Delta} R_2NH + HX$$

$$R_2NH + R-X \xrightarrow{\Delta} R_3 N + HX$$

$$R_3N + R-X \xrightarrow{\Delta} R_4N + X^-$$

These are nucleophilic substitution reactions, the primary or secondary amine acts as nucleophile and perform nucleophilic substitution at on alkyl halide. The process of converting an amine (1°, 2°, 3°) into quaternary ammonium salt on treatment of excess of alkyl halide is called exhaustive alkylation. Alkylation preceds via SN¹

reaction mechanism. So it is not good for 3° R–X, because they undergoes elimination reaction. At each stage of reaction an HX is formed. This can protonate the amine formed by making co–ordinate bond, therefore stop the reaction before completion.

Therefore for the neutralization of acid and for liberating nucleophile, a base such as NaHCO₃ is added.

IV) Quaternary ammonium salt:

These are analogous to ammonium salt.

Definition : These are tetra alkyl derivatives of ammonium salt, obtained by replacing four hydrogen atoms from ammonium salt by four same or different alkyl groups. They are represented as, R_4 N⁺ X⁻.

Preparation: Quaternary ammonium salt is prepared from trialkyl amine and alkyl halide.

$$R_3N + R-X \xrightarrow{\Delta} R_4 N^+X^-$$

quaternary ammonium salt

1. Action of moist Ag₂O on quaternary ammonium salt: When quaternary ammonium salt is heated with moist silver oxide gives quaternary ammonium hydroxide and ppt of silver halide.

$$R_4N^+X^- + AgOH \xrightarrow{AgO + H_2O} R_4N^+OH^- + AgX$$

e.g.

i) When tetra methyl ammonium iodide is heated with moist silver oxide gives tetramethyl ammonium hydroxide.

$$(CH_3)_4N^+I^- + AgOH \xrightarrow{AgO+H_2O}$$
 $(CH_3)_4N^+OH^- + AgI$

ii) When tetraethyl ammonium iodide is heated with moist silver oxide gives tetraethyl ammonium hydroxide.

$$(C_2H_5)_4N^+I^- + AgOH \xrightarrow{AgO+H_2O}$$

 $(C_2H_5)_4N^+OH^- + AgI$

2. Action of heat on quaternary ammonium hydroxide:

The quaternary ammonium hydroxides are heated at 400 K gives 3^o amine, alcohol or alkene.

e.g.
$$(CH_3)_4N^+OH^- \xrightarrow{400K} (CH_3)_3N + CH_3OH$$

Hofmann's elimination: If one of the alkyl group is other than methyl then quaternary

ammonium hydroxide on heating gives 3° amine, alkene and water. In these reactions methyl group retained on nitrogen atom. The pyrolysis quaternary ammonium hydroxide to give alkene is called Hofmann's elimination reaction. This can be used for the elucidation of structure of amines. The alkene formed against Saytzeff rule or less substituted alkene is major product.

e.g.
$$[(CH_3)_3N-CH_2CH_3]^+ OH^- \xrightarrow{400K}$$

 $(CH_3)_3N + CH_2 = CH_2 + H_2O$

13.6 ELECTROPHILIC SUBSTITUTION OF ARYL AMINE

The NH₂ group is powerful benzene ring activating group. Due to strong activating effect of – NH₂ group the reaction can not stop at monosubstitution stage. To stop reaction at monosubstitution stage the activating effect of –NH₂ has to be reduced. This can be done by acetylation. Acetyl group is electron withdrawing group and therefore lone pair of electron on nitrogen is withdrawn towards the carbonyl group as shown as follows. This method is known as protection of amino group by acetylation and can be used to control the electrophilic substitution reaction

Therefore, the lone pair of electron on nitrogen is less available and the activating power of $-\mathrm{NH}_2$ group is reduced. This also prevent di and tri substituted products. The acetyl group removed by acid hydrolysis to get back the amine.

1. Halogenation (Bromination):

By protecting NH, group by acetylation

o-bromo aniline (minor) p-bromo aniline (major)

2. Nitration

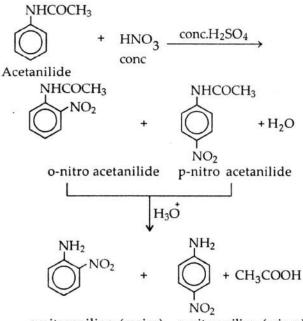
Aromatic amines cannot be nitrated directly because they undergoes oxidation with HNO₃ (oxidising agent) to give partial oxidative product of ring (black mass).

However, under controlled condition nitration of aniline gives unexpectedly 47% m—nitro aniline in addition to o— and p—nitro aniline.

m-nitro aniline o-nitro aniline p-nitro aniline

The reason for that the formation of 47% m–nitroaniline is that the strongly acidic condition. Under acidic condition aniline gets protonated to give anilinium ion ($C_6H_5NH_3^+$). The NH_3^+ group is deactivating and meta directing.

To solve this problem the nitration is carried out by protecting NH₂ group by acetylation. The acetylation deactivates the ring and therefore controls the reaction.



o-nitroaniline (major) p-nitroaniline (minor)

3. Sulphonation:

When aniline is heated with cone. H₂SO₄ at 473 k gives p-amino benzene sui phonic acid (sulphanilic acid) as a major product. Sulphanilic acid exist a as salt called dipolar or Zwitter ion. It is produced by the reaction between an acidic group and basic group in same molecule.

$$NH_2$$
 $+H_2SO_4$
 $-H_2O$
 SO_3H
 SO_3
 SO_3H
 SO_3
 $SUlphanilic acid zwitter ion$

4. Friedel Craft reaction:

Aniline does not give Friedel Craft reaction due to salt formation with AlCl₃ (Lewis acid). Due to this nitrogen of aniline carried positive charge and hence acts as strong deactivating group for further reaction.

Note: NH₂⁺ Cl is ring deactivating group.

Section—III: Benzene Diazonium Salt

13.0 INTRODUCTION

The compounds in which $N_2^+ X^-$ group is directly attached to benzene nucleus are known

as benzene diazonium salt.

The diazoniumsalt have general formula ArN_2^+X , where X- may be F, Cl, Br, I.

The N_2^+ group $(-N^+ \equiv N)$ is known as diazonium group.

e.g. $C_6H_5N_2^+Cl^-$ benzenediazonium chloride. Aliphatic diazonium salt $R-CH_2N_2^+X^-$ are highly unstable because of absence of resonance. $R-CH_2N_2^+X^-$ decompose to give alcohol with liberation of N_2 gas.

Aromatic diazonium salt are stable by resonance.

13.1 PREPARATION METHOD

From diazotisation:

13.2 CHEMICAL PROPERTIES

- A] Substitution reactions: They under goes nucleophilic substitution reaction.ln which N₂ + X is replaced by another nucleophiles i.e. OH-, H-F-, Cl-Br-, I-, CN-, NO₂ etc.
- 1. Replacement by -OH group (Acid hydrolysis):

These on acid hydrolysis give phenol.

$$H_2O$$
 H_2O H_2O

2. Reduction (Replacement of by -H atom)

$$N_2^+CI^-$$
+ $H_3PO_2 + H_2O$ \longrightarrow $+ H_3PO_3$

Hypophosphorous acid
+ $N_2 + HCI$
 $N_2^+CI^-$
+ CH_3-CH_2-OH \longrightarrow $+ CH_3CHO + HCI$

3. Replacement of N₂X by Cl or Br atom:

a) Sandmeyers reaction (Replacement by Cl or Br atom) or CN group: Freshly prepared solution of dizonium salt is mixed with cuprous chloride or cuprous bromide to give chlorobenzene or bromobenzene respectively.

$$C_{6}H_{5}N_{2}^{+}Cl^{-} + Cu_{2}Cl_{2} \longrightarrow \bigcirc + N_{2} + Cu_{2}Cl_{2}$$

$$Br$$

$$C_{6}H_{5}N_{2}^{+}Br^{-} + Cu_{2}Br_{2} \longrightarrow \bigcirc + N_{2} + Cu_{2}Br_{2}$$

$$CN$$

$$C_{6}H_{5}N_{2}^{+}Br^{-} + CuCN/HCN \longrightarrow \bigcirc + N_{2} + CuBr/HBr$$

b) Gattermann reaction: When benzene diazonium salt is reacted with Cu + HCl or Cu + HBr gives chlorobenzone or bromobenzone respectively. The yield of Gattermann reaction is less than Sandmeyers reaction.

$$C_6H_5N_2^+Cl^- \xrightarrow{Cu+HCl} Cl + N_2 + CuCl$$

$$C_6H_5N_2^+Cl^- \xrightarrow{Cu+HBr} C_6H_5-Br+N_2 + CuCl$$

4. Replacement by iodine:

$$C_6H_5N_2^+Cl^- + KI \xrightarrow{\Delta} C_6H_5-I + N_2 + KCl$$

5. Replacement by fluorine (Balz–Schiemanns reaction): When benzene diazonium chloride is treated with fluoroboric acid (HBF₄) give benzene diazonium fluoroborate, which on heating gives fluoro benzene.

$$C_{6}H_{5}N_{2}^{+}Cl^{-} + HBF_{4} \xrightarrow{-HCl}$$

$$C_{6}H_{5}N_{2}^{+}BF_{4}^{-} \xrightarrow{\Delta} C_{6}H_{5}^{-}F + N_{2} + BF_{3}$$

6. Replacement by nitro group:

When benzene diazonium fluoroborate is heated with aqueous NaNO₂ solution in the presence of copper powder to give nitrobenzene.

- **B]** Azo coupling reaction: It react with certain aromatic compound gives azo compounds having general formula $C_6H_5 N = N C_6H_5$. This reaction is called azo coupling rection.
 - The diazonium ion act as electrophile because of positive charge on nitrogen atom. It react with nucleophilic atomatic compounds activated by electron donating groups like –OH, NR₂, NHR and –NH₂. These are strong nucleophile react with aromatic diazonium salt.
- a) When benzene diazonium chloride neacts with phenol in the presence of alkaline medium to form p-hydroxy azobenzene (orange dye).

$$N^+ \equiv NCl + H - OH - OH - KOH - OH + KCl + H2O$$

p-hydroxy azobenzene (orange dye)

b) When benzene diazonium chloride is reacted with aniline in the presence of alkali to give p aminoazobenzene (yellow dye).

$$N^{+} \equiv NCI^{-} + H \longrightarrow NH_{2} \xrightarrow{KOH} NH_{2} + HCI$$

p-amino azobenzene (yellow dye)

c)
$$N^+ \equiv NCl + H - CH_3 \xrightarrow{CH_3} \xrightarrow{KOH}$$
 $N = N - CH_3 \xrightarrow{CH_3} + HCl$

p-N, N- dimethyl amino azobenzene (yellow dye)

Note:

- i) All azo compounds are coloured and uses as dyes.
- ii) These are electrophilic substitution reaction.
- iii) Coupling occurs at only para position with respect to electron donating group hydroxyl, amino, NH-R, NR, group etc.

OOO



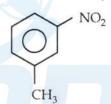
MULTIPLE CHOICE QUESTIONS

SECTION - I: NITRO ALKANES

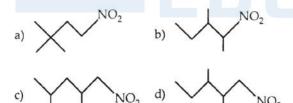
INTRODUCTION, CLASSIFICATION, NOMENCLATURE

- 1. Nitrocompounds are
 - a) derivatives of alkane
 - b) derivatives of benzene
 - c) nitroderivative of ammonia
 - d) both a and b
- 2. IUPAC name of the following compound is

- a) 2-nitropropane
- b) 2-methyl 2-nitropropane
- c) 2-ni trobutane
- d) 2-methyl 1-nitropropane
- 3. IUPAC name of the following compound is



- a) p-nitro toluene
- b) o-nitro toluene
- c) m-nitro toulene
- d) methyl nitrobenzene
- 4. Which of the following is 2,3-dimethyl 1-nitropentane



- 5. Which of the following is ambidentate group?
 - a) NH,
- b) OH
- c) NO₂
- d) OR
- 6. IUPAC name of the following compound is

$$\label{eq:CH2} \begin{split} \mathrm{CH_2} = \mathrm{CH} - \mathrm{CH} - \mathrm{NO_2} \\ | \\ \mathrm{CH_3} \end{split}$$

- a) 3-methyl 3-nitro prop-l-ena
- b) 1-methyl 1-nitro prop-2-ene

- c) 3-nitro but-1-ene
- d) 2-nitro but-3-ene
- 7. Which of the following is 30 nitroalkane

$$d) \hspace{0.2in} \bigwedge^{\hspace{0.2in} NO_2}$$

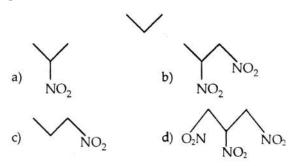
- 8. CH_3-NO_2 , and $CH_3-O-N=O$ are
 - a) position isomers
- b) metamers
- c) linkage isomers
- d) geometrical isomers
- 9. IUPAC name of following compound is

- a) 3,4-dinitro aniline
- b) 4-amino 1,2-dinitro benzene
- c) 4,5-dinitro aniline
- d) 4,5-dinitro benzyl amine

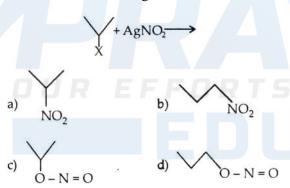
PREPARATION METHODS

- 10. Which of the following method is not meant for the synthesis of nitroalkane?
 - a) nitration of alkane
 - b) oxidation of oxime
 - c) oxidation of 30 alkyl amine
 - d) reduction of oxime
- 11. Which of the following does not undergoes nitration?
 - a) 🔨
- b) CH₃NH₂
- c) +
- d) \/
- 12. Which of the following is nitrating agent?
 - a) HNO₂
- b) AgNO₃
- c) HNO₂
- d) KNO₂
- 13. Vapour phase nitration of propane produces how many products
 - a) 1
- b) 2
- c) 3
- d) 4

- Vapour phase nitration of alkane gives
 - a) nitroalkane
- b) dinitroalkane
- c) trinitroalkane
- d) tetranitroalkane
- 15. Liquid phase nitration of alkane gives
 - a) mononitroalkane
- b) polynitroalkane
- c) alkane nitrite
- d) dialkyl nitrite
- 16. Liquid phase nitration of following compound produces.

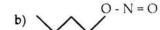


- 17. Which of the following gives acetone 1-nitropropane on acid hydrolysis?
 - a) 2-methyl 1-nitroprop-1-ene
 - b) 1-nitroprop-1-ene
 - c) 3-methyl 2-nitro but-2-ene
 - d) 2-methyl 3-nitro pent-2-ene
- 18. Product of the following reaction is



- 19. Alkyl halide and silver nitrite produces.
 - a) silver oxide
- b) nitro paraffins
- c) dinitroparaffins
- d) alkyl nitrite
- 20. Which of the following is obtained when 1-halobutane is heated with AgNO,





d)
$$O - N = O$$

21. Product 'B' of the following reactions is

$$CH_3 - CH_3 + Br_2 \xrightarrow{AlBr_3} A \xrightarrow{AgNO_2}$$

- a) CH₃ CH₂ ONO b) CH₃ CH₂ NO₂

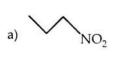
$$\begin{array}{c|cccc} CH_2-CH_2 & CH_2-CH_2 \\ c) & | & | & d) & | & | \\ NO_2 & NO_2 & ONO & ONO \end{array}$$

22. Product of the following reaction is

 $R - X + KNO_2 \xrightarrow{\text{dimethyl sulphoxide}} ?$

- a) R-NO₂
- b) R-ONO
- c) R-OH
- d) R-NH,
- 23. Product of the following reaction.

