12

ORGANIC COMPOUNDS CONTAINING NITROGEN

AMINES

INTRODUCTION :

Hydrocarbon derivatives of ammonia are called 'Amine'. Classification of amines is done on the basis of number of alkyl groups attached to nitrogen atom.

$NH_3 \xrightarrow[+R]{-H} R\text{–}NH_2$ 1° or Primary amine
$[C_nH_{2n+1}NH_2]$ $\text{–}NH_2$ ⇒ Amino

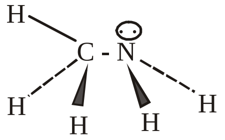
$NH_3 \xrightarrow[+2R]{-2H} R_2NH$ 2° or Secondary amine
$[(C_nH_{2n+1})_2NH]$ $>NH$ ⇒ Imino

$NH_3 \xrightarrow[+3R]{-3H} R_3N$ 3° or Tertiary amine

$[(C_nH_{2n+1})_3N]$ $-\overset{|}{N}-$ ⇒ Nitrilo

When all the alkyl group in 2° and 3° amines are identical, then they are called simple amines, and if nonidentical, they are called mixed amines.

Structure of an Alkyl amine :

Methylamine


Overlapping	Bond formation
$C(sp^3) – H (S)$	σ(3)
$C(sp^3) – N (sp^3)$	σ(1)
$N(sp^3) – H (s)$	σ(2)
lone pair	(1)

PREPARATION

1. Ammonolysis of Alkyl halides (Hofmann's method)

$$R\text{–}X + H\text{–}NH_2 \xrightarrow[\text{Pressure}]{\Delta,\ 100°C} R\text{–}NH_2HX \xrightarrow[\text{Alkali}]{\Delta} R\text{–}NH_2$$

(Excess)

On taking the alkyl halides in excess, the primary amines gets further alkylated to form 2° & 3° amines and finally quaternary ammonium salt.

$$R\text{–}NH_2 \xrightarrow[\Delta]{RX} R_2NH \xrightarrow[\Delta]{RX} R_3N \xrightarrow{RX} R_4\overset{\oplus}{N}\overset{\ominus}{X}$$

Note :

(i) This reaction is an example of a nucleophilic substitution reaction in which ammonia molecule (NH_3) acts as a nucleophile.

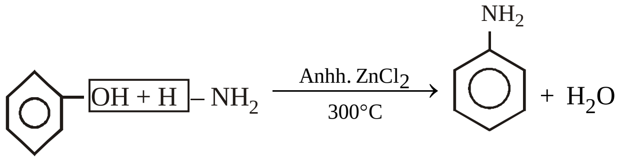
(ii) The order of reactivity of haloalkanes in ammolysis reaction is RI > RBr > RCl

2. Ammonolysis of alkanols :

When a mixture of an alcohol and ammonia vapours are passed over heated alumina (400°C) or thoria (ThO_2) Under pressure of 100 atm. a mixture of 1°, 2° & 3° amines is obtained.

$$R\text{–}OH + H\text{–}NH_2 \xrightarrow[400°C,\ 100atm]{Al_2O_3} R\text{–}NH_2$$

$$\xrightarrow{R-OH} R_2NH \xrightarrow{R-OH} R_3N$$



Note : (i) 1° amines can be obtained in excess by using ammonia in excess.

(ii) In this process, quaternary ammonium hydroxide is not formed because the realeased water molecule gets absorbed by alumina and there by the $\overset{\ominus}{OH}$ is not available for the formation of quarternary compound.

3. Reduction :

(i) By nitroalkanes :

$$R\text{–}NO_2 + 6H \xrightarrow{Sn+HCl} R\text{–}NH_2 + H_2O$$

The following reductants can be used

(a) Metal + Acid (b) $LiAlH_4$ or $NaBH_4$

(c) Raney nickel + H_2, etc

(ii) By Alkyl cyanides (Mendius Reaction) :

$$R - C \equiv N + 4H \xrightarrow{Na+C_2H_5OH} R\text{–}CH_2 - NH_2$$

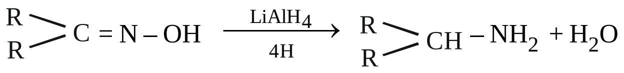
(50% yield)

Note : The yield can be increased to about 90% by using more powerful reductant, as $LiAlH_4$ or $NaBH_4$.