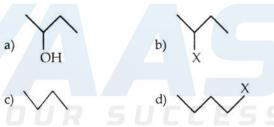
 $\text{CH}_3\text{CHClCH}_3 + \text{NaNO}_2 \xrightarrow{\text{N, N-dimethyl}} \text{formamide}$







24. Compound 'A' on halogenation gives B. Which is reacted with NaNO₂ in dimethyl sulphoxide gives 2-nitrobutane. The compound 'A' is



25. Compound 'A' is reacted with HX produces 'B' which is heated with silver nitrate gives 2nitropropane. The compound 'A' is





- d) both b and c
- Sodium salt of a-halo carboxylic acid is heated with sodium nitrite and followed by hydrolysis gives
 - a) amides
- b) nitroparaffins
- c) amines
- d) alcohols
- 27. Product of the following reaction is

- a) 2-nitropropane
- b) 1-nitropropane
- c) propanamine
- d) propanal
- 28. Find out product D in the following sequence of reaction

$$CH_3-CH_2-COOH + Na \longrightarrow A \xrightarrow{Br_2/Red.P.} B$$

$$\xrightarrow{NaNO_2} C \xrightarrow{H_2O} D$$





- 29. Tertiary alkyl amines on oxidation by KMnO gives
 - a) 1° nitroalkane
- b) 2° nitroalkane
- c) 3° nitroalkane
- d) 3° alcohols
- 30. State the product available by the following reaction

$$NH_2 \xrightarrow{KMnO_4} NI$$

- 31. Nitroparaffins are obtained by oxidation of
 - a) 3° amines
 - b) α –halocarboxylic acid
 - c) acid amide
 - d) 3° alkyl amines
- 32. α –nitroalkene is converted into nitroalkane by a) oxidation
 - b) treating it with KNO, and followed by hydrolysis
 - c) acid hydrolysis
 - d) alkaline hydrolysis
- 33. Acid hydrolysis of following compound gives

$$NO_2 \xrightarrow{H_3O^+} ?$$

- a) CH_3 – $CH = CH_1$, and CH_3 NO_2
- b) $CH_2 = CH_2$ and $C_2H_5 NO_2$
- c) CH₃-CO-CH₃ and CH₃ NO₂
- d) CH₃-CHOH-CH₃ and CH₃ NO₅
- 34. In which of the following reaction product

- obtained has less number of carbon atom than reactants?
- 1. acid hydrolysis of α –nitroalkene
- 2. oxidation of aldehydes
- 3. oxidation of ketones
- 4. oxidation of 3° alkyl amine
- a) 2, 3
- b) 1, 4
- c) 2, 4
- d) 1, 3
- 35. Reaction involved during conversion of 3° alkyl amine to 3° nitro alkane
 - a) hydrolysis
- b) reduction
- c) oxidation
- d) pyrolysis
- 36. Find out A in the following reaction

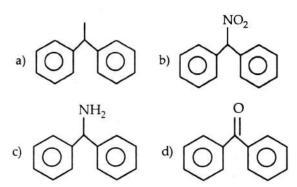
$$CH_3$$
- $CH = CH$ - CH_2 - $NO_2 \xrightarrow{A}$

$$CH_3$$
- $CHO + CH_3$ - CH_2 - NO_2

- a) KMnO₄
- b) H,O+
- c) LiAlH₄
- d) PCC
- 37. Oxidation of oxime produces
 - a) 1° amines
- b) nitro alkanes
- c) aldehydes
- d) ketones
- 38. Aldoxime on oxidation by trifluoroperoxy acetic acid gives
 - a) 1° amines
- b) 2° amines
- c) 1° nitroparaffins d) 2° nitroparaffins
- 39. Ketoxime on oxidation by trifluoroperoxy acetic acid gives
 - a) 1° nitroparaffins b) 2° nitroparaffins
 - c) 3^{0} nitroparaffins d) 1° amines
- 40. Product of the following reaction is



- 41. Product of the following reaction will be trifluoroperoxy?



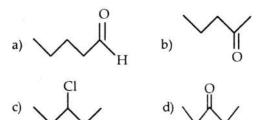
- 42. Propionaldoxime is reacted with trifluoroperoxy acetic acid gives
 - a) propan-1-amine
- b) propan-2-amine
- c) 1-nitropropane
- d) 2-nitropropane
- 43. Acetoxime on reaction with trifl uoroperoxy acetic acid gives
 - a) 1-nitropropane
- b) 2-nitropropane
- c) propionic acid
- d) isobutyric acid
- 44. The reagent used to convert alkyl halide to nitroalkane are
 - 1. AgNO,
 - 2. KMnO₄ in dimethylsulphoxide
 - 3. acidic KMnO₄
 - 4. HNO₃
 - a) 1, 4
- b) 2, 3
- c) 1, 3
- d) 1
- 45. Ketoximes are oxidised into 2⁰-nitroalkane by using
 - a) KMnO₄
 - b) K₂Cr₂O₇ + dil.H₂SO₄
 - c) trifluoroperoxy acetic acid
 - d) pyridinium chlorochromate
- 46. During conversion of oxime to nitroparaffins, which reaction is involved?
 - a) reduction
- b) oxidation
- c) acid hydrolysis
- d) alkaline hydrolysis
- 47. Find out final product of the following reaction

$$A \xrightarrow{OJ} B$$

$$A \xrightarrow{IOJ} B$$

$$A \xrightarrow{$$

48. The unknown organic compound reacts with hydroxyl amine and followed by oxidation using trifluoroperoxy acetic acid gives 3–nitro pentane. The unknown organic compound is



49. Product A in the following reaction is

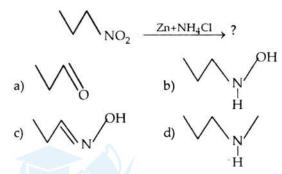
 $H_2C = NOH \xrightarrow{\text{trifluoroperoxy acetic acid}} A$

- a) formic acid
- b) nitromethane
- c) methyl nitrite
- d) methanal
- 50. 1-nitro prop-1-ene on acid hydrolysis gives
- a) nitroethane and formaldehyde
 - b) nitroethane and formic acid
 - c) nitromethane and acetic acid
 - d) nitromethane and acetaldehyde

CHEMICAL PROPERTIES

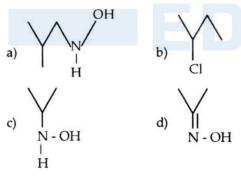
- 51. 1°, 2° and 3° nitroalkanes can be distinguished by
 - 1. acid hydrolysis
 - 2. halogenation
 - 3. reaction with nitrous acid
 - a) 1, 3
- 0) 1, 2
- c) only 3
- d) 1, 2, 3
- 52. Reduction of nitroalkane produces
 - 1] 10-amines
 - 2] N-alkyl hydroxyl amine
 - 3] oxime
 - a) 1,3
- b) 1,2
- c) only 1
- d) 1, 2, 3
- 53. Nitroalkanes are reduced by $Zn + NH_4Cl$ gives
 - a) 1° amines
 - b) Nvalkyl hydroxyl amine
 - c) oxime
 - d) amide
- 54. During conversion of nitroalkane to N-alkyl hydroxyl amine, which of the following reducing agent is used?
 - a) Sn + conc. HCl
- b) H₂/Ni
- c) $Zn + NH_4C1$
- d) SnCl₂ + HCl
- 55. Nitroalkane is reduced by stannous chloride and HCl gives

- a) 2° amine
- b) only oxime
- c) only N-alkyl hydroxyl amine
- d) mixture of oxime and N-alkyl hydroxyl amine
- 56. SnCl₂ + HCl convert
 - a) -CHO to -CH₂-OH
 - b) >C = O to >CH-OH
 - c) -NO₂ to -NH₂
 - d) $-NO_2$ to = NOH
- 57. Product of the following reaction is



- 58. Reduction of the following compound would yield mixture of N-ethyl hydroxyl amine and acetaldoxime
 - a) $C_2H_5-NO_2$
- b) C₂H₅-CONH₂
- c) CH₃-NO₂
- d) CH₃-CONH₂
- 59. Find out 'A' in the following reaction:

$$\bigvee_{NO_2} \xrightarrow{Z_n + NH_4Cl} A$$



- 60. The compound obtained by catalytic hydrogenation of nitrobenzene is
 - a) aniline
- b) benzaldoxime
- c) benzyl nitrite
- d) phenyl nitrite
- 61. N-isopropyl hydroxyl amine is obtained by reduction of

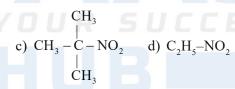
a)
$$\bigvee_{NO_2}$$
 and $Zn + NH_4Cl$

b)
$$\bigvee_{NO_2}$$
 and $SnCl_2 + HCl$

c)
$$\bigvee_{NO_2}$$
 and Fe + conc.HCl

d)
$$\bigvee_{NO_2}$$
 and H_2/Ni

- 62. Acid hydrolysis of 30-nitroalkane gives
 - a) ketones
- b) carboxylic acids
- c) aldehydes
- d) no product
- 63. 2⁰-nitroparaffins on acid hydrolysis will give
 - a) aldehydes
- b) carboxylic acids
- c) ketones
- d) amide
- 64. Which of the following doesn't undergoes acid hydrolysis?
 - a) CH₃ –NO₂
- b) CH₃ CH CH₃

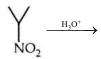


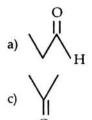
- 65. The acid hydrolysis which of the following will gives acetic acid
 - 1] CH₃ -CN
 - 2] CH₃ -CH₂ -NO₂
 - 3] CH₃ CH CH₃ | | NO₂
 - 4] (CH₃)₃C-NO₂
 - a) only 1, 3
- b) 1 and 2
- c) only 2, 4
- d) 1, 2, 4
- 66. Propionic acid is obtained by acid hydrolysis of
 - a) \bigvee_{NO_2}
-) Y



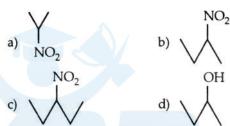


67. The product formed in following reaction is

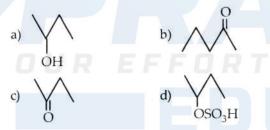




Which of the following compound will not gives ketone on acid hydrolysis

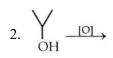


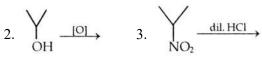
69. 2-Nitrobutane is heated with dil.H₂SO₄ gives



70. Which of the following reaction will give acetone?

1.
$$CH_3 - CN + CH_3MgX \xrightarrow{dry ether}$$





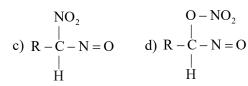
- a) 1, 2
- b) 1, 3
- c) 2, 3
- d) 1, 2, 3
- 71. Chlorination of nitro methane gives
 - a) methyl chloride
 - b) chloropicrin
 - c) dichloronitromethane
 - d) CCl₄
- 72. In halogenation of nitroalkane
 - a) all halogen are replaced by halogens

- b) all α –H are replaced by halogens
- c) all β-H are replaced by halogens
- d) only one α –H is replaced by halogen
- 73. Halogenation of nitroparaffins is the characteristic reaction of
 - a) α –H atoms
- b) β -H atoms
- c) γ-H atoms
- d) δ -H atoms
- 74. Which of the following is nitrolic acid

a)
$$R - C - N = O$$

 $R - C - N = O$
 R

b) $R - C - N = C$



75. The following structure shown below is



- a) nitroform of nitrolic acid
- b) aci form of nitrolic acid
- c) pseudo nitrol
- d) nitroethanol
- 76. Product of following reaction will be

$$CH_3 - CH_2 - NO_2 + Cl_2 \xrightarrow{NaOH} ?$$

- a) CH₃-CHCl-NO, b) ClCH₂-CH₂-NO,
- c) $CH_3-CCl_2-NO_2$ d) $Cl_3C-CH_2-NO_2$
- 77. Product in the following sequence of reaction

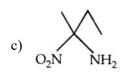
$$R_{3}C-NH_{2} \xrightarrow{KMnO_{4}} A \xrightarrow{Cl_{2}/NaOH} B$$

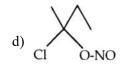
- a) CCl_3-NO_2 b) $R-CH-NO_2$
- c) R,CCl-NO,
- d) no product
- 78. In the reaction

$$CH_3$$
- CH_2 - $Br + NaNO_2 \xrightarrow{dimethyl sulphoxide} A$

The product B is

- a) CH₃-CH₂-NO₂ b) CH₃-CCl₂-NO₂

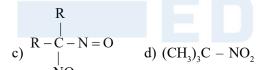




- 79. Which of the following compound does not react with alkaline bromine

- 80. 1° nitroalkane react with HNO, gives
 - a) dinitroalkane
 - b) nitrolic acid
 - c) N-alkyl hydroxyl amine
 - d) nitrosoamine
- 81. Nitrosonitroalkane is obtained by 2^o-nitroalkane with
 - a) HNO,
- b) HNO,
- c) AgNO,
- d) KNO,
- 82. Which of the following will undergoes tau tomerisation?

a)
$$R - C - N = O$$
 b) $C = C - C(CH_3)_3$ $C - C - C(CH_3)_3$



- 83. Nitrolic acid is formed from nitrous acid and what?







- 84. Blue coloured pseudonitrol is formed from nitrous acid and what
 - a) CH₃-NO,
- b) CH₃ CH CH₃ | NO₂

- c) $C_{2}H_{5}-NO_{5}$
- d) (CH₂),NH
- 85. Which of the following does not react with nitrous acid?
 - 1. CH₃-NH₂
- 2. (CH₃),N
- 3. $C_{2}H_{5}-NH_{2}$
- 4. (CH₃)₂NH
- 5. $(CH_3)_3C-NO_2$ 6. $C_2H_5-NO_2$
- a) 2, 3
- b) 4, 5
- c) 5, 6
- d) 2.5
- 86. The following compound is

$$CH_3 \\ CH_3 - C - N = O$$

$$NO_2$$

- a) pseudonitrol
- b) nitrolic acid
- c) nitronic acid
- d) nitroso isopropyl nitrite
- 87. Compound formed when nitroethane reacts with nitrous acid
 - a) ethanamine
 - b) nitroso nitroethane
 - c) dimethyl nitroso amine
 - d) ethanol
- 88. Pseudonitrol is formed from nitrous acid and what?



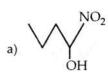




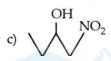
- 89. Red colour sodium salt is obtained by nitrolic acid react with
 - a) Na₂SO₄
- b) NaOH
- c) NaHSO₃
- d) CH₂COONa
- 90. Aci form of nitrolic acid is
 - a) red colour
- b) blue colour
- c) yellow colour
- d) white colour
- 91. Nitroalkane condensed with aldehyde and ketone to form nitroalcohol. The main condition of nitroalkane is
 - a) absence of α –H atoms
 - b) absence of β -H atoms
 - c) presence of α –H atoms
 - d) it must be tertiary

- 3-nitro 2-methyl butan-2-o1 is the condensation products of
 - a) ethanal and nitromethane
 - b) acetone and nitro methane
 - c) acetone and nitroethane
 - d) methanal and 1-nitropropane
- 93. Product of the following reaction will be

$$\bigvee_{\mathbf{H}}^{\mathbf{O}} + \mathbf{CH}_3 - \mathbf{NO}_2 \xrightarrow{\text{alc. KOH}}$$

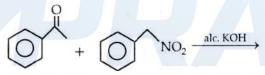








- 94. When carbonyl compounds react with nitroalkane. The reaction proceeding through
 - a) carbocation
- b) carbon free radical
- c) carbene
- d) carbanion
- 95. Product of following reaction will be

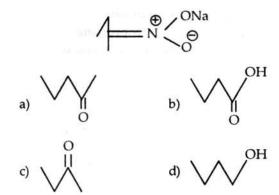


- a) 1, 2—diphenyl ethanol
- b) 1, 1-diphenyl ethanol
- c) 2, 3-diphenyl 3-nitropropan-2-o1
- d) 1, 1-diphenyl 2-nitroethanol
- 96. α –H atom of nitroalkane is
 - a) acidic
- b) basic
- c) neutral
- d) can't be predicted
- 97. Nef-carbonyl synthesis is used to produce
 - a) carboxylic acids or esters
 - b) aldehydes or ketones
 - c) alcohols or ethers
 - d) oxime or amide
- 98. The product of the following reaction will be





99. The compound obtained by reacting following compound with H₂SO₄.



100. Which of the following is Nef-carbonyl synthesis

a) H–CHO + CH
$$_3$$
 –NO $_2$ $\xrightarrow{\text{alc. KOH}}$

b) R-COC1
$$\xrightarrow{\text{Pd-BaSO}_4}$$
 quinoline

c) R-C-OH
$$\xrightarrow{\text{LiAlH}_4}$$

d)
$$R_2C = N$$

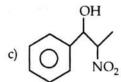
ONa

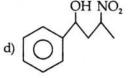
H₂SO₄

- 101. Which of the following does not condense with aldehydes or ketones
 - a) CH₃-NO,
- b) $C_2H_5-NO_2$
- c) $(CH_3)_2CH-NO_2$ d) $(CH_3)_2C-NO_2$
- 102. Product of the following reaction is

$$\begin{array}{c}
OH & \xrightarrow{PCC} A & \xrightarrow{i) C_2H_5-NO_2} B
\end{array}$$

a)
$$OH$$
 OH OH OH OH OO_2





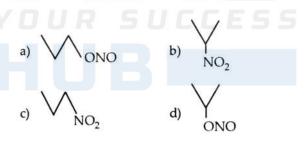
103. Reagent 'A' in the following reaction is