(iii) By Oximes :

$$R\text{–}CH{=}N\text{–}OH \xrightarrow[4H]{LiAlH_4} R\text{–}CH_2\text{–}NH_2 + H_2O$$

(Aldoxime)

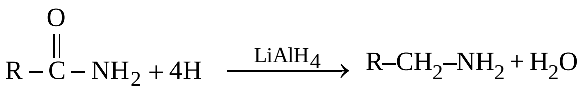


$$R_2C = N - OH \xrightarrow[4H]{LiAlH_4} R_2CH - NH_2 + H_2O$$

(Ketoxime) (2° amine)

Reductant, which can be used are Na + C_2H_5OH, $LIAlH_4$, $NaBH_4$, Ni/H_2

(iv) By Acid Amides :



$$R - \overset{\overset{O}{\|}}{C} - NH_2 + 4H \xrightarrow{LiAlH_4} R\text{–}CH_2\text{–}NH_2 + H_2O$$

(v) By Reductive Amination of carbonyl compounds :

$$R-CH=O+H_2NH \xrightarrow[-H_2O]{} R\text{–}CH\text{=}NH \xrightarrow[Ni]{H_2} R-CH_2-NH_2$$

$$R_2C=O+H_2NH \xrightarrow[-H_2O]{} R_2C\text{=}NH \xrightarrow[Ni]{H_2} R_2CH_2-NH_2$$

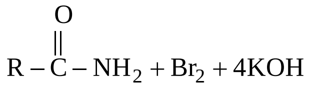
Note : If carbonyl compound is in excess, secondary amine is formed

$$R-CH_2-NH_2+O=CH-R \xrightarrow[-H_2O]{}$$

$$[R\text{–}CH_2\text{–}N\text{=}CH\text{–}R] \xrightarrow[H_2]{Ni} R\text{–}CH_2\text{–}NH\text{–}CH_3\ (2^{\circ}\text{Amine})$$

4. By Hydrolysis :

(i) Hofmann's Bromaamide reaction :



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2+Br_2+4KOH$$

$$\longrightarrow R\text{–}NH_2+2KBr+K_2CO_3+2H_2O$$

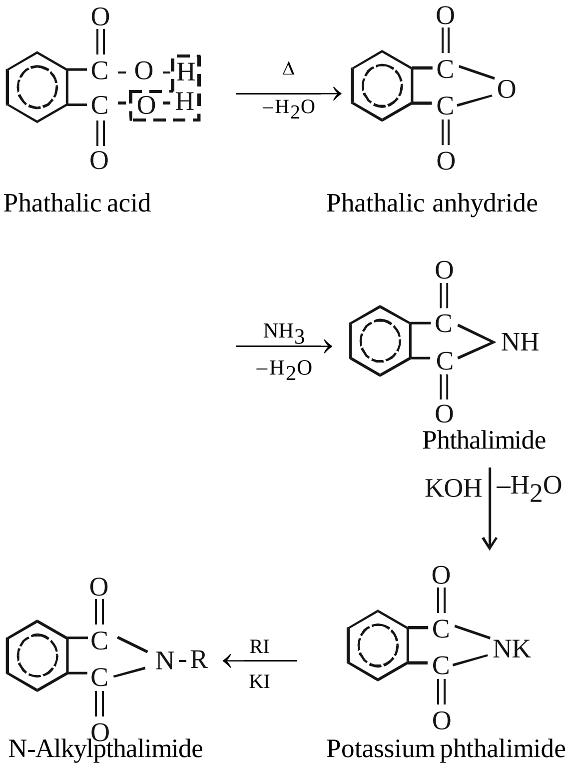
$$CH_3CONH_2+Br_2+4KOH$$

$$\longrightarrow CH_3NH_2+2KBr+K_2CO_3+2H_2O\ \text{[Lab method]}$$

$$C_6H_5CONH_2+Br_2+4KOH$$

$$\longrightarrow C_6H_5NH_2+2KBr+K_2CO_3+2H_2O$$

(ii) Gabriel phthalimide reaction :



Phathalic acid

Phathalic anhydride

Phthalimide

N-Alkylpthalimide

Potassium phthalimide

$$R\text{ - }NH_2+\text{Phthalic acid} \xleftarrow{2H_2O}$$

Amine

Note : The reaction is best used for the preparation of pure 1° Amines.

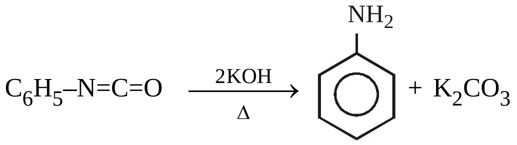
(iii) Alkyl Isocyanides :

$$R\text{–}N{\equiv}C+2H_2O \xrightarrow{HCl} R\text{–}NH_2+HCOOH$$

$$C_6H_5NC+2H_2O \xrightarrow{\text{dil. Acid}} C_6H_5NH_2+HCOOH$$

(iv) Alkyl Isocyanates (Wurtz Method) :

$$R\text{–}N\text{=}C\text{=}O \xrightarrow[\Delta]{2KOH} R\text{–}NH_2+K_2CO_3$$



$$C_6H_5\text{–}N\text{=}C\text{=}O \xrightarrow[\Delta]{2KOH} C_6H_5NH_2 + K_2CO_3$$

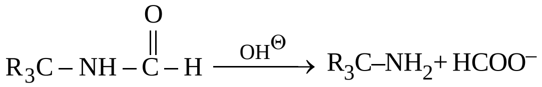
(v) Leuckart reaction : 1° Amines are formed on heating carbonyl compounds with ammonia formate or formamide. The reaction involve reductive amination.

$$>C\text{=}O+HCOONH_4 \longrightarrow >CHNHCHO+H_2O+CO_2$$

$$\xrightarrow[\text{Hydrolysis}]{H^{\oplus}} HCHO+>CH_2\text{–}NH_2$$

(vi) Ritter reaction :

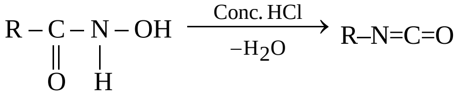
$$R_3C\text{–}OH \xrightarrow[\text{Conc. }H_2SO_4]{\text{HCN or NaCN}} R_3C\overset{\oplus}{N}\equiv\overset{\ominus}{C} \xrightarrow{HOH}$$



$$R_3C-NH-\overset{\overset{\displaystyle O}{\|}}{C}-H \xrightarrow{OH^{\ominus}} R_3C\text{–}NH_2+HCOO^-$$

(vii) Lossen Rearrangement :

Isocyanates are formed by dehydrative rearrangement of hydroxamic acids. Hydrolysis of Isocyanate then gives 1° amines.

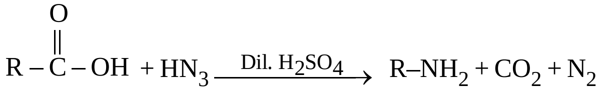


$$\underset{\underset{\displaystyle O}{\|}}{R-C}-\underset{\underset{\displaystyle H}{|}}{N}-OH \xrightarrow[-H_2O]{\text{Conc. HCl}} R\text{–}N\text{=}C\text{=}O$$

Hydroxamic acid

$$\xrightarrow{2KOH} R\text{–}NH_2+K_2CO_3$$

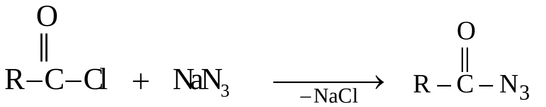
(viii) Schmit reaction :