$\begin{array}{c} \text{OH} \\ \text{H-CHO} + \text{CH}_3 - \text{NO}_2 & \xrightarrow{\text{A}} \text{H-C-CH}_2 - \text{NO}_2 \\ \mid \\ \text{H} \end{array}$

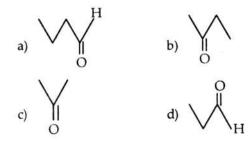
- a) 20% KOH
- b) 50% KOH
- c) ale. KOH
- d) SnCl, + HCl
- 104. Which of the following compound does not react with NaNO, and HCl
 - a) $C_6H_5-NH_2$
- b) $CH_3 CH_2 NO_2$
- c) C₂H₅ -NH₂
- d) (CH₃), C-NO,
- 105. Hydrolysis of CH_3 – CH_2 – CH_2 – NO_2 with 85% H_2SO_4 gives
 - a) CH₃ -CH₂ -CH₃ -OH
 - b) CH₃ -CH₂ -COOH
 - c) CH₃ CH₂ CH₃
 - d) CH_3 –CH, –CH = NOH
- 106. Depending upon the reducing agent, the reduction of nitro paraffins may gives
 - 1. 1°-amine
 - 2. 2°-amine
 - 3. 3°-amine
 - 4. N-alkyl hydroxyl amine
 - a) only 1
- b) 1, 2, 3
- c) only 2
- d) 1, 4
- 107. Primary nitrocompounds react with nitrous acid to form nitrolic acid which dissolve in NaOH to give
 - a) yellow solution
- b) red solution
- c) blue solution
- d) colourless solution
- 108. The different behavior 1°, 2°, 3° nitroalkanes on the basis of
 - a) Victor Mayer's test b) Lucas test
 - c) Hinsberg test
- d) Tollen's test
- 109. Which of the following is not nitro compounds
 - a) $C_6H_5-NO_2$
- b) (CH₃),CH–NO,
- c) $CH_3-O-N = O$
- d) (CH₃), C-NO,
- 110. In Nef-carbonyl synthesis of 1°-nitro alkane on treatment with NaOH followed by acidification with 50% H₂SO₄ gives
 - a) aldehydes
- b) esters
- c) ketones
- d) carboxylic acids
- 111. Which of the following isomerism is exhibited in nitro ethane?
 - a) geometrical
- b) optical
- c) tautomerism
- d) chainisomerism

- 112. Nitroalkanes are acidic only towards
 - a) Na₂CO₃
- b) C,H,-OH
- c) NaOH
- d) NH₃
- 113. Reduction of nitroalkane in neutral medium (Zn + NH₄Cl) forms mainly
 - a) R NH,
- b) R NH OH
- c) R-N = N-C1
- d) $CH_3 CH = N OH$
- 114. A nitrogenous compound is treated with nitrous acid and the product so formed is further treated with NaOH solution which produces blue colouration. The nitrogenous compound is
 - a) \bigvee_{NH_2}
- b) \\/
- c) \Mono
- d) NO₂
- 115. In Nef-carbonyl synthesis of 2-nitropropane on treatment with strong alkali and followed by acidification with 50% H₂SO₄ gives a product, which will give
 - a) Tollen's test
- b) Haloform test
- c) Hinsberg test
- d) Carbyl amine reaction
- 116. $C_3H_7NO_2 + NaOH \rightarrow A \xrightarrow{50\%H_2SO_4} B$

Hence compound 'B' will give positive Tollen's test. The structure of C₃H₇NO₂ will be



117. Sodium salt of aci form of ethyl methyl nitronic acid is treated with 50% H₂SO₄ gives



118. A nitroalkane reacts with HNO₂ to yield a product which is insoluble in NaOH and give blue colour

on treatment with alkali. The nitroalkane could

a)
$$CH_3 - CH_2 - NO_2$$
 b) $(CH_3)_3C - NO_2$

c)
$$CH_3 - CH - C_2H_5$$
 d) $(CH_3)_2CH - CH_2 - NO_2$
NO₂

119. An aliphatic nitro compound turn red with the addition of conc.NaOH, followed by addition of excess HNO₂. The colour disappear with the addition of excess acid but reappear if the solution is made alkaline. The aliphatic nitro compound is

a)
$$CH_3 - CH_2 - NO_2$$
 b) $CH_3 - CH - CH_3$

$$|
NO_3$$

c)
$$CH_3$$

 $CH_3 - C - NO_2$
 $CH_3 - CH - C_2H_5$
 CH_3
 NO_2

120. The product obtained in the following reaction

$$CH_3-NO_2 + Cl_2 + NaOH \longrightarrow$$

- c) Cl₃C NO₂
- d) all of these
- 121. What is the product when nitrobenzene is treated with zinc dust and ammonium chloride
 - a) benzene
 - b) aniline
 - c) phenyl hydroxyl amine
 - d) azobenzene
- 122. The conversion of nitroalkane to primary amine is carried out by
 - a) reduction
- b) oxidation
- c) hydrolysis
- d) dehydration
- 123. Compound which does not tautomerise and does not show acidic property is
 - a) CH₃-NO₂
- b) C₂H₅-NO₂
- c) (CH₃)₂CH-NO, d) (CH₃)₂C-NO,

124. R-
$$CH_2$$
 - NO_2 $\xrightarrow{Dil. H_2SO_4}$ $A + B$

- A, B are respectively
- a) R-COOH, NH₂OH
- b) R-COOH, NH₄OH
- c) RCONHOH, NH,
- d) RCONH,, ROOH

COC

ANSWERS - MCQ'S

SECTION - I: NITRO ALKANES

1.	d)	2.	b)	3.	c)	4.	d)	5.	c)	6.	c)	7.	c)	8.	c)	9.	a)	10.	d)
11.	b)	12.	c)	13.	d)	14.	a)	15.	b)	16.	d)	17.	d)	18.	a)	19.	b)	20.	a)
21.	b)	22.	a)	23.	b)	24.	c)	25.	d)	26.	b)	27.	b)	28.	a)	29.	c)	30.	c)
31.	d)	32.	c)	33.	c)	34.	d)	35.	c)	36.	b)	37.	b)	38.	c)	39.	b)	40.	d)
41.	b)	42.	c)	43.	b)	44.	d)	45.	c)	46.	b)	47.	b)	48.	d)	49.	b)	50.	d)
51.	d)	52.	d)	53.	b)	54.	c)	55.	d)	56.	d)	57.	b)	58.	a)	59.	c)	60.	a)
61.	a)	62.	d)	63.	c)	64.	c)	65.	b)	66.	a)	67.	c)	68.	d)	69.	c)	70.	d)
71.	b)	72.	b)	73.	a)	74.	c)	75.	b)	76.	c)	77.	d)	78.	b)	79.	c)	80.	b)
81.	b)	82.	a)	83.	a)	84.	b)	85.	d)	86.	a)	87.	b)	88.	d)	89.	b)	90.	b)
91.	c)	92.	c)	93.	c)	94.	d)	95.	c)	96.	a)	97.	b)	98.	d)	99.	c)	100.	d)
101.	d)	102.	c)	103.	c)	104.	d)	105.	b)	106.	d)	107.	b)	108.	a)	109.	c)	110.	a)
111.	c)	112.	c)	113.	b)	114.	d)	115.	b)	116.	c)	117.	b)	118.	c)	119.	a)	120.	d)
121.	c)	122.	a)	123.	d)	124.	a)												



MULTIPLE CHOICE QUESTIONS

SECTION - II: AMINES

INTRODUCTION, CLASSIFICATION, NOMENCLATURE, ISOMERISM

- 1. Amines are
 - a) mono alkyl derivative of ammonia
 - b) dialkyl derivative of ammonia
 - c) trialkyl derivative of ammonia
 - d) all of these
- 2. A secondary amine is
 - a) a compound with two carbon atoms and an –NH, group
 - b) a compound containing two –NH, groups
 - c) a compound in which hydrogens of NH, have been replaced by two alkyl groups
 - d) a compound with an -NH₂ group on carbon atom in number two position
- Which of the following is secondary amine?

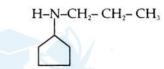
 - a) Sec. butyl amine b) Iso propyl amine
 - c) Diethyl amine
- d) All of these
- Which of the following is not tertiary amine?
 - a) $(CH_2)_2N$
- b) $(C_{2}H_{5})_{3}N$
- c) $(C_2H_5)_2NCH_2$
- d) (CH₂), CNH₂
- (CH₂)₂CHNH₂ is
 - a) 1° amines
- b) 2° amines
- c) 3° amines
- d) all of these
- Nitrogen atom in amines is
 - a) sp²-hybridised
- b) sp-hybridised
- c) sp³-hybridised
- d) sp²-d-hybridised
- 3° amines contain
 - a) nitrile group
- b) imino group
- c) nitro group
- d) amino group
- 8. Tertiary amine contains
 - a) -NH, group
- b) > NH group
- c) N group
- d) none of these
- 9. IUPAC name of the following compound is



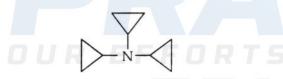
- a) m-nitroarene amine
- b) 3-nitroaniline
- c) 3-amino nitrobenzene
- d) m-arnino nitrobenzene

- 10. Imino group is present in
 - a) 1° amine
 - b) 2° amine
 - c) 3° amine
 - d) quaternary ammonium salt
- 11. Secondary amines are represented by
 - a) –NH,
- b) > NH
- c) N
- d) -NO
- 12. All amines have general formula
 - a) $C_n H_{2n} N H_2$
- b) $C_n H_{2n} N$
- c) $C_n H_{2n+3} N$
- d) $C_n H_{2n+2} N$
- 13. The IUPAC name for, (CH₃)₂NC(CH₃)₃
 - a) N, N-dimethyl 2-methyl 1-propanamine
 - b) N, N-dimethyl 2-methyl 2-propanamine
 - c) dimethyl t-butyl amine
 - d) N, N-dimethyl 2-butanamine
- 14. The structural formula of N-methyl methanamine
 - a) (CH₃),CHNH,
- b) (CH,),NH
- c) (CH₂),N
- d) CH, NH,
- 15. IUPAC name of CH₃N(C₂H₅), is
 - a) diethyl methyl amine
 - b) diethyl methanamine
 - c) N-methyl diethanamine
 - d) ethyl methyl amine
- 16. IUPAC name of 1° amine is
 - a) alkyl amine
- b) dialkanamine
- c) alkanamine
- d) trialkanamine
- 17. IUPAC name ethyl methyl amine is
 - a) ethyl methanamine b) methyl ethanamine
 - c) diethanamine
- d) dimethanamine
- 18. What is IUPAC name of compound when imino group is attached to ethyl and n-propyl group?
 - a) N-Ethyl isopropyl amine
 - b) N-Ethyl 2-propanamine
 - c) N-Ethyl 1-propanamine
 - d) N-Ethyl 1-butanamine
- 19. IUPAC name of following compound is
 - $(CH_3)_2 N C_2H_5$
 - a) ethyl methyl methanamine
 - b) N, N-dimethyl ethanamine
 - c) ethyl dimethanamine
 - d) methyl ethanamine
- 20. IUPAC name of isobutyl amine is

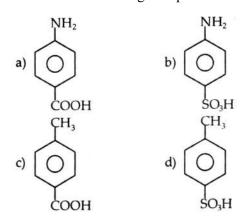
- a) 2-methyl, 2-propanamine
- b) 2-methyl, 2-butanamine
- c) 2-methyl, 1-propanamine
- d) 2-propanamine
- 21. IUPAC name of t-butyl amine is
 - a) 2-methyl 2-propanamine
 - b) trimethanamine
 - c) N, N-dimethyl methanamine
 - d) N-methyl diethanamine
- 22. How many metamers are possible for formula C₅H₁₃N?
 - a) 5
 - b) 6
 - c) 7
 - d) 8
- 23. IUPAC name of the following compound is



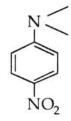
- a) N-cyclopentyl propan-1-amine
- b) N-propyl cyclopentanamine
- c) 1-amino cyclopentane
- d) Cyclopentyl amine
- 24. Following compound can be named as



- a) N,N-dicyclopropyl cyclopropanamine
- b) tricyclopropyl amine
- c) N,N-dicyclopropyl amino cyclopropane
- d) all of these
- 25. Which of the following is sulphanilic acid



26. IUPAC name of the following compound is

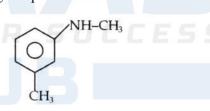


- a) 4-nitro N,N-dimethyl aniline
- b) 4-nitro N,N-dimethyl benzenamine
- c) dimethyl nitrobenzene
- d) both a and b
- 27. Class of the following compound is

- a) 1° amine
- b) 2°- amine
- c) 3°- amine
- d) amide
- 28. IUPAC name of the following compound is



- a) 1, 2-diaminobenzene
- b) o-Phenylene diamine
- c) diphenyl amine
- d) both a and b
- 29. Following compound can be named as

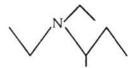


- a) N-methyl 3-methyl aniline
- b) N-methyl 3-methyl benzenamine
- c) dimethyl phenyl amine
- d) both a and b
- 30. IUPAC name of the following compound is

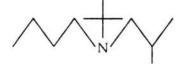


- a) 2-chloro pentanamine
- b) 4-chloro pentan-1-amine
- c) 4-chloro pent-2-en-1-amine
- d) 2-chloro pent-3-en-5-amine
- 31. Hybridised state of N-atom in trimethyl amine is
 - a) sp^3
- b) sp²

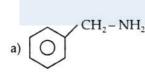
- c) sp
- d) sp^3-d
- 32. IUPAC name of the following compound is

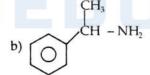


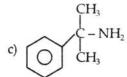
- a) N-N-dimethyl pentan-2-amine
- b) N,N-diethyl butan-2-amine
- c) N,N-diethyl 1-methyl butan-1-amine
- d) N,N-diethyl butan-1-amine
- 33. IUPAC name of the following compound is

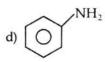


- a) N-(1,1-dimethyl ethyl) N-(2-methyl propyl) butan-1-amine
- b) N(butyl) N–(1,1–dimethyl ethyl)2–methyl propan–1–amine
- c) N-butyl,N-(2-methyl propyl) 2-methyl propan-1-amine
- d) N-butyl N-2-methyl propyl 2-methyl butan -1-amine
- 34. Which of the following is incorrect IUPAC name?
 - a) N-(propyl) propan-2-amine
 - b) N-(2-propyl) propan-1-amine
 - c) dimethyl ethanamine
 - d) N-ethyl cyclohexanamine
- 35. Which of the following is benzyl amine?