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH+HN_3 \xrightarrow{\text{Dil. }H_2SO_4} R\text{–}NH_2+CO_2+N_2$$

$$C_6H_5COOH+N_3H \xrightarrow{\text{Dil. }H_2SO_4} C_6H_5NH_2+N_2+CO_2$$

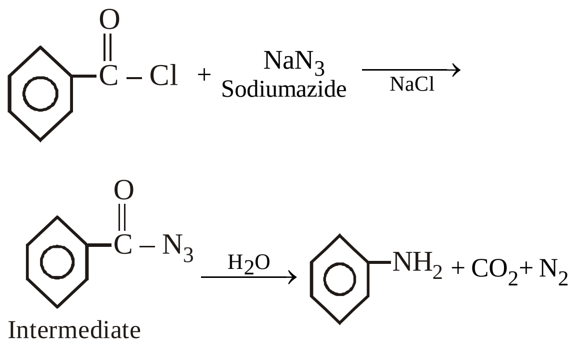
(ix) Curtius reaction :



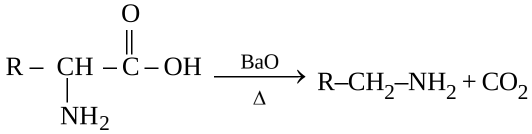
$$R\text{–}\overset{\overset{\displaystyle O}{\|}}{C}\text{–}Cl + NaN_3 \xrightarrow[-NaCl]{} R-\overset{\overset{\displaystyle O}{\|}}{C}-N_3$$

$$\xrightarrow{HOH} R\text{–}NH_2+CO_2+N_2$$

Sodium azide



(x) From decarboxylation of ~-aminoacids :



$$R-\underset{NH_2}{\underset{|}{CH}}-\overset{O}{\overset{||}{C}}-OH \xrightarrow[\Delta]{BaO} R–CH_2–NH_2 + CO_2$$

PHYSICAL PROPERTIES

(i) Physical state : Lower aliphatic amines = Gases
Intermediate members = Liquid (Fishy odour)
higher member = solids

(ii) Solubility : Lower aliphatic amines (up to C_6) = soluble in water because of H-bonding Higher amines (> C_6) = Insoluble in water

$$\text{Solubility} \propto \frac{1}{\text{Molecular weight}}$$

(iii) Boiling point – b.p. of alcohols & carboxylic acids > b.p. of amines > b.p. of alkanes and
b.p. of 1° amine > 2° amine > 3° amine

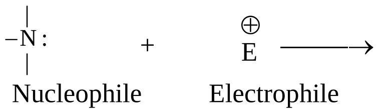
Explanation :

(i) Primary and secondary amines form inter molecular H-bonds. While tertiary amines do not form inter molecular H-bonds. As a result, 1° & 2° amines show high B.P. than 3° amines.

(ii) H-bonding in amines is through nitrogen atoms while in alcohols and carboxylic acids, it is through oxygen atoms and nitrogen is less electronegative than oxygen. So H-bonding in amines is weaker than that in carboxylic acids and alcohols.

CHEMICAL PROPERTIES

(i) Basic nature of amines : Basic nature arises due to presence of lone pair of e^- on the N-atom, which can be shared with an electron deficient species (an electrophile).



$$-\overset{|}{\underset{|}{N}}: \quad + \quad \overset{\oplus}{E} \longrightarrow$$

Nucleophile Electrophile

Basic strength of amines depends on combined effect of two factors

+ I effect : Base strength ∝ +I effect

$$\text{Steric hindrance : Base strength} \propto \frac{1}{\text{Sterichindrance}}$$

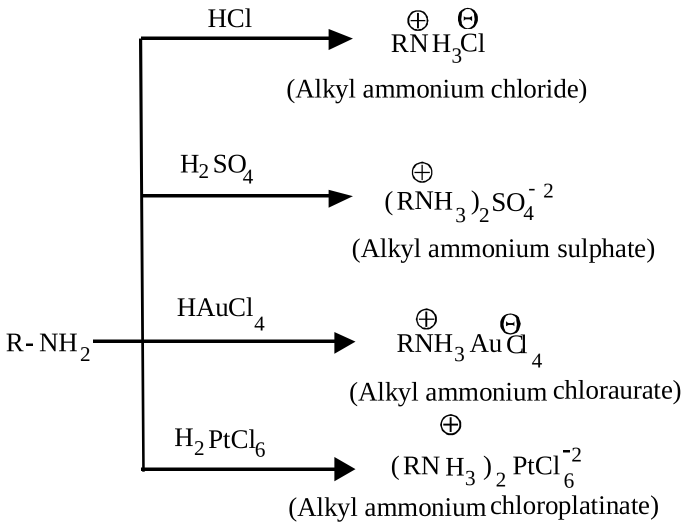
Since both the factors work in opposite direction, the factor which is more predominant is more effective in deciding the base strength of amines.

Order of basic character of amines is

(i) R = CH_3 – $R_2NH > RNH_2 > R_3N > NH_3$
(ii) R = C_2H_5 – $R_2NH > RNH_2 > NH_3 > R_3N$
(iii) R = $(CH_2)_2CH$ – $R–NH_2 > NH_3 > R_2NH > R_3N$
(iv) R = $(CH_3)_3C$ – $NH_3 > RNH_2 > R_2NH > R_3N$

Reactions showing basic nature :

Salts are formed on reacting amines with strong acids



$$R-NH_2 \xrightarrow{HCl} R\overset{\oplus}{N}H_3\overset{\ominus}{Cl}$$

(Alkyl ammonium chloride)

$$R-NH_2 \xrightarrow{H_2SO_4} (R\overset{\oplus}{N}H_3)_2SO_4^{-2}$$

(Alkyl ammonium sulphate)

$$R-NH_2 \xrightarrow{HAuCl_4} R\overset{\oplus}{N}H_3\,Au\overset{\ominus}{Cl}_4$$

(Alkyl ammonium chloraurate)

$$R-NH_2 \xrightarrow{H_2PtCl_6} (R\overset{\oplus}{N}H_3)_2\,PtCl_6^{-2}$$

(Alkyl ammonium chloroplatinate)

(ii) Reaction with water : Give alkaline solution in water.

$$R–NH_2 + H_2O \longrightarrow R\overset{\oplus}{N}H_3\overset{\ominus}{O}H \rightleftharpoons R\overset{\oplus}{N}H_3 + \overset{\ominus}{O}H$$

Aqueous sol^n of alkylamine precipitate hydroxides of heavy metals

$$3R\overset{\oplus}{N}H_3\overset{\ominus}{O}H + FeCl_3 \longrightarrow Fe(OH)_3 + 3R\overset{\oplus}{N}H_3\overset{\ominus}{Cl}$$

$$3R\overset{\oplus}{N}H_3\overset{\ominus}{O}H + AlCl_3 \longrightarrow Al(OH)_3 + 3R\overset{\oplus}{N}H_3\overset{\ominus}{Cl}$$

(iii) Alkylation :

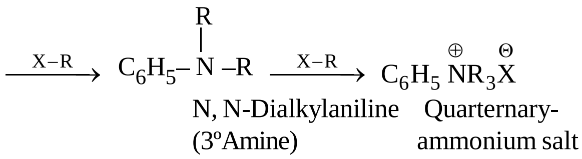
$$R-NH_2 \xrightarrow[-HX]{RX} R_2(NH) \xrightarrow[-HX]{RX} R_3N$$

$$\xrightarrow{RX} R_4\overset{\oplus}{N}\overset{\ominus}{X}$$

(Tetra alkyl ammonium halide)

$$C_6H_5NH–H + X–R \xrightarrow[-HX]{} C_6H_5NH–R$$

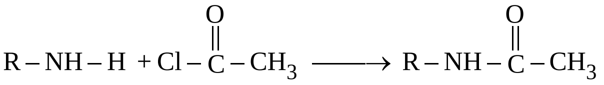
N-Alkylaniline (2°Amine)



$$\xrightarrow{X–R} C_6H_5-\overset{R}{\overset{|}{N}}-R \xrightarrow{X–R} C_6H_5\overset{\oplus}{N}R_3\overset{\ominus}{X}$$

N, N-Dialkylaniline (3°Amine) Quarternary-ammonium salt

(iv) Acetylation :

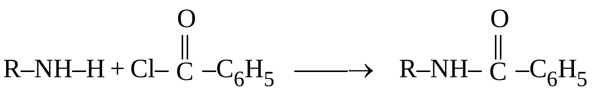


$$R-NH-H + Cl-\overset{O}{\overset{||}{C}}-CH_3 \longrightarrow R-NH-\overset{O}{\overset{||}{C}}-CH_3$$

(N - Alkylacetamide)

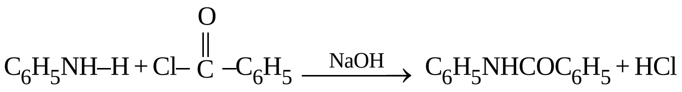
Note : Acetanilide is an important compound which is used in protection of $–NH_2$ group of aniline.