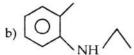
- 36. Tertiary alkyl amine is
 - a) 1°-amine
- b) 2°-amine
- c) 3°-amine
- d) quaternary salt
- 37. How many metamers are possible for molecular formula $C_4H_{11}N$.
 - a) 0
- b) 2

c) 3

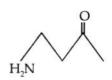
- d) 4
- 38. Molecular formula C₃H₀N can show

- 1) chain isomerism
- 2) position isomerism
- 3) functional isomerism
- 4) metamerism
- a) 1, 3
- b) 3, 4
- c) 1, 2
- d) 2, 3
- 39. In which of the following imino group is present IUPAC name of the following compound is

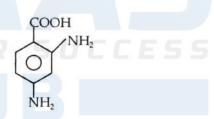




- c) NH₂
- d) (C₆H₅)₃N
- 40. IUPAC name of the following compound is



- a) 1-amino butan-3-one
- b) 4-amino butan-2-one
- c) 3-oxo-butan-1-amine
- d) 2-oxo butan-4-amine
- 41. IUPAC name of the following compound is



- a) 4-carboxyl phenylene diamine
- b) 1-carboxyl phenylene diamine
- c) 2,4-diamino benzoic acid
- d) 4-carboxyl 3-amino aniline
- 42. $(CH_3)_3C-NH_3$ and $(CH_3)_3N$ are
 - 1) pair of optical isomers
 - 2) identical
 - 3) chain isomers
 - 4) function isomers
 - 5) not identical
 - a) 1, 4
- b) only 4
- c) only 5
- d) all of these
- 43. Which of the following statement is not true about $(CH_3)_3N$?
 - a) It's IUPAC name is trimethanamine

- b) N-atom is sp³-hyridised state
- c) it has pyramidal structure
- d) It contain imino group
- 44. IUPAC name of the following compound is



- a) N-ethyl heptan-2-amine
- b) N-methyl 1-rnethyl heptan-1-amine
- c) heptyl ethyl amine
- d) heptyl methyl amine
- 45. Following compound can be named as



- a) N-ethyl 1-methyl cyclohexyl amine
- b) N-ethyl N-methyl cyclohexyl amine
- c) N-ethyl N-methyl cyclohexanamine
- d) N-cyclohexyl N-methyl ethanamine
- 46. Total number of isomeric 1°,2°, 3° amines can be calculated by formula
 - a) $I = 2^{n}$
- b) $I = 2^{n-2}$
- c) $I = 2^{n-3}$
- d) $I = 2^{n-1}$
- 47. Ethyl amine and dimethyl amines are
 - a) metamers
- b) position isomers
- c) chain isomers
- d) functional isomers
- 48. Which isomerism is not present in amines?
 - a) Functional
- b) Position
- c) Chain
- d) Cis and trans
- 49. How many 2° amines are possible for molecular formula C₄H₁₁N ?
 - a) 2
- b) 3
- d) 5
- 50. How many 3° amines are possible for molecular formula C₄H₁₁N?
 - a) 1
- b) 2

c) 3

- d) 4
- 51. Molecular formula C₄H₁₁N shows
 - a) chain isomerism
- b) position isomerism
- c) functional isomerism d) all of these
- 52. $C_4H_{11}N$ represents
 - a) 1° amines
- b) 2° amines
- c) 3° amines
- d) all of these
- 53. In general formula of amines. If n = 3 the amine

- may be
- a) 1° and 2°
- b) 1° and 3°
- c) 2° and 3°
- d) 1°, 2° and 3°
- 54. Isomerism shown by amines is / are
 - a) chain
- b) position
- c) functional
- d) all of these
- 55. Which of the following is not isomer of C₂H₀N?
 - a) $(CH_2)_2N$
- b) (CH₃),CHNH,
- c) C₂H₅NHCH₂
- d) (CH₂), CNH₂
- 56. How many primary amines are possible for the formula C₄H₁₁N?
 - a) 1
- b) 2

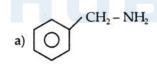
- c) 3
- d) 4
- 57. C₃H₀N represents
 - a) 1° amine
- b) 2° amine
- c) 3° amine
- d) all of these
- 58. Molecular formula C₂H₇N represents
 - a) 2° and 3° amines b) 1° and 2° amines
 - c) only 1° amines
- d) only 2° amines
- 59. Molecular formula C₂H₇N shows which type of isomerism?
 - a) Position
- b) Functional
- c) Chain
- d) Optical
- 60. n-butyl amine and isobutyl amine are
 - a) chain isomers
- b) position isomers
- c) optical isomers
- d) functional isomers

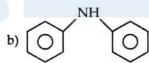
PREPARATION METHODS

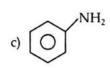
- 61. The reduction of alkyl cyanide with sodium and alcohol is called
 - a) Mendius reduction
 - b) Clemmensons reduction
 - c) Catalytic reduction
 - d) none of these
- 62. Aldoxime on reduction with Na + C₂H₅OH form
 - a) 1° amines
- b) 2° amines
- c) 3° amines
- d) alcohols
- 63. Acetoxime on reduction and followed by acetylation gives
 - a) ethyl amine
 - b) isopropyl amine
 - c) monoacetyl isopropyl amine
 - d) diacetyl isopropyl amine
- 64. The reduction of which of the following gives 1-propanamine?
 - a) C₃H₇CN
- b) $C_2H_5CH = NOH$
- c) CH₂NO₂
- d) CH, COCH,

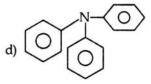
- 65. The reduction of acetaldoxime gives
 - a) CH₃-CH₂-NH₃
- b) CH₂-NH₂
- c) (CH₃)₃C-NH₅
- d) CH₂-NH-CH₃
- 66. Which of the following reagent is used to convert -CN group to -CH₂NH₂ group?
 - a) CrO,
- b) Na + C_2H_5OH
- c) H₃PO₄
- d) Al₂O₃
- 67. Which of the following compound give methanamine on reduction?
 - a) HCN
- b) HCHO
- c) CH, CN
- d) HCOOH
- 68. On reduction with Sn + conc. HCl of C₂H₅NO₂ yields
 - a) esters
- b) secondary alcohol
- c) primary amine
- d) secondary amine
- 69. The reaction of CH₂CN to CH₂CH₂NH₂ is called
 - a) Mendius reduction
 - b) Rosenmund reduction
 - c) Hoffman reduction
 - d) Clemmenson reduction
- 70. –NO, group is converted into –NH, group by the reaction
 - a) dehydration
- b) alkaline hydrolysis
- c) reduction
- d) decarboxylation
- 71. Which of the following reactions does not yield an amine?
 - a) RX + NH₂ \longrightarrow
 - b) RCH = N-OH + H, $\xrightarrow{\text{Ni}}$
 - c) RCN + H₂O $\xrightarrow{H^+}$
 - d) R-NO₂ + 4H $\xrightarrow{\text{Sn + conc.HCl}}$
- 72. Ethylamine can be obtained by the action of
 - a) $NH_3 + C_2H_5I$
- b) $C_2H_2CN + 4H$
- c) both 'a' and 'b'
- d) HCHO + NH₂
- 73. Which of the following compounds gives a primary amine on reduction?
 - a) Nitroalkane
- b) Oximes
- c) Alkyl cyanides
- d) All of these
- 74. Excess of bromo ethane reacts with alcoholic ammonia to give,
 - a) ethyl amine
- b) diethyl amine
- c) triethyl amine
- d) all of these
- 75. Ketoxime on reduction gives
 - a) 1° amines
- b) 2° amines
- c) 3° amines
- d) all of these

- 76. Acetonitrile is treated with sodium and ethanol gives
 - a) methyl amine
- b) acetic acid
- c) ethyl amine
- d) methanal
- 77. Acetoxime on reduction gives,
 - a) dimethyl amine
- b) isopropyl amine
- c) ethyl methyl amine d) ethyl amine
- 78. $R-NO_2 \xrightarrow{Sn + conc.HCl} X$. In this reaction X is
 - a) R-Cl
- b) R-NH,
- c) R-SnCl₂
- d) R-NH, + Cl-
- 79. CH₂NH₂ is obtained from NH₂ by
 - a) Hoffmans reaction b) Cannizzaros reaction
 - d) none of these c) Wurtz reaction
- 80. Which of the following does not give primary amine on reduction?
 - a) RNO,
- b) RCHO
- c) $R_{a}C = NOH$
- d) RCN
- 81. 2–nitro 2–methyl propane on reduction gives
 - a) (CH₃)₃N
- b) (CH,),NH
- c) (CH₂)₂CNH₂
- d) (CH₂)₂CHCH₂NH₂
- 82. n-propyl cyanide on reduction gives
 - a) n-butyl amine
- b) n-propyl amine
- c) isobutyl amine
- d) t-butyl amine
- 83. Which of the following is Mendius reduction?
 - a) RNO₂ + 6H \rightarrow
 - b) RCN + 4H \rightarrow
 - c) RCH = NOH + 4H \rightarrow 4) PNC + 2H \rightarrow
 - d) RNC + 2H, \rightarrow
- 84. Benzyl halide on ammonolysis produces









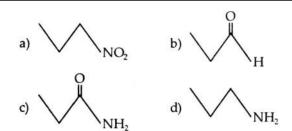
85. The production (C) in following sequence of reaction

$$\begin{array}{c}
O \\
OH
\end{array}$$

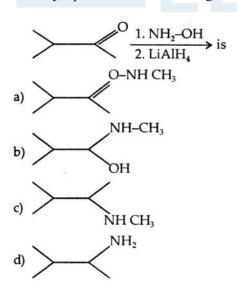
$$\begin{array}{c}
O \\
OH
\end{array}$$

$$A \xrightarrow{\text{heat}} B$$

 $Na+C_2H_5-OH$ C

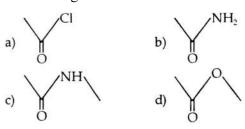


- 86. Methyl amine is formed by reduction of
 - a) nitroethane
- b) methyl cyanide
- c) formamide
- d) Acetaldoxime
- 87. Ethyl amine is obtained by the action of sodium hypobromite on the following amide
 - a) formamide
- b) propanamide
- c) acetamide
- d) butanamide
- 88. For alkylation of ammonia which of the following is not used
 - a) CH₂-X
- b) CH₃-CH₂-X
- c) $(CH_3)_2CH-X$
- d) $(CH_3)_2C-X$
- 89. Hofmann's hypobromite reaction is affords a method of
 - a) preparation of 1°alcohol
 - b) preparation of mixture of amines
 - c) stepping down the series
 - d) stepping up a series
- 90. A primary amine is formed from amide, bromine and alkali. The 1°-amine has
 - a) one carbon less than amide
 - b) one carbon more than amide
 - c) one hydrogen less than amide
 - d) one hydrogen more than amide
- 91. The major product in the following reaction



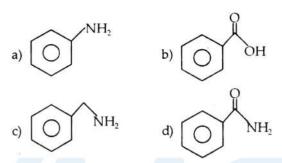
92. Which of the following will undergoes Hofmann's

reaction to give a 1°-amine?

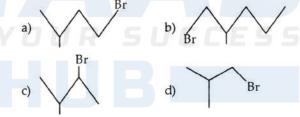


93. State the product available by the following reaction

$$\begin{array}{c|c} & & & \\ \hline & & 1. \text{ NH}_2\text{-OH} \\ \hline & 2. \text{Zn+CH}_3\text{-COOH} \\ \end{array}$$



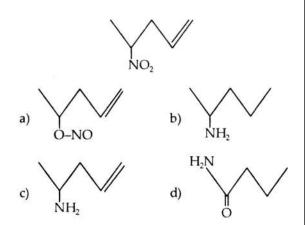
94. Potassium phthalimide react with 'A' which on hydrolysis gives 2–methyl propan–1–amine. What is 'A'?



- 95. Reduction of nitoparaffin gives
 - a) 1°-amine
- b) 2°-amine
- c) 3°-amine
- d) amide
- 96. Tertiary amine can be obtained by
 - a) Gabriel phthalimide synthesis
 - b) hydrolysis of cyanide
 - c) Thermal decomposition of quaternary ammonium salt
 - d) Reduction of nitroalkane by Zn + NH₄Cl
- 97. Which of the following may be prepared by Gabriel Phthalimide synthesis
 - a) Aliphatic 1°-amine b) Aromatic 1°-amine
 - c) Aliphatic 2°-amine d) Aromatic 2°-amine
- 98. A $\xrightarrow{\text{Reduction}}$ 1° amine.

The compound A may be

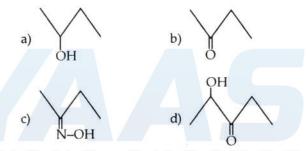
- 1) R-NC
- 2) R-CN
- 3) R-CONH,
- 4) R-NO,
- a) 1, 2
- b) 3, 4
- c) 2
- d) 2, 3, 4
- 99. Aniline is obtained by
 - a) Reduction of benzaldoxime
 - b) treating benzamide with NaOBr
 - c) treating acetophenone with hydroxyl amine
 - d) treating phthalimide with R-X
- 100. From Gabriel phthalimide synthesis aromatic primary amine cannot be prepared
 - a) Ar-X do not undergoes nucleophilic substitution reaction
 - b) Ar–X is stable due to resonating structures
 - c) Ar–X is highly reactive due to C–X bond is very weak
 - d) Ar-X is not stable
- 101. Potassium phthalimide is reacted with ethyl halide and followed by acid hydrolysis gives
 - a) ethanol
- b) nitroethane
- c) ethanamine
- d) diethyl amine
- 102. In Hofmann's hypobromide reaction
 - a) The alkyl group in amide migrate to nitrogen atom
 - b) The alkyl group in amide migrate to oxygen atom
 - c) There is a no migration of alkyl group of amide
 - d) Hydrogen atom is migrated to carbonyl oxygen atom of amide
- 103. Following compound on reduction by using Fe+cone. HCl. gives



104. Product of the following reaction is

105. Find out (B) in the following reaction

106. Compound 'A' is oxidised by trifluoroperoxy acetic acid gives 'B' followed by reduction with Fe+cone. HCl gives butan-2-amine. The compound 'A' is



107. Product of the following reaction is

$$OH \xrightarrow{1. NH_3/A} ?$$

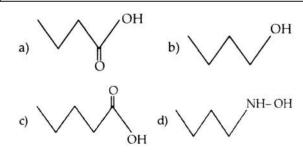
$$a) O NH_2$$

$$b) O NH_2$$

$$c) O NH-OH$$

108. Compound A in the following reaction is

$$A \xrightarrow{NH_3/\Delta} B \xrightarrow{Br_2 + KOH} Butan-1$$
-amine

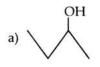


BASIC NATURE AND PROPERTIES

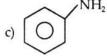
- 109. Amine are basic is nature according to
 - a) Arrhenious theory
 - b) Lewis theory
 - c) Lowry-Bronsted theory
 - d) all of these
- 110. In chemical reaction of amines, which act as
 - a) electrophiles
- b) nucleophiles
- c) neutral
- d) acid
- 111. Aniline is less soluble in water than ethyl amine
 - a) Resonance stabilization of benzene ring
 - b) resonance stabilization of anilium ion
 - c) more hydrophobic nature of C₆H₅ group than C,H, group
 - d) more hydrophilic nature of C₆H₅ group than C,H, group
- 112. Amines have higher B.P. than corresponding alkane or ethers due to
 - a) intermolecular hydrogen bonding
 - b) intramolecular hydrogen bonding
 - c) high polar nature of C-N bond
 - d) Lone pair of electron on nitrogen atom
- 113. In isomeric amine correct order of B.P. is
 - a) $1 > 2^{\circ} > 3^{\circ}$
- b) $3^{\circ} > 2^{\circ} > 1^{\circ}$
- c) $2^{\circ} > {}^{\circ} > 1^{\circ}$
- d) $1^{\circ} > 3^{\circ} > 2^{\circ}$
- 114. Which of the following has lowest B.P.
 - a) CH₃-CH₂-CH₂-NH₃

- c) C₂H₅-NH-CH₃
- d) (CH,),N
- 115. All amines are soluble in
 - a) water
- b) HCl
- c) CS₂
- d) CCl₄
- 116. Amines have lower B.P. than
 - a) ethers
- b) alkanes

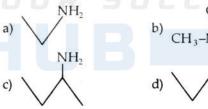
- c) alcohols
- d) alkyl halide
- 117. Which of the following is more soluble in water



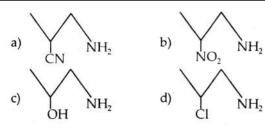




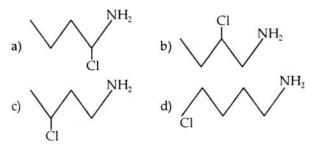
- 118. Basicity of amines in gaseous state is
 - 1) (CH₃)₃N
- 2) CH,-NH,
- 3) (CH₂), NH
- 4) NH,
- a) 1 > 2 > 3 > 4
- b) 1 > 3 > 2 > 4
- c) 3 > 1 > 2 > 4
- d) 2 > 3 > 1 > 4
- 119. Basicity of following amines in aqueous medium
 - 1) CH₃-NH₃
- 2) (CH₃), NH
- 3) (CH₂)₂N
- 4) NH,
- a) 1 > 2 > 3 > 4
- b) 3 > 2 > 1 > 4
- c) 2 > 1 > 3 > 4
- d) 2 > 3 > 1 > 4
- 120. In gaseous state the basicity of amine is
 - a) $1^{\circ} > 2^{\circ} > 3^{\circ} > NH_{1}$
 - b) $3^{\circ} > 2^{\circ} > 1^{\circ} > NH_{3}$
 - c) NH₃ > 3° > 1° > 2°
 - d) $2^{\circ} > 1^{\circ} > NH_{3} > 3^{\circ}$
- 121. Which of the following is more basic in gaseous state?