(v) Benzoylation : (Schotten - Bauman reaction)



$$R\text{–}NH\text{–}H + Cl\text{–}\overset{O}{\overset{\|}{C}}\text{–}C_6H_5 \longrightarrow R\text{–}NH\text{–}\overset{O}{\overset{\|}{C}}\text{–}C_6H_5$$

(N - Alkyl benzamide)



$$C_6H_5NH\text{–}H + Cl\text{–}\overset{O}{\overset{\|}{C}}\text{–}C_6H_5 \xrightarrow{NaOH} C_6H_5NHCOC_6H_5 + HCl$$

Benzanilide

(vi) Acidic behaviour :

$$2RNH_2 + 2Na \longrightarrow 2R\overset{\ominus}{N}H\overset{\oplus}{N}a + H_2$$

(N - Alkyl sodamide)

$$2C_6H_5NH_2 + 2Na \longrightarrow 2C_6H_5\overset{\ominus}{N}H\overset{\oplus}{N}a + H_2$$

(Sodium anilide)

(vii) With Grignard's reagent :

$$R\text{–}NH\text{–}H + X\text{–}Mg\text{–}R' \longrightarrow R'\text{–}H + R\text{–}NHMgX$$

(Alkane)

$$C_6H_5NH-\boxed{H + R}MgX \longrightarrow R\text{–}H + C_6H_5NHMgX$$

(Alkane)

(viii) With Tilden's reagent :

Tilden reagent = NOCl

$$R\text{–}NH_2 + O\text{=}N\text{–}Cl \longrightarrow R\text{–}Cl + N_2 + H_2O$$

(Alkylchoride)

(ix) With Hinsberg's reagent :

The compound in which sulphonyl chloride group is directly attached to an aromatic ring are called "Hinsberg's reagents".

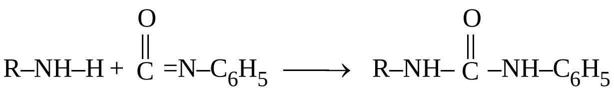
$$R\text{–}NH\text{–}H + Cl\text{–}SO_2\text{–}C_6H_5 \longrightarrow C_6H_5\text{–}SO_2\text{–}NH\text{–}R + HCl$$

(N–Alkylbenzene Sulphonamide)

$$C_6H_5NH-\boxed{H \ + \ Cl}SO_2-C_6H_5 \longrightarrow C_6H_5NH\text{–}SO_2\text{–}C_6H_5$$

(H.B.R.) N-Phenylbenzene sulphonamide

(x) With Phenyl isocyanate :

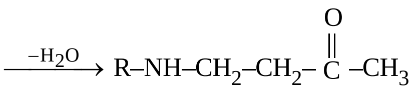


$$R\text{–}NH\text{–}H + \overset{O}{\overset{\|}{C}}\text{=}N\text{–}C_6H_5 \longrightarrow R\text{–}NH\text{–}\overset{O}{\overset{\|}{C}}\text{–}NH\text{–}C_6H_5$$

(N–Alkyl–N'–Phenylurea)

(xi) Mannich reaction :

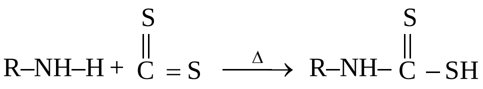
$$R\text{–}NH_2 + HCHO + CH_3COCH_3$$



$$\xrightarrow{-H_2O} R\text{–}NH\text{–}CH_2\text{–}CH_2\text{–}\overset{O}{\overset{\|}{C}}\text{–}CH_3$$

(Mannich base)