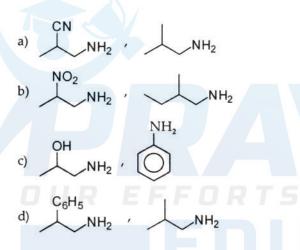
- CH3-N-CH3
- 122. Which of the following is correct statement about basicity of amines?
 - 1) smaller the value of pKb weaker the base
 - 2) Electron donating groups increase the basicity of amines
 - 3) Electron withdrawing groups decrease the basicity of amines
 - 4) Aromatic amines are more basic than aliphatic amines
 - a) 1, 4
- b) 2, 3
- c) 2, 4
- d) 1, 3
- 123. Which of the following is less basic in aqueous medium is



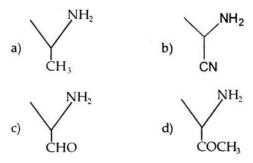
124. Which of the following is more basic in aqueous medium is



125. In which of the fallowing 1^{st} is more basic than 2^{nd}



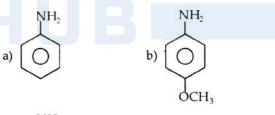
- 126. Which of the following has more pKb value?
 - a) CH₃-NH₂
- b) $C_2H_5-NH_2$
- c) Cl-CH₂-NH₂
- d) HO-CH₂-NH₂
- 127. Which of the following has more kb value?



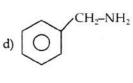
- 128. Aryl amines are less basic than alkyl amine and ammonia which is due to
 - a) In aryl amine lone pair of electron on nitrogen is conjugation with benzene ring and thus making

less available for protonation

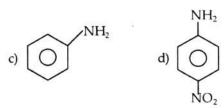
- b) less stability of anilium ion than alkyl ammonium ion
- c) Aniline forms hydrogen bond with water
- d) In aniline intermolecular hydrogen bonding is present
- 129. Correct order of B.P. of amine is
 - a) $CH_3-NH_2 > (CH_3)_2NH > (CH_3)_3N$
 - b) $(CH_3)_3NH > CH_3-NH_3 > (CH_3)_3N$
 - c) $(CH_3)_3N > (CH_3)_2NH > CH_3-NH_3$
 - d) $(CH_{3})_{3}NH > (CH_{3})_{3}N > CH_{3}-NH_{3}$
- 130. Mark the correct statement
 - a) methyl amine is slightly acidic
 - b) methyl amine is less basic than ammonia
 - c) methyl amine is more basic than ammonia
 - d) methyl amine form salt with alkalies
- 131. The conjugate base of (CH₃)₂NH₂⁺ is
 - a) (CH₂),NH
- b) $(CH_{2})_{2}N^{+}$
- c) $(CH_{2})_{2}N^{+}$
- d) $(CH_3)_2N^-$
- 132. Which of the following is conjugate base of (CH₃)₃NH⁺?
 - a) $(CH_3)_3N^+$
- b) (CH₃)₃N
- c) (CH₃),NH
- d) $(CH_{2})_{2}N^{+}H$
- 133. Which of the following shares lone pair of electron less easily?
 - a) methyl amine
- b) benzyl amine
- c) aniline
- d) diethyl amine
- 134. Which of the following is more basic in aqueous medium?







- 135. Among the following most basic compound in aqueous medium is
 - a) C₂H₅-NH₂
- b) CH₂- NH₂



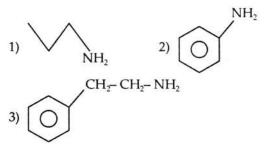
- 136. The correct order of basicity of following compound in aqueous medium is
 - 1) $(C_{2}H_{2})_{2}NH$
- 2) C₂H₅-NH₂
- 3) (CH₂),NH
- 4) CH₂NH₂
- a) 1 > 2 > 3 > 4
- b) 3 > 1 > 2 > 4
- c) 2 > 1 > 3 > 4
- d) 1 > 3 > 2 > 4
- 137. Product of the following reaction is

$$\begin{bmatrix} \operatorname{CH_3} & & \\ -\operatorname{CH_3} - \operatorname{N} - - \operatorname{CH} - \operatorname{CH_2} - \operatorname{CH_3} \\ -\operatorname{CH_3} & \operatorname{CH_3} \end{bmatrix}^{+} \operatorname{OH^{-}} \xrightarrow{\Delta}$$

- a) $(CH_2)_2NH + CH_2-OH + CH_3-CH = CH-CH_3$
- b) $(CH_3)_3N+CH_3-CH = CH-CH_3$
- c) $(CH_3)_3N + CH_2 = CH_2 CH_3 + H_2O$
- d) $(CH_2)_2NH + CH_2 OH + CH_2 = CH CH_2 CH_2$
- 138. Which of the fallowing has highest pKb value in aqueous medium?

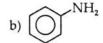
 - a) CCl₃-CH₂-NH₂ b) CCl₃-CH₂-CH₂-NH₃

 - c) CF₃-CH₂-NH₂ d) CF₃-CH₂CH₂-NH₃
- 139. Which of the following is insoluble in dil HCl?
 - a) Aniline
- b) ethyl amine
- c) triphenyl amine
- d) dimethyl amine
- 140. Arrange the following amines in the decreasing order of their basicity in aqueous medium



- a) 1 > 3 > 2
- b) 3 > 2 > 1
- c) 1 > 2 > 3
- d) 2 > 1 > 3
- 141. Which of the following is least basic in aqueous medium?

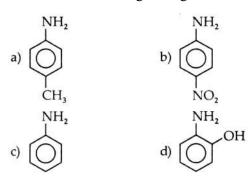




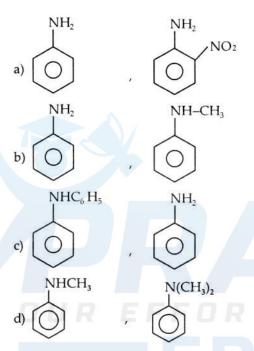
- - NHCH,
- 142. The less basic amine in aqueous medium is
 - a) $(C_2H_5)_2NH$
- b) $(C_{2}H_{5})_{3}N$
- c) $(CH_2)_2NH$
- d) (CH₂)₂N
- 143. Which of the following factor influence the basicity aliphatic amines in aqueous medium?
 - 1) Inductive effect of alkyl groups
 - 2) Solvation effect
 - 3) Steric effect
 - a) 1, 3
- b) 1, 2
- c) 2, 3
- d) 1, 2, 3
- 144. Which of the following is more basic in aqueous medium?
 - a) CH,-NH,
- b) CH₃-CHNH₂-CH₃
- c) (CH₂),NH
- 145. Identify the incorrect statement about the basic nature of amines
 - a) Aralkyl amines are less basic than ammonia
 - b) Aniline is more basic than ammonia
 - c) p-nitroaniline is more basic than para amino benzoic acid
 - d) p-amino phenol is less basic than para methyl aniline
- 146. In which of the following first is more basic than

a)
$$\bigvee_{NH_2}^{NH_2}$$
 $\bigvee_{NH_2}^{NH_2}$ $\bigvee_{NO_2}^{NH_2}$ $\bigvee_{NO_2}^{NH_2}$ $\bigvee_{NO_2}^{NH_2}$ $\bigvee_{NO_2}^{NH_2}$ $\bigvee_{NO_2}^{NH_2}$ $\bigvee_{NO_2}^{NH_2}$ $\bigvee_{NO_2}^{NH_2}$ $\bigvee_{NO_2}^{NH_2}$

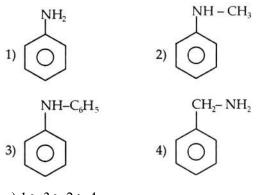
147. Which of the following has highest Kb value



148. Which of the following first is more basic than second?



149. Correct order of basicity of following compound second is



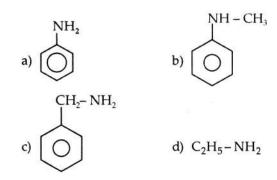
a)
$$1 > 3 > 2 > 4$$

b)
$$4 > 2 > 1 > 3$$

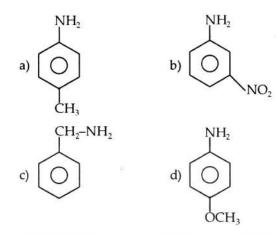
c)
$$4 > 3 > 2 > 1$$

d)
$$4 > 1 > 2 > 3$$

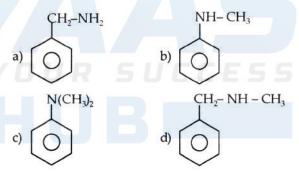
150. Which of the following has highest pKb value



151. Which of the following amine is easily protonated?



152. Which of the following amine has less tendency to accept proton form acid



- 153. Which of the following has maximum steric effect?
 - a) (CH₃)₂N
- b) (CH₂)₂NH
- c) CH₃NH₂
- d) C₂H₅NH₂
- 154. Consider the following amines
 - 1) n-butyl amine
 - 2) ethyl dimethyl amine
 - 3) diethyl amine

the correct sequence of boiling point is

a)
$$1 > 3 > 2$$

b)
$$1 > 2 > 3$$

c)
$$2 > 3 > 1$$

d)
$$2 > 1 > 3$$

155. Which of the following reacts with nitrous acid to form an alcohol?

Compounds Containing Nitrogen

- a) CH₃CH₂NH₂
- b) (CH₃)₂NH
- c) (CH₃)₃ N
- d) $(C_2H5)_3N$
- 156. Which of the following will not answer Carbyl amine reaction?
 - a) Ethyl amine
- b) Methyl amine
- c) Aniline
- d) Dimethyl amine
- 157. The correct order of basic strength of amines in aqueous medium is
 - 1) $C_2H_5NH_2$
- 2) (CH₃)₂NH
- 3) $(C_2H_5)_2NH$
- 4) $(C_2H_5)_2N$
- a) 3 > 2 > 1 > 4
- b) 2 > 3 > 4 > 1
- c) 3 > 4 > 2 > 1
- d) 1 > 3 > 2 > 4
- 158. A substance (A) is soluble in dil. HCl and produces obnoxious smell with alcoholic potash and haloform. Which type of compound behave like this.
 - a) Alcohol
- b) 1° amine
- c) 2° amine
- d) 3° amine
- 159. Which of the following reaction is given by only primary amine?
 - a) With HONO
 - b) With CHX₃ and alcoholic potash
 - c) With acetyl chloride
 - d) With CH₃I
- 160. Which of the following compound give nitrosoamine with HNO₂?
 - a) 1° amines
- b) 2° amines
- c) 3° amines
- d) All of these
- 161. The compound, which does not react with CH₃COCl is
 - a) RNH₂
- b) R,NH
- c) R₂N
- d) all of these
- 162. Steric effect of methyl group reduces basic character of
 - a) 3° amines
- b) 1° amines
- c) 2° amines
- d) none of these
- 163. A carbon compound which is soluble in conc. HCl solution, on treatment with sodium nitrite give a ni trogen gas
 - a) C₂H₅NH₂
- b) CH₃NH₂
- c) CH₃CH₂CH₂NH₃, d) all of these
- 164. $R_2NH + HNO2 \xrightarrow{\text{cold}} R_2N N = O + H_2O$

This reaction is,

- a) electrophilic addition
- b) electrophilic substitution
- c) nucleophilic addition

- d) nucleophilic substitution
- 165. Which of the following species is formed when ethanamine is reacted with conc. HCl?
 - a) $C_2H_5NH_2^+Cl^-$
- b) C₂H₅NH₃+Cl-
- c) $(C_2H_5)_2NH_2+C1$
- d) C₂H₅NH⁺Cl⁻
- 166. Amines behave as
 - a) Lewis acids
 - b) Lewis bases
 - c) aprotic acids
 - d) amphoteric compounds
- 167. Which of the following alkyl halide is used as a methylating agent?
 - a) CH₃I
- b) C₂H₅Br
- c) C₂H₅Cl
- d) C₆H₅Cl
- 168. Action of nitrous acid with ethyl amine produces
 - a) ethane
- b) ammonia
- c) ethyl alcohol
- d) nitroethane
- 169. The correct order of basicity of the following compound in aqueous medium is
 - 1) NH₃
- 2) CH, CH, NH,
- 3) $(CH_3)_2NH$
- 4) $(C_2H_5)_2N$
- a) 2 > 3 > 1 > 4c) 4 > 3 > 1 > 2
- b) 4 > 3 > 2 > 1d) 3 > 2 > 1 > 4
- 170. Secondary amine forms insoluble nitrosoamine with
 - a) HNO₃
- b) HNO,
- c) CH,COCl
- d) HCl
- 171. Primary, secondary and tertiary amines are distinguished by the action of
 - a) HNO₂
- b) HNO
- c) dil. HCl
- d) dil. H,SO,
- 172. Consider the nitrogen atom in amines, which one of the following statement is correct?
 - a) It is sp³-hybridised b) It is sp²-hybridised
 - c) It is sp^3 -hybridised d) It is sp^2 -d hybridised
- 173. In tertiary amines the valency of nitrogen atom is
 - a) 3
- b) 4
- c) 5
- d) 2
- 174. The reagent which does not react with $(C_2H_5)_3N$ is / are
 - a) CH₃COCl
- b) (CH₃CO)₂O
- c) NaOH
- d) all of these
- 175. An aliphatic primary amine reacts with HNO₂ in cold to form
 - a) a nitrile
- b) an alcohol
- c) a diazonium salt
- d) a secondary amine
- 176. Carbylamine reaction is given only by

Compounds Containing Nitrogen

- a) primary amines
- b) secondary amines
- c) tertiary amines
- d) quaternary amines
- 177. Which of the following is more basic?
 - a) Methenamine
- b) Ethanamine
- c) Propan-2-amine
- d) Phenyl methanamine
- 178. Hinsberg reagent is
 - a) Cu⁺⁺ + OH⁻
- b) C₆H₅SO₇ Cl
- c) C₆H₅ NHNH₂
- d) SOCl,
- 179. Which one of the following pair can consume same amount of acetyl chloride?
 - a) Acetyl ethyl amine and ethyl amine
 - b) Acetyl ethyl amine and diethyl amine
 - c) Ethyl amine and diethyl amine
 - d) Methyl amine and trimethyl amine
- 180. The basic character of amines is due to
 - a) presence of nitrogen atom
 - b) lone pair of electrons on nitrogen atom
 - c) tetrahedral structure
 - d) high electronegativity of nitrogen
- 181. All amines are basic in nature because,
 - a) they possess lone pair of electron on nitrogen
 - b) they give OH- ion in aqueous medium
 - c) they form salt with acid
 - d) all of these
- 182. Isocyanide test is used for the detection of
 - a) primary alcohols
- b) secondary alcohols
- c) primary amines
- d) secondary amines
- 183. C₂H₅NH₂ and CH₃NHC₂H₅ can be distinguished by
 - a) Hoffmann's reaction
 - b) Williamson's reaction
 - c) Wurtz's reaction
 - d) Carbyl amine reaction
- 184. Ethyl amine reacts with excess of methyl iodide to give
 - a) ethyl methyl amine
 - b) ethyl dimethyl amine
 - c) ethyl trimethyl ammonium iodide
 - d) all of these
- 185. How many molecules of CH₃I will react with CH₃NH₂ to form tetra methyl ammonium iodide?
 - a) 2
- b) 3
- c) 4
- d) 5
- 186. Following 1° amine has chiral centre CH₃CHNH₂C₂H₅

- This on reaction with NaNO₂ + HCl forms
- a) 1° alcohol with retention of configuration
- b) 2° alcohol with inverted configuration
- c) racemic mixture of 2° alcohol
- d) racemic mixture of 1° alcohol
- 187. Acetylation of amine is done in the presence of
 - a) CH, COCl
- b) CH₃CONH₂
- c) CH, COOCH,
- d) all of these
- 188. Which of the following is more basic?
 - a) CH₂NH₂
- b) (CH₃)₂NH
- c) $(CH_3)_3N$
- d) NH₃
- 189. Which of the following is acetylating agent?
 - a) CH₂COCH₂
- b) CH₃CONH₂
- c) (CH₃CO)₂O
- d) CH₃COONa
- 190. Which of the following has lowest Kb value?
 - a) Benzenamine
 - b) N-methyl aniline
 - c) N, N-dimethyl aniline
 - d) N, N-dimethyl methanamine
- 191. Which of the following amine does not give alcohol with HNO₂?
 - a) C₂H₅NH₂
- b) CH₂CHNH₂CH₃
- c) CH, NHCH,
- d) (CH₃)₃CNH₂
- 192. The best methylating agent is
 - a) CH₃Cl
- b) CH₃Br
- c) CH₃F
- d) CH₃I
- 193. Triethyl amine reacts with HCl and NaNO₂ give,
 - a) triethyl nitroso amine
 - b) ethyl alcohol and diethyl nitroso amine
 - c) three molecules of ethyl alcohol
 - d) no product
- 194. About amines some statements are given below,
 - 1. they possess two lone pair of electrons on nitrogen atom
 - 2. these are monoacidic base
 - 3. their basicity is one
 - 4. they can accept proton

Among the above, true statement(s) is/are

- a) only 2 and 3
- b) only 3 and 4
- c) only 2, 3 and 4
- d) all of these
- 195. Primary amine forms
 - a) diacetyl derivative
 - b) triacetyl derivative
 - c) monoacetyl derivative
 - d) all of these
- 196. The unpleasant smelling isocyanide are also called

- a) nitriles
- b) cyanide
- c) carbyl amine
- d) ethers
- 197. The conversion of 1° amine to 3° amine. The process involved may be called,
 - a) reduction
- b) alkylation
- c) oxidation
- d) hydrogenation
- 198. Which of the following can not be acetylated?
 - a) CH₃NH₂
- b) (CH₃),NH
- c) $(CH_3)_3N$
- d) (CH₃),CNH,
- 199. Trimethyl amine on acetylation gives
 - a) trimethyl acetyl amine
 - b) triacetyl methyl amine
 - c) diacetyl dimethyl amine
 - d) none of these
- 200. Amines are polar compounds because of the
 - a) hydrogen bonding
 - b) difference in electronegativity between C, H and N
 - c) -NH, group
 - d) alkyl group
- 201. Which of the following amine will not give effervescence with HNO₂?
 - a) CH₃NH₂
- b) C,H,NH,
- c) (CH₃),CHNH,
- d) $(CH_3)_2NH$
- 202. Tertiary amines does not react with CH₃COCl, because of
 - a) least basic
 - b) no hydrogen atom on nitrogen
 - c) three alkyl groups
 - d) all of these
- 203. Which is soluble in NaNO₂ and dil HCl forming salt?
 - a) (CH₃)₃ CNH₂
- b) (CH₃), CHNH,
- c) (CH₃), NH
- d) (CH₃)₃ N
- 204. Which type of bond is formed when amines donate lone pair to proton?
 - a) Covalent bond
- b) Ionic bond
- c) Co-ordinate bond
 - d) Electrovalent bond
- 205. Primary amines on treatment with HNO₂ give
 - a) primary alcohol
- b) secondary alcohol
- c) tertiary alcohol
- d) all of these
- 206. The general formula of quaternary ammonium compound is
 - a) R–NH₂
- b) R₂N
- c) $R_{\downarrow}N^{+}X^{-}$
- d) NH₄X
- 207. N, N dimethyl acetamide is

- a) $(CH_3)_2NCOCH_3$ b) $CH_3N(COCH_3)_2$
- c) CH₃CONH₂
- d) C,H₅N(COCH₃)₂
- 208. Which of the following has fishy smell?
 - a) CH₃NH₂
- b) C,H,NH,
- c) (CH₃),NH
- d) $CH_3(CH_2)_4NH_2$
- 209. $(CH_3)_2CHNH_2$ is reacted with excess acetic anhydride, the compound formed is
 - a) (CH₃)₂CHNCOCH₃
 - b) (CH₃)₂CHN(COCH₃)₂
 - c) $(CH_3)_2CHOH$
 - d) (CH₃),CHN(COOCH₃),
- 210. Acetylation of amine is
 - a) nucleophilic addition
 - b) nucleophilic substitution
 - c) electrophilic addition
 - d) electrophilic substitution
- 211. The bond(s) present in quaternary ammonium salt is/are
 - a) covalent
 - b) ionic
 - c) covalent, co-ordinate and ionic
 - d) covalent and co-ordinate
- 212. Amines form salt with H₂SO₄, the molar ratio of
 - a) 2 : 2
- b) 2:1
- c) 1:2
- d) 2:3
- 213. The maximum number of moles of an acetylating agent, consumed by a mole of each of 1°, 2° and 3° amines are respectively
 - a) 2, 3 and 4
- b) 1, 2 and 3
- c) 2, 1 and 0
- d) 0, 2 and 1
- 214. The number of moles of nitrogen obtained by the complete reaction of one mole of C₂H₅NH₂ with nitrous acid is
 - a) 2
- b) 3
- c) 4
- d) 1
- 215. Three moles of CH₃I are made to react with one mole of ammonia. The product formed is
 - a) 1° amine
 - b) 2° amine
 - c) 3° amine
 - d) quaternary ammonium salt
- 216. Which of the following reaction shows the basic nature of amines?
 - a) RNH₂ + HCl
- b) RNH₂ + CH₂COCl
- c) RNH₂ + HNO₂
- d) $RNH_2 + (CH_3CO)_2O$
- 217. Select the correct statement about the following reaction.

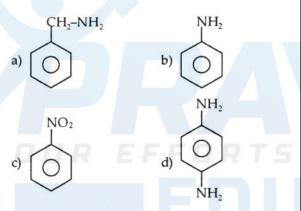
$$[(CH_3)_3NCH_2-CH_3]^+OH^-$$

$$(CH_3)_3N + CH_2 = CH_2 + H_2O$$

- a) This is called Hofmann elimination reaction
- b) OH- ion function as base
- c) Less substituted alkene is major product
- d) All of these are correct
- 218. Which of the following alkyl halides is used as a methylating agent?
 - a) C₂H₅Cl
- b) CH,COCl
- c) (CH,CO),O
- d) CH₃I
- 219. Consider the following reaction

$$CH_3$$
-CONH, \xrightarrow{I} CH_3 -NH, \xrightarrow{II} CH_3 NC

- a) Reaction I is called Hofmann's hypobromide reaction.
- b) Reaction II is called carbyl amine reaction.
- c) Reaction I and II are Hofmann reaction.
- d) Both 'a' and 'b' are correct statements.
- 220. Anilinium hydrochloride is obtained from HCl and what



- 221. Optical active amine of molecular formula $C_4H_{11}N$ on reaction with nitrous acid gives
 - a) bu tan-1-ol
 - b) 2-methyl propan-1-ol
 - c) 2-methyl propan-2-ol
 - d) butan-2-ol
- 222. What will be the major product when propan—2—amine is treated with nitrous acid?
 - a) propan-1-ol
- b) propan–2–ol
- c) propene
- d) cyclopropane
- 223. The residue insoluble in KOH obtained in the Hinsberg's test corresponds to
 - a) 1°-amine
- b) 2°-amine
- c) 3° –amine
- d) cannot be predicated
- 224. Two compound A and B treated with nitrous acid

$$\begin{array}{ccc} \operatorname{CH_3} - \operatorname{CH} - \operatorname{CH_3} & & \operatorname{CH_3} - \operatorname{CH_3} - \operatorname{CH_2} - \operatorname{NH_2} \\ & & | \\ & \operatorname{NH_2} & & \end{array}$$

The corresponding stable carbocation intermediated are respectively

a)
$$A = \bigvee_{\Theta}$$

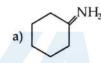
Α

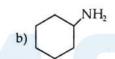
В

$$A = \bigoplus_{\Theta}$$

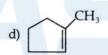
$$B = \bigoplus$$

- d) A =
- 225. Product (B) of the following reaction is









- 226. C₆H₅-NH₂ + CHCl₃ + KOH nitrogen containing compound + 3KCl + H₂O. The nitrogen containing compound is
 - a) $C_6H_5-NH_3-C1$
- b) C₆H₅-CN
- c) C₆H₅-NC
- d) $C_6H_5-NO_2$
- 227. In order to distinguish between C₂H₅-NH₂ and C₆H₅-NH₂, which of the following reagent is useful
 - a) Hinsberg's reagent b) HNO₂
 - c) CHCl₃ + KOH
- d) NaOH
- 228. Which of the following is more basic amine?
 - a) (CH₃),NH
- b) $(C_{2}H_{5})_{3}N$
- c) (CH₃)₃N
- d) $C_2H_5NH_2$
- 229. Methyl alcohol is prepared form heating of
 - a) (CH₃)₄NOH
- b) (CH₃)₃N-C₂H₅OH
- c) $CH_3-CH_2-NH_2$
- d) CH₃-NH-CH₃
- 230. Which of the following reacts with Hinsberg reagent to form a product soluble in KOH
 - a) 1°-amine
- b) 2°-amine
- c) 3°-amine
- d) quaternary amine

231. Thermal decomposition of

$$\begin{bmatrix} \mathrm{CH_3} \\ \mathrm{CH_3} - \mathrm{N} & ---- \mathrm{CH} - \mathrm{CH_2} - \mathrm{CH_3} \\ | & | & | \\ \mathrm{CH_3} & \mathrm{CH_3} \end{bmatrix}^{\!+} \quad \mathrm{OH^- \ gives}$$

- a) CH_3 – $CH = CH_2$ b) $CH_2 = CH_2$
- c) CH₃-CH₃
- d) CH₃-CH₂-CH₃
- 232. 1°,2°,3°–amines can be distinguished by using
 - a) NaNO₂ + HCl
- b) CH,COCl
- c) C₆H₅SO₂Cl
- d) all of these
- 233. All three amines $1^{\circ}, 2^{\circ}, 3^{\circ}$ are react with
 - 1) H,O
- 2) R-X
- 3) HCl
- 4) (CH₂CO)₂O
- a) 1, 2
- b) only 4
- c) 1, 2, 4
- d) 1, 2, 3
- 234. N,N-dimethyl anilinium acetate obtained from

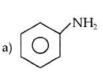
a)
$$N < \frac{CH_3}{CH_3} + (CH_3CO)_2O \longrightarrow$$

b)
$$N \leq_{CH_3}^{CH_3} + CH_3COCI \longrightarrow$$

c)
$$N < CH_3 + CH_3COOH \longrightarrow$$

d)
$$NH-CH_3$$
 + CH_3COOH \longrightarrow

235. N-phenyl ethanamide is obtained from CH₂COCl and what

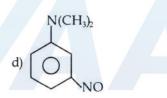


236. Aniline reacts with NaNO₂ + dil.HCl gives

- a) phenol
- b) chlorobenzene
- c) dichlorobenzene
- d) benzene diazonium chloride
- 237. N-N-dimethyl phenyl amine reacts with nitrous acid gives

$$a) \ \ \, \bigcap^{\textstyle N \ (CH_3)_2 NO^{\star}_2}$$

b)
$$NH_2$$
 $NH (CH_3)_2NO_2$



238. Which of the following compound produces alkene on heating

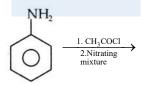
$$\begin{pmatrix}
CH_3 \\
-
CH_3 - N - CH_3 \\
-
CH_3
\end{pmatrix}^{\dagger} OH^{-1}$$

b) $(CH_3)_3C - X$

c)
$$\begin{bmatrix} CH_3 \\ CH_3 - N - CH_2 - CH_3 \\ CH_3 \end{bmatrix}^{\dagger} OH^{-}$$

- 239. –NH, group in aniline is
 - a) only o-directing
- b) only p-directing

- c) only m-directing
- d) o and p directing
- 240. Strong activating effect of –NH₂ group is reduced by using
 - a) CH₃COCl
- b) CH₃Cl
- c) CH,ONa
- d) CH₃-CHO
- 241. During electrophilic substitution reaction protection of -NH₂ group can be done by
 - a) reduction
- b) oxidation
- c) alkylation
- d) acylation
- 242. Aniline is reacted with Br₂/water gives (without protecting –NH₂ group)
 - a) o-bromo aniline
 - b) p-bromo aniline
 - c) mixture of o- and p-bromo aniline
 - d) 2,4,6-tribomoaniline
- 243. When bromination of aniline is carried out by protecting –NH₂. The product is
 - a) o-bromoaniline
 - b) 2, 4, 6-tribromo aniline
 - c) p-bromo aniline
 - d) mixture of o- and p-bromo aniline
- 244. Aniline on nitration gives
 - a) o-nitroaniline
 - b) p-nitroaniline
 - c) m-nitroaniline
 - d) mixture of o,p,m nitroaniline
- 245. Aniline on nitration unexpectedly gives
 - a) o-nitroaniline
- b) p-nitroaniline
- c) m-nitroaniline
- d) o-dinitro benzene
- 246. Product of the following reaction will be

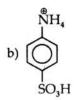


- a) o-nitroaniIine as major product
- b) p-nitroaniline as major product
- c) m-nitroaniline as major product
- d) o-amino acetophenone is major product
- 247. Which of the following exist as a zwitter ion?
 - a) sulphanilic acid
- b) sulphonic acid
- c) phthalic acid
- d) Terephthalic acid
- 248. Aniline is heated with cone. H₂SO₄ gives
 - a) o-amino benzene sulphonic acid
 - b) p-amino benzene sulphonic acid
 - c) m-amino benzene sulphonic acid

- d) isophthalic acid
- 249. Following is zwitter ion of



NH₂OH a) SO₃H



c) ONH₂
SO₃H



- 250. Aniline donot reacts with
 - a) Br, + water
 - b) conc.NHO,
 - c) conc.H₂SO₄
 - d) CH₃-Cl in the presence of AlCl₃
- 251. Which of the following reaction is not occur in aniline
 - a) bromination
- b) sulphonation
- c) nitration
- d) Friedel-Craft reaction
- 252. What is the main reason for aniline which does not gives Feridel Craft reaction
 - a) Aniline is stabilized by resonance
 - b) NH₂ group of aniline react with AlCl₃ to give

ring deactivating NH2Cl

- c) lone pair of electron on nitrogen never conjugate with benzene ring
- d) it is a Lewis base

 $\xrightarrow{\text{H}_3\text{O}^+}$ C

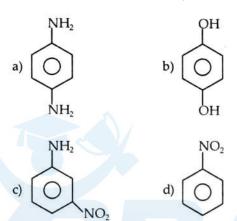
What is 'C' as a major product?





d)
$$\bigcap_{Br}^{NH_2}$$

254. Aniline react with cone HNO, gives



- 255. Bromination of aniline gives 2,4,6-tribromoaniline, where as nitration of aniline gives m-nitroaniline. In case of nitration m-derivatives is formed
 - a) In presence of strong acid NH, group protonated to form NH3 which is m-directing
 - b) m-nitroaniline is more stable than o-and pnitroaniline
 - c) nitro group cannot enter at o and P position because of steric factor
 - d) The mechanism of bromide and nitration is different
- 256. Aniline is reacted with acetic anhydride gives
 - a) phenol
- b) acetamide
- c) acetanilide
- d) benzene
- 257. An organic formula C₄H₁₁N does not react with C₆H₅SO₂Cl but react with one mole of methyl iodide to form salt. The structure of 'X' is

$$CH_3$$
a) $CH_3 - N - CH_2 - CH_3$

b)
$$CH_3 - CH - C_2H_5$$

 \mid
 NH_2

c)
$$CH_3$$
 $\stackrel{C}{\underset{|}{\overset{|}{C}-NH_2}}$ CH_3

d)
$$C_2H_5 - NH-C_2H_5$$

- 258. Which medium change the directive influence of NH, in nitration reaction of aniline?
 - a) Strongly basic
- b) Strongly acidic
- c) Neutral
- d) Weakly acidic
- 259. What is 'D' int he following reaction?

$$C_2H_5-NO_2 \xrightarrow{\text{LiAlH}_4} A \xrightarrow{C_2H_5Br} B$$

$$\xrightarrow{C_2H_5Br} C \xrightarrow{H_2SO_4} I$$

- a) $[(C_2H_5)_3NH]_2^+SO_4^{2-}$
- b) [(C₂H₅)₃NH]₃+SO₄²⁻
- c) $(C_2H_5)_3NH^+SO_4^{2-}$
- d) $(C_2H_2)_2N^+$ OH-
- 260. Product 'B' in the following reaction

Ethane nitrile
$$\xrightarrow{\text{Na} + \text{C}_2\text{H}_5\text{OH}} A \xrightarrow{\text{NaNO}_2 + \text{HCl}} B$$

- a) C₂H₅Cl
- c) C₂H₂OH
- b) C₂H₅NH₂ d) CH₃CH₂CH₂OH
- 261. Which of the following amine is most basic in nature?
 - a) 2,4-dichloro aniline
 - b) 2,4—dimethyl aniline
 - c) 2,4—dinitro aniline
 - d) 2,4-dibromo aniline
- 262. Which of the following amine can not be prepared by Gabriel phthaliamide synthesis?
 - a) Secondary propyl amine
 - b) Tertiary butyl amine
 - c) 2-phenyl ethyl amine
 - d) N-methyl benzyl amine
- 263. Chloropicrin is used as
 - a) antiseptic
- b) antibiotic
- c) insecticide
- d) anaesthetic