(xii) Hofmann's Mustard oil reaction (HMO reaction) :



$$R\text{–}NH\text{–}H + \overset{S}{\overset{\|}{C}}=S \xrightarrow{\Delta} R\text{–}NH\text{–}\overset{S}{\overset{\|}{C}}-SH$$

1° amine

$$\xrightarrow{HgCl_2} R\text{–}N\text{=}C\text{=}S + 2HCl + HgS$$

(Alkyl isothiocyanate) (Black ppt)

(xiii) With aldehydes :

$$R\text{–}NH_2 + CH_3\text{–}CH\text{=}O \xrightarrow{\Delta} R\text{–}N\text{=}CH\text{–}CH_3 + H_2O$$

(Acetaldehyde) (Schiff's base)

$$R\text{–}NH_2 + O\text{=}CH\text{–}C_6H_5 \xrightarrow{\Delta} R\text{–}N\text{=}CH\text{–}C_6H_5 + H_2O$$

(Benzaldehyde)

$$C_6H_5N\boxed{H_2 \ + \ O}=CH-C_6H_5 \longrightarrow C_6H_5N\text{=}CH\text{–}C_6H_5 + H_2O$$

Benzalaniline or
Benzylidineaniline
(Schift's base / Aniline)

$$C_6H_5N\boxed{H_2 \ + \ O}=CH-CH_3 \rightarrow C_6H_5N\text{=}CH\text{–}CH_3$$

(Ethylidine aniline)
(Schift's base/Aniline)

(xiv) Hofmann carbylamine reaction (Isocyanide test) :

$$R\text{–}NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} R\text{–}NC + 3KCl + 3H_2O$$

(Alkyisocyanide)

$$C_6H_5NH_2 + CHCl_3 + 3KOH \longrightarrow C_6H_5NC + 3KCl + 3H_2O$$

Phenylisocyanide
Having offensive smell

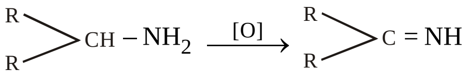
Note : The product alkyli isocyanide has very foul offensive smell. This reaction is used as a test of 1° amines and is called Isocyanide test.

(xv) Oxidation :

(i) Primary amines : Primary aliphatic amine on oxidation with $KMnO_4$ followed by hydrolysis give aldehydes, ketones and nitroalkanes.

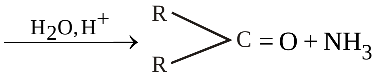
$$RCH_2NH_2 \xrightarrow{[O]} R\text{–}CH\text{=}NH \xrightarrow{H_2O,H^+} + RCHO + NH_3$$

Alkyl amine Aldimine Aldehyde



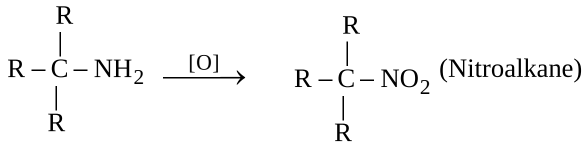
$$\begin{matrix}R\\R\end{matrix}\!\!>CH-NH_2 \xrightarrow{[O]} \begin{matrix}R\\R\end{matrix}\!\!>C=NH$$

Ketimine



$$\xrightarrow{H_2O,H^+} \begin{matrix}R\\R\end{matrix}\!\!>C=O + NH_3$$

Ketone



$$R-\overset{R}{\underset{R}{C}}-NH_2 \xrightarrow{[O]} R-\overset{R}{\underset{R}{C}}-NO_2$$

(Nitroalkane)

(ii) Secondary amines : Secondary aliphatic amines on oxidation with $KMnO_4$ give tetra alkyl hydrazine.

$$2R_2NH \text{ (2°- amine)} \xrightarrow[-H_2O]{[O]} R_2N\text{–}NR_2 \text{ (Tetraalkylhydrazine)}$$

(iii) Tertiary amines : Tertiary amine are not oxidised by $KMnO_4$ but are oxidised by Caros acid or ozone or H_2O_2 to corresponding N–oxides.

$$R_3N: \ + \ [O] \longrightarrow [R_3N \longrightarrow O]$$

3° amine amine oxide

(xvi) Distinction between 1°, 2° and 3° amines :