OOO

ANSWERS - MCQ'S

SECTION - II : AMINES

												_							$\overline{}$
1.	d)	2.	c)	3.	c)	4.	d)	5.	a)	6.	c)	7.	a)	8.	c)	9.	b)	10.	b)
11.	b)	12.	c)	13.	b)	14.	b)	15.	c)	16.	c)	17.	b)	18.	c)	19.	b)	20.	c)
21.	a)	22.	b)	23.	b)	24.	d)	25.	b)	26.	d)	27.	b)	28.	a)	29.	d)	30.	c)
31.	a)	32.	b)	33.	a)	34.	a)	35.	a)	36.	a)	37.	c)	38.	d)	39.	b)	40.	b)
41.	c)	42.	c)	43.	d)	44.	a)	45.	c)	46.	d)	47.	d)	48.	d)	49.	b)	50.	a)
51.	d)	52.	d)	53.	d)	54.	d)	55.	d)	56.	d)	57.	d)	58.	b)	59.	b)	60.	a)
61.	a)	62.	a)	63.	d)	64.	b)	65.	a)	66.	b)	67.	a)	68.	c)	69.	a)	70.	c)
71.	c)	72.	a)	73.	d)	74.	d)	75.	a)	76.	c)	77.	b)	78.	b)	79.	a)	80.	b)
81.	c)	82.	a)	83.	b)	84.	a)	85.	d)	86.	c)	87.	b)	88.	d)	89.	c)	90.	a)
91.	d)	92.	b)	93.	c)	94.	d)	95.	a)	96.	c)	97.	a)	98.	c)	99.	b)	100.	a)
101.	c)	102.	a)	103.	c)	104.	b)	105.	c)	106.	c)	107.	b)	108.	c)	109.	d)	110.	b)
111.	c)	112.	a)	113.	a)	114.	d)	115.	b)	116.	c)	117.	a)	118.	b)	119.	c)	120.	b)
121.	b)	122.	b)	123.	b)	124.	d)	125.	c)	126.	c)	127.	a)	128.	a)	129.	b)	130.	c)
131.	a)	132.	b)	133.	c)	134.	d)	135.	a)	136.	d)	137.	c)	138.	c)	139.	c)	140.	a)
141.	b)	142.	d)	143.	d)	144.	c)	145.	b)	146.	d)	147.	a)	148.	a)	149.	b)	150.	a)
151.	c)	152.	b)	153.	a)	154.	a)	155.	a)	156.	d)	157.	c)	158.	b)	159.	b)	160.	b)
161.	c)	162.	a)	163.	d)	164.	b)	165.	b)	166.	b)	167.	a)	168.	c)	169.	b)	170.	b)
171.	b)	172.	a)	173.	a)	174.	d)	175.	b)	176.	a)	177.	b)	178.	b)	179.	b)	180.	b)
181.	d)	182.	c)	183.	d)	184.	d)	185.	b)	186.	c)	187.	a)	188.	b)	189.	c)	190.	a)
191.	c)	192.	d)	193.	d)	194.	c)	195.	a)	196.	c)	197.	b)	198.	c)	199.	d)	200.	b)
201.	d)	202.	b)	203.	d)	204.	c)	205.	d)	206.	c)	207.	a)	208.	d)	209.	b)	210.	b)
211.	c)	212.	b)	213.	c)	214.	d)	215.	c)	216.	a)	217.	d)	218.	d)	219.	d)	220.	b)
221.	d)	222.	ь)	223.	b)	224.	c)	225.	b)	226.	c)	227.	b)	228.	b)	229.	a)	230.	a)
231.	b)	232.	d)	233.	d)	234.	c)	235.	a)	236.	d)	237.	c)	238.	c)	239.	d)	240.	a)
241.	d)	242.	d)	243.	d)	244.	d)	245.	c)	246.	b)	247.	a)	248.	b)	249.	c)	250.	d)
251.	d)	252.	b)	253.	c)	254.	c)	255.	a)	256.	c)	257.	a)	258.	b)	259.	a)	260.	c)
261.	b)	262.	d)	263.	c)														
1																			





BRAIN TEASERS

SECTION - II: AMINES

1. Identify the end product (Y) in the following reaction series

 $CH_{3}CN \xrightarrow{Na+C_{2}H_{5}OH} X \xrightarrow{HNO_{2}} Y$

- a) CH₃OH
- b) CH₃OCH₃
- c) C₂H₅OH
- d) $CH_3ON = O$
- 2. An optical inactive amine (A) C₄H₁₁N on treatment with HNO₂ give an alcohol (B). The alcohol (B) on heating with conc. H₂SO₄ at 453K 1-butene. Identify (A).
 - a) CH₃CH₂CH(NH₂)CH₃
 - b) CH₃CH₂CH₂CH₂NH₂
 - c) CH₃NHCH₂CH₂CH₃
 - d) C₂H₅NHC₂H₅
- 3. The compound (A) C₄H₁₁N which is optically active, dissolved in conc. HCl and released nitrogen with HNO₂. What is the compound (A)?
 - a) CH,CH,CH,CH,NH,
 - b) CH,CHNH,CH,CH,
 - c) C₂H₅NHC₂H₅
 - d) CH₃NHCH(CH₃),
- In the following reaction RX + KCN

 —[△]
 which of the following isomeric compound is formed
 - a) RCN
- b) RNC
- c) RNH₂
- d) ROR
- 5. In the reaction

$$C_2H_5NH_2 \xrightarrow{HC1+NaNO_2} A \xrightarrow{HC1} B \xrightarrow{KCN} C$$

The final product C is

- a) propane nitrile
- b) ethane nitrile
- c) propyl amine
- d) formo nitrile
- 6. The total number of electrons around the nitrogen atom in amines are,
 - a) 8
- b) 7
- c) 4
- d) 3
- 7. The end product of the reaction,

Ethyl amine $\xrightarrow{\text{HNO}_2}$ A $\xrightarrow{\text{PCl}_5}$ B $\xrightarrow{\text{excess NH}_3}$ C

- a) ethyl amide
- b) ethyl amine
- c) methyl amine
- d) acetamide
- 8. Identify the product Y in the series

 $CH_{3}CH_{2}CH_{2}CN \xrightarrow{\quad NaHg + H_{2}O \quad} X \xrightarrow{\quad HCl + NaNO_{2} \quad} Y$

- a) 1-propanol
- b) 2-propanol
- c) 1-butanol
- d) 2-butanol
- 9. Identify the product Y in the series

 $(CH_3)_2CH = NOH \xrightarrow{Na+C_2H_5OH} X \xrightarrow{HNO_2} Y$

- a) 2-propanol
- b) 2-propanamine
- c) 2-butanol
- d) 1-propanol
- 10. Compound X is treated with NH₂OH and followed by reduction gives

 NH_2 $(CH_3)_2CHCH_2CH$ $CH_2(CH_3)_3$ The compound X is,

NOH
|
a) (CH₃),CHCH, CCH CH,C(CH₃)₃

CN | b) (CH₃)₂CHCH₂CH CH₂C(CH₃)₃

c) (CH₃)₂CHCH₂CH CH₂C(CH₃)₃

d) $(CH_3)_2CHCH_2CCCH_3)_3$

- 11. The type(s) of bond in RNC is / are
 - a) covalent
 - b) ionic
 - c) ionic and co-ordinate
 - d) covalent and co-ordinate
- 12. The unknown compound is taken in vessel soluble in dilute HCl and small amount of NaNO₂ is added, nitrogen gas is evolved. The unknown compound is
 - a) 1° amines
- b) alcohols
- c) 2° amines
- d) carboxylic acids
- 13. Which of the following is not capable of forming hydrogen bond?
 - a) CH₃NH₂
- b) (CH₃)₃CNH₂
- c) CH₃NHCH₃
- d) (CH₂)₂N
- 14. The amine which form co-ordinate bond with Lewis acid is / are
 - a) RNH,
- b) R₂NH
- c) R₂N
- d) all of these

- 15. Quaternary ammonium halide is heated with moist silver oxide gives
 - a) quaternary ammonium hydroxide
 - b) ammonium hydroxide
 - c) alcohol
 - d) alkene

- 16. Quaternary ammonium hydroxide containing all groups are methyl, on heated gives
 - a) trimethyl amine
- b) methanol
- c) both 'a' and 'b'
- d) ethanol



ANSWERS - BRAIN TEASERS

SECTION - II: AMINES

1	1.	c)	2.	b)	3.	b)	4.	b)	5.	a)	6.	a)	7. b)	8.	c)	9	. a)	10.	d)
1	11.	d)	12.	a)	13.	d)	14.	d)	15.	a)	16.	c)	**						

QUESTIONS ASKED IN MHT-CET

SECTION - II: AMINES

- 1. When formaldoxime is treated with Na in C₂H₅OH it will give?
 - a) Formaldehyde
- b) Methyl amine
- c) Methanol
- d) Formic acid
- 2. The odour of amine is
 - a) odourless
- b) pungent
- c) fishy
- d) garlic like
- 3. IUPAC name of ethyl methyl amine is
 - a) ethyl methanamine b) methyl ethanamine
 - c) propanamine
- d) 2-amino propane
- 4. When ethyl amine is treated with acetyl chloride, forms?
 - a) C₂H₅NH
- b) C,H,CHO
- c) CH₃NHCH₃
- d) C₂H₅NHCOCH₃
- 5. Which of the following cannot be acetylated?
 - a) CH₃NH₂
- b) (CH₃)₂NH
- c) (CH₂),N
- d) $C_2H_5NH_2$
- 6. Iso-propyl amine on acetylation gives
 - a) (CH₂)₂CH–NCOCH₃
 - b) (CH₂)₂CH–NHCOCH₂
 - c) $(CH_3)_2CHN(COCH_3)_2$
 - d) (CH_3) , $CHN(OCH_3)$,
- 7. In acetylation of amines one or more hydrogen atoms are removed from
 - a) carbon atom only
 - b) nitrogen atom only
 - c) both carbon and nitrogen atoms
 - d) from acetyl chloride only
- 8. Final product of methylation of ethyl amine is
 - a) tri ethyl methyl amine

- b) ethyl tri methyl amine
- c) tri ethyl methyl ammonium halide
- d) ethyl tri methyl ammonium halide
- 9. n–propyl amine reacts with HNO, gives
 - a) iso-propyl alcohol
 - b) n-propyl alcohol
 - c) n-propyl nitrosoamine
 - d) none of these
- 10. IUPAC name of isopropyl amine is
 - a) 2-amino propane
 - b) 2-propanamine
 - c) 2,2-methyl ethanamine
 - d) dimethanamine
- 11. Which of the following compound reacts with nitrous acid to form alcohol?
 - a) R,NH
- b) RNH
- c) R-CONH₂
- d) R,N
- 12. Acetaldoxime on reduction with Na/C₂H₅OH gives
 - a) 2-propanol
- b) ethylamine
- c) acetaldehyde
- d) ethanol
- 13. Acetonitrile on reduction gives
 - a) propanamine
- b) methanamine
- c) ethanamine
- d) acetic acid
- 14. The functional group present in secondary amine is
 - a) amino group
- b) imino group
- c) nitrile group
- d) oxime group
- 15. Final product of methylation of ethyl amine and ethyl methyl amine is
 - a) ethyl trimethyl amine
 - b) triethyl methyl amine
 - c) triethyl methyl ammonium halide

- d) ethyl trimethyl ammonium halide
- 16. What is the product of reaction between diethyl amine and nitrous acid?
 - a) Diethyl amine nitrite
 - b) Diethyl nitroso amine
 - c) Diethyl alcohol
 - d) Diethyl nitrate
- 17. IUPAC name of C₂H₅CH(CH₃)NH₂
 - a) ethyl methyl amine b) methyl ethyl amine

- c) 2-butanamine
- b) 1-butanamine
- 18. Which of following is most basic amine?
 - a) C₂H₅NH₂
- b) $(C_2H_5)_2N$
- c) $(C_2H_5)_2$ NH
- d) NH₃
- 19. Which of following forms C₂H₅NH₂I on reduction?
 - a) C₂H₅CN
- b) CH,CHO
- c) CH₂CN
- d) CH₂NC

CCC

ANSWERS - QUESTIONS ASKED IN MHT-CET

b) c) 3. b) d) 5. c) c) 7. b) b) 10. b) 15. d) 12. b) 13. c) 14. b) 16. b) 17. c) 18. c) 19. c) 11. **b**)

MULTIPLE CHOICE QUESTIONS

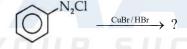
SECTION-III: DIAZOIUM SALT

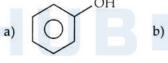
- 1. Aliphatic diazonium chloride an decomposition gives
 - a) 1°-amines
- b) alcohols
- c) aldehydes
- d) alkanes
- 2. IUPAC name of the following compound is



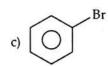
- a) 3-oxo benzene diazonium chloride
- b) 3-hydroxy benzene diazonium chloride
- c) 3-nitro chlorophenol
- d) 4-hydroxy benzene diazonium chloride
- 3. Diazotization of aniline gives
 - a) nitrobenzene
 - b) dinitrobenzene
 - c) benzaldehyde
 - d) benzene diazonium chloride
- 4. Which of the following is incorrect about benzene diazonium chloride?
 - a) These are colour less crystalline solid
 - b) These are readily soluble in water
 - c) It's aqueous solution conduct electricity
 - d) It does not decompose in dry state
- 5. $-N \equiv N$ -group in benzene diazonium chloride is
 - a) o-directing
- b) p-directing
- c) m-directing
- d) none of these

- 6. Benzene diazonium chloride on acid hydrolysis gives
 - a) benzene
- b) phenol
- c) benzoic acid
- d) benzaldehyde
- 7. Replacement of $-N_2^+Cl^-$ from benzene diazonium chloride by hydrogen atom can be done by using
 - a) H_3PO_2
- b) C, H₅-OH
- c) CH,-CHO
- d) both a and b
- 8. Product of the following reaction is











- 9. Replacement by $-N_2^+Cl^-$ from benzene diazonium chloride by iodine can be done by using
 - a) HI
- b) NaOI
- c) PI,
- d) KI
- 10. Which of the following is Sandmeyer's reaction

a)
$$OH + H_2O \xrightarrow{SiO_2} OH + HCI$$

b)
$$N_2^+Cl^ Cl$$
 $+ N_2 + CuCl$

c)
$$OH$$
 OH OH CHO

$$CI + N_2 + CuC$$

$$OH OH$$
 CHO

11. Which of the following is Gattermann reaction?

a)
$$OH + H_2O \xrightarrow{SiO_2} OH + HCI$$

b) $OH + N_2+ CuCI$

c) $OH + N_2+ CuCI$

OH OH OH

CHO

CHO

- 12. Sandmeyer's reaction of benzene diazonium chloride is used in the preparation of
 - a) chlorobenzene
- b) benzene
- c) phenol
- d) iodobenzene
- 13. In Balz-Schiemann's reaction reagent used is
 - a) H₃BO₃
- b) BF₄
- c) HBF₄
- d) HF
- 14. Balz-Schiemann's reaction is used to convert
 - a) Aromatic aldehyde to aldol
 - b) benzene to chlorobenzene
 - c) chlorobenzene to phenol
 - d) benzene diazonium chloride to fluorobenzene
- 15. Product of the following reaction is

a)
$$\bigcirc$$
 CI \bigcirc HBF₄ $\stackrel{\Delta}{\longrightarrow}$?

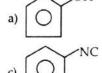
b) \bigcirc F

c) \bigcirc d) \bigcirc NH₂

- 16. Sandmeyer's reaction convert benzene diazonium chloride to
 - 1) chlorobenzene
- 2) bromobenzene
- 3) toluene
- 4) nitrobenzene

- a) 1, 4
- b) 2, 3
- c) 2, 3, 4
- d) 1, 2, 3
- 17. Benzene diazonium chloride convert phenyl cyanide by using
 - a) H-NC
- b) AgCN
- c) CuCN
- d) CH₂-CN
- 18. Product of the following reaction is

$$\begin{array}{c}
N_2^+\text{Cl}^- \\
& \xrightarrow{\text{HBF}_4} A \xrightarrow{\text{NaNO}_2/\text{Cu}} B
\end{array}$$



19. Product 'B' in the following reaction is









20. Which of the following undergoes coupling reaction with benzene diazonium chloride?





21. Product of the following reaction is

$$C_6H_5-N_2C1 + C_6H_5-NH_2 \longrightarrow$$

a)
$$N = N$$

c)
$$N = N$$
 NH_2

$$N = N - NH_2$$

$$N = N - NH_2$$

22. Orange colour compound is obtained when benzene diazonium chloride and what

 In the reaction of aniline a coloured product was obtained

$$\begin{array}{c}
NH_2 \\
Na NO_2 \\
HCI
\end{array}
A
\begin{array}{c}
CH_3 \\
CH_3
\end{array}$$

a)
$$N = N - CH_3$$

b) $N = N - CH_2N - CH_3$

c)
$$CH_3$$
 CH_3 CH_3 CH_3 CH_3 CH_3 CH_3

- 24. Gattermann reaction is modified form of
 - a) diazotizations reaction
 - b) Hofmann's bromide reaction
 - c) Sand meyers reaction
 - d) Ullman reaction

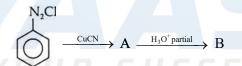
25. Product D in the fallowing sequence of reaction

 $\xrightarrow{\text{HNO}_2} D$

26. Product 'B' in the following reaction

- a) benzoic acid
- b) benzaldehyde
- c) benzonitrile
- d) aniline

27. Product 'C' in the following reaction



KOBr C

- a) benzoic acid
- b) benzaldehyde
- c) benzonitrile
- d) aniline
- 28. $-N_2^+X^-$ is replaced by CN using
 - a) HCN
- b) CuCN
- c) CH, CN
- d) both 'a' and 'b'
- 29. $C_6H_5-N_2^+X^-$ is converted into benzene by using
 - a) H₃PO₂
- b) H₃PO₃
- c) H₃PO₄
- d) HPO₃
- 30. Azo coupling reaction is not possible with
 - a) C₆H₅OH
- b) C₆H₅NH₂
- c) C₆H₅NHCH₃
- d) C₆H₅NO₂

COC



10. (d) Reduction of oxime produces 1⁰ amines.

17. (d)
$$CH_3 - C = C - NO_2 + H - OH \xrightarrow{H^+}$$

$$CH_2$$

$$CH_3$$

$$CH_2$$

$$CH_3$$

$$CH_3$$

 $CH_3 - C = O + CH_3 - CH_2 - CH_2 - NO_2$

21. (b)
$$CH_3-CH_3+Br_2 \xrightarrow{AlBr_3} CH_3-CH_2-Br+HBr$$

 $CH_3-CH_2-Br+AgNO_2 \xrightarrow{AgBr+CH_3-CH_2-NO_2}$

28. (a)
$$CH_3-CH_2-COOH + 2Na \longrightarrow CH_3-CH_2-COONa + H_2$$

$$CH_3$$
- CH_2 - $COONa + Br_2 \xrightarrow{Red P}$

OUR EFBFORT

$$CH_3$$
- CH - $COONa + NaNO_2$ \longrightarrow Br

$$CH_3$$
- CH - $COONa$ + H_2O \longrightarrow NO_2

33. (c)
$$CH_3 - C = CH - NO_2 + H.OH \xrightarrow{H^+}$$

 $CH_3 - COCH_3 + CH_3 - NO_2$

40. (d)
$$CH_3$$
- CH - CH = NOH $\xrightarrow{Trifluoroperoxy}$ acetic acid CH_3
 CH_3 - CH - CH - CH_2 - NO_2

47. **(b)**
$$CH_3-C-CH_2-CH_3+NH_2-OH \xrightarrow{-H_2O}$$

NOH
$$CH_3-C-CH_2-CH_3 \xrightarrow{Trifluoroperoxy acetic acid}$$

$$CH_3-C-CH_2-CH_3 \xrightarrow{NO_2}$$

$$CH_3-CH-CH_2-CH_3$$

48. (d)
$$CH_3-CH_2-C-CH_2-CH_3+NH_2-OH \xrightarrow{-H_2O}$$

NOH
 \parallel
 $CH_3-CH_2-C-CH_2-CH_3 \xrightarrow{Oxidation}$
 NO_2
 $CH_3-CH_2-CH_2-CH_2-CH_3$

50. (d)
$$CH_3$$
- CH = CH - NO_2 + H_2O $\xrightarrow{H^+}$ CH_3 - NO_2 + CH_3 - CHO

58. (a)
$$CH_3-CH_2-NO_2+4(H) \xrightarrow{SnCl_2+HCl} CH_3-CH_2-NH-OH+CH_3-CH=NOH$$

64. (c) 3^0 nitroalkane does not undergo acid hydrolysis because of absence of α -H atom.

65. (b)
$$CH_3-CN \xrightarrow{H_3O^+} CH_3-COOH + NH_3$$

$$CH_3-CH_2-NO_2 \xrightarrow{H_3O^+} CH_3-COOH+NH_2-OH$$

66. (a) Primary nitroalkane on acid hydrolysis gives acid.

$$CH_3$$
- CH_2 - CH_2 - NO_2 + H.OH $\xrightarrow{H^+}$ CH_3 - CH_2 - $COOH$ + NH_2 - OH

67. (c) Secondary nitroalkane on acid hydrolysis gives ketone.

$$\begin{array}{c}
2CH_3-CH-CH_3+H.OH \xrightarrow{H^+}\\
NO_2
\end{array}$$

$$2CH_3-C$$
 $-CH_3 + N_2O + 2H_2O$
 0

78. **(b)**
$$CH_3-CH_2-Br+NaNO_2 \xrightarrow{\text{dimethyl}} \frac{\text{dimethyl}}{\text{sulphoxide}}$$

CH₃-CH₂-NO₂
$$\xrightarrow{\text{Cl}_2 + \text{NaOH}}$$
 CH₃-CCl₂-NO₂ In above reaction α -H atom of nitroalkane are replaced by Cl.

tautomerisation.

- 83. (a) Primary nitroalkane produces nitrolic acid with HNO₂.
- 84. (b) Secondary nitroalkane gives blue coloured pseudonitrol with HNO₂.
- 85. (d) Tertiary nitroalkane and tertiary amine does not react with nitrous acid.

99. (c)
$$2CH_3-CH_2-C=N$$
ONa
 $+2H_2SO_4$

$$\begin{array}{c}
\text{OH} \\
\downarrow \\
\text{C-CH-NO}_2 \\
\downarrow \\
\text{ii) Alc. KOH}
\end{array}$$

- 114. (d) Secondary nitroalkane gives blue coloured pseudonitrol, which do not undergo tautomerisation. Hence blue colour is retained when treated with NaOH.
- means aldehyde.

 Aldehydes are prepared by Nef-carbonyl synthesis from 10-nitroalkane.

116. (c) Compound B gives positive Tollen's test,

HINT & SOLUTIONS - MCQ'S

- 37. c) Three metamers are possible for formula $C_4H_{11}N$.
 - 1. CH₃-NH-CH₂-CH₂-CH₃
 - 2. CH₃-NH-CH(CH₃)₂
 - 3. $C_2H_5-NH-C_2H_5$
- **38. d)** Molecular formula C₃H₉N can show position and functional isomerism,

$$\begin{array}{c} CH_3\text{-}CH_2\text{-}CH_2\text{-}NH_2\text{-}and \ CH_3 - CH - CH_3 \\ & \mid \\ NH_2 \end{array}$$

are position isomers.

1⁰, 2⁰, 3⁰-amines are functional isomers.

- 39. b) NH group is imino group.
- 41. c) -COOH group is principal functional group
 Hence name of the compound is according to
 COOH group.
- **42. c)** These are not identical because they have different molecular formula.
- 48. d) Cis trans isomerism is possible in that compounds containing C=C, C=N, N=N. Amines are single bonded compounds.
- b) It is a Mendius reduction which convert –CN group to –CH₂–NH₂ group.
- **62.** a) Aldoxime or ketoxime on reduction gives only 10-amines.

63. d)
$$CH_3 - C = NOH \xrightarrow{Na + C_2 H_5 OH}$$

$$CH_3$$
 $CH_3 - CH - NH_2 \xrightarrow{2CH_3COCl}$

diacetyl isopropyl amine

- **64. b)** $CH_3 CH_2 CH = NOH + 4(H) \xrightarrow{Na + C_2H_5 OH} CH_3 CH_2 CH_2 NH_2 + H_2O$
- 67. a) $H-C = N + 4(H) \xrightarrow{Na+C_2H_5-OH} CH_3-NH_2$.
- **71. b)** Alkyl cyanide on acid hydrolysis gives carboxylic acids.
- **80. b)** Aldehyde on reduction gives 1° alcohols.

81. c)
$$CH_3$$
 $CH_3 - C - NO_2 + 6[H] \xrightarrow{Fe+HCl}$
 CH_3

$$CH_3$$
 $CH_3 - C - NH_2 + 2H_2O$
 CH_3

84. a)
$$\longleftrightarrow$$
 + NH₃ \longleftrightarrow CH₃-NH₂ + HX

alc. and excess

85. d) CH_3 - CH_2 - $COOH + NH_3 \longrightarrow$

$$CH_3$$
- CH_2 - $COONH_4 \xrightarrow{\Delta} -H_2O$

$$CH_3-CH_2-CONH_2 \xrightarrow{Na+C_2H_5OH}$$

$$CH_3-CH_2-CH_2-NH_2$$

88. d) 3° alkyl halide is not used in alkylation of ammonia because it undergo elimination reaction with alc. NH₃.

91. d)
$$CH_3 - CH - C - CH_3 + NH_2 - OH \xrightarrow{-H_2O}$$

$$CH_3$$
 NOH
$$CH_3 - CH - C - CH_3 \xrightarrow{LiAlH_4}$$

- 92. b) Amide gives 1° amines by Hoffmann's degradation method.
- 94. d) 1-bromo, 2 methyl propane gives 2-methyl propan-1-amine by Gabrial phathalimide synthesis.
- 97. a) Only 1° aliphatic amines can be prepared by Gabriel Phthalimide synthesis.
- 98. c) Alkyl cyanide, and nitroalkane gives 1° amine on reduction. Amide also give 1° amine but not reduction method.

group.

105. c)
$$CH_3 \xrightarrow{CH_3} CH_3 \xrightarrow{CH_3} CH_3 \xrightarrow{CH_3} CH_3 \xrightarrow{CH_3} CH_3 \xrightarrow{CH_3} CH_3$$

$$\xrightarrow{H_2+Ni} CH_3 - C-NH_2$$

$$CH_3 - C-NH_2$$

$$CH_3$$

106. c)
$$CH_3 - C - CH_2 - CH_3 + [O] \xrightarrow{\text{Triflurope roxy} \\ \parallel \\ NOH$$

$$CH_3 - CH - CH_2 - CH_3 \xrightarrow{Fe+conc.HCl} NO_2$$

Butan-2-amine

107. b)
$$OOOH + NH_3 \xrightarrow{\Delta} OOOH_2$$

108. c)
$$CH_3-CH_2-CH_2-COOH+NH_3 \xrightarrow{\Delta} -H_2O$$

$$CH_3-CH_2-CH_2-CONH_2 \xrightarrow{Br_2+KOH} CH_3-CH_2-CH_2-CH_2-NH_2$$
Butan-1-amine

111. c) C₆H₅ - group is more water hating than C₂H₅ group.

112. a) Primary and secondary amines have intermolecular hydrogen bonding because of presence of hydrogen atoms attached to nitrogen atom.

113. a) In isomeric compounds normal compounds have higher B.P. than branched compounds. But in amines active hydrogen atoms are different. 3° amines = \ge N group = 0 active H-atoms Hence B.P. order is 1°> 2° > 3°

- **115. b)** Amine are basic in nature. Hence these are soluble in acid forming salt.
- 116. c) In alcohols oxygen is more electronegative than nitrogen in amines. Hence alcohol forms strong intermolecular hydrogen bonding than amines, leads to higher B.P. than amines.
- 117. a) Alcohols are more soluble in water than amines because they form strong hydrogen bond with water.
- 123. b) Electron withdrawing groups decrease the basicity of amines. Strong electron withdrawing groups decrease more basicity of amines.

NO₂ is strong withdrawing group than CN, Cl, and OH.

- 124. d) When electron withdrawing group goes away from -NH₂ group, the basicity of amine increases.
- 125. c) Aliphatic amines are more basic than aromatic amines.
- 126. c) More the Pkb value less the basicity. The -Cl atom is electron withdrawing which decreases the basicity of amines.
- **127. a)** Electron donating group increases the basicity of amines. Methyl group is electron donating.
- 131. a) $(CH_3)_2 NH + H^+ \longrightarrow (CH_3)_2 NH_2^+$ conjugate base conjugate acid
- **133. c)** Weak base can share lone pair of electron less easily. Aniline is weak base than other.
- 134. d) Aralkyl amines are more basic than any aromatic amines. Benzyle amine is aralkyl amine.
- 135. a) Aliphatic amines are more basic than aralkyl amines and aromatic amines.
- 146. d) Electron withdrawing groups decreases the basicity of amine.More the electron withdrawing power of the group less the basicity.

-NO₂ group has more electron withdrawing power than F. Hence p-fluoroaniline is more basic than p-nitro aniline.

156. d) Carbyl amine reaction is characteristics reaction of primary amine. Dimethyl amine is secondary amine, does not give Carbylamine reaction. gives nitrosoamine.

161. c) Because of absence of hydrogen atom attached to nitrogen atom.

163. d) All primary amine gives N₂ gas with NaNO₂ + HCl.

164. b) In this reaction H⁺ is replace by NO⁺. Hence it is electrophilic substitution reaction.

169. b) Triethyl amine has more Kb value hence it is more basic than dimethyl amine.

180. b) Basicity of amines depends upon the sharing of lone pair of electrons.

191. b) Secondary amine does not give alcohol with nitrous acid.

192. d) CH₃-I is best methylating agent because of C-I bond length is more than that of C-Cl, C-Br, C-F bond length.

203. d) Tertiary amine soluble in NaNO₂ + HCl forming water soluble salt.
 (CH₃)₃ N + HNO₂ → (CH₃)₃ NH⁺Cl⁻

220. b)
$$NH_2 + HCl \longrightarrow NH_3^+Cl^-$$

Anilinium hydrochloride

221. d) Secondary butyl amine is optically active, reacts with nitrous acid to give butan-2-ol.

$$CH_3 - CH - CH_2 - CH_3 + HNO_2 \xrightarrow{Cold}$$
 NH_2

$$CH_3 - CH - CH_2 - CH_3 + N_2 + H_2O$$
OH

224. c) Isopropyl amine produces isopropyl carbocation while n-propyl amine produces n-propyl carbocation.

225. b)
$$O + NH_2 - OH \longrightarrow N - OH$$

$$LiAlH_4 \longrightarrow NH_2$$

226. c) It is a carbylamine reaction gives isocyanide (C_6H_5NC) .

227. **b)** $C_2H_5-NH_2+HNO_2 \xrightarrow{COId} C_2H_5-OH+N_2+H_2O$ $C_6H_5-NH_2+HNO_2+HCl \xrightarrow{Cold} C_6H_5-N_2^+Cl^-+2H_2O$

229. a) (CH_3) - $NOH \xrightarrow{\Delta} CH_3$ - $OH + (CH_3)N$

234. c)
$$\bigcirc \stackrel{CH_3}{\longrightarrow} ^{CH_3}_{CH_3} + CH_3COOH \longrightarrow$$

N, N -dimethyl anilinium acetate

235. a)
$$\bigcirc$$
 + CH₃-COCI \longrightarrow NH-COCH₃

N-Phenyl ethanamide or Acteanilinde

237. c)
$$N(CH_3)_2$$
 + HNO_2 $Cold$ NO + H_2O

p-nitroso N, N-dimethyl phenyl amine

238. c)
$$\begin{bmatrix} CH_3 \\ CH_3 - N - CH_2 - CH_3 \\ CH_3 \end{bmatrix}^{+} OH^{-\Delta}$$

$$(CH_3)_3N + H_2O + CH_2 = CH_2$$

250. d) Aniline does not undergoes Friedel Craft reaction because AlCl₃ bonded with -NH₂ to form -NH₂⁺ Cl⁻

253. c)
$$NH_2 + CH_3COCI \xrightarrow{-HCl}$$

$$NH CO CH_3 \xrightarrow{Br_2/CH_3COOH}$$

$$NH CO CH_3 \xrightarrow{H_3O^+}$$

$$\bigcup_{Br} NH_2$$

258. b) Strong acidic medium change the directive influence of -NH₂ group and gives unexpectedly m-nitro aniline.

259. a)
$$C_2H-NO_2 \xrightarrow{\text{LiAlH}_4} C_2H_5-NH_2 \xrightarrow{C_2H_5Br} -HBr$$

$$(C_2H_5)-NH \xrightarrow{C_2H_5Br} (C_2H_5)_3 N \xrightarrow{H_2SO_4}$$

$$[(C_2H_5)_3NH]_2^+SO_4^{2-}$$

260. c)
$$CH_3$$
- $CN \xrightarrow{Na+C_2H_5OH} CH_3$ - CH_2 - NH_2

$$\xrightarrow{NaNO_2+HCl} CH_3$$
- CH_2 - $OH+H_2O+N_2$

YOUR SUCCESS HUBBEE