(i) Reaction with HNO_2 :

(a) Primary amines react with nitrous acid to produce nitrogen gas [seen as bubbles]:

$$C_2H_5NH_2 + HONO \longrightarrow C_2H_5OH + N_2\uparrow + H_2O$$

(b) Secondary amines react with nitrous acid to produce a yellow oily layer.

$$(C_2H_5)_2N{-}H + HONO \longrightarrow (C_2H_5)_2N-N{=}O + H_2O$$

N – nitrosodiethyl amine
(yellow oil)

(c) Tertiary amines react with nitrous acid to form soluble nitrite:

$$(C_2H_5)_2N + HONO \longrightarrow (C_2H_5)_3\overset{\oplus}{N}HNO_2^{\ominus}$$

Triethylammoniumnitrite (soluble)

(ii) Reaction with benzene sulphony chloride :

(a) Primary amines react with benzenesulphonyl chloride to form a precipitate which is soluble in NaOH solution.

$$C_6H_5SO_2Cl + H_2NC_2H_5 \longrightarrow C_6H_5SO_2NHC_2H_5 + HCl$$

N-ethyl sulponamide (precipitate)

(b) Secondary amines react with benzene sulphonyl chloride to give a precipitate which is insoluble in NaOH solution.

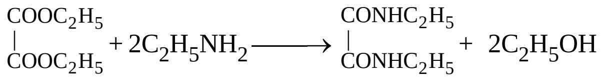
$$C_6H_5SO_2Cl + HN(C_2H_5)_2 \longrightarrow C_6H_5SO_2(C_2H_5)_2 + HCl$$

N, N-diethyl sulphonamide
(precipitate)

(c) Tertiary amines do not react with benzenesulphonyl chloride as they do not possess replaceable hydrogen.

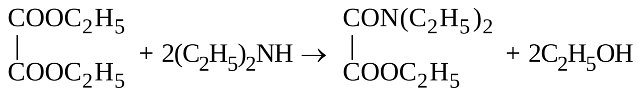
(iii) Reaction with diethyloxalate (Hofmann's method)

Primary amines react to form solid crystalline oxamide. Secondary amines react to give oily dialkyl oxamic ester. Tertiary amines do not react as they do not contain a replaceable H atom.



$$\begin{array}{l}COOC_2H_5\\ |\\ COOC_2H_5\end{array} + 2C_2H_5NH_2 \longrightarrow \begin{array}{l}CONHC_2H_5\\ |\\ CONHC_2H_5\end{array} + 2C_2H_5OH$$

(solid)



$$\begin{array}{l}COOC_2H_5\\ |\\ COOC_2H_5\end{array} + 2(C_2H_5)_2NH \rightarrow \begin{array}{l}CON(C_2H_5)_2\\ |\\ COOC_2H_5\end{array} + 2C_2H_5OH$$

(liquid)

Diethyl oxalte + tertiary amine ⟶ No reaction.

SPECIAL POINTS RELATED TO ANILINE

- "Unverdorbon" was the discoverer of Aniline.
- Aniline was first obtained from distillation of "Indigo".
- "Runge" showed its presence in coal-tar.
- The name aniline was given by "Fritzsche".

METHODS OF PREPARATION

(i) Lab method :

$$C_6H_5NO_2 + 6H \xrightarrow{Sn+HCl} C_6H_5NH_2 + 2H_2O$$

$$Sn + 4HCl \longrightarrow SnCl_4 + 4H$$

$$C_6H_5NO_2 + 6H \longrightarrow C_6H_5NH_2 + 2H_2O$$

$$SnCl_4 + 2HCl \longrightarrow H_2SnCl_6 \text{ (Chlorostannic acid)}$$

$$C_6H_5NH_2 + \frac{SnCl_4 + 2HCl}{(H_2SnCl_6)} \rightarrow (C_6H_5\overset{\oplus}{N}H_3)_2\overset{\ominus 2}{SnCl_6}$$

$$\xrightarrow{8NaOH} C_6H_5NH_2 + Na_2SnO_3 + 6NaCl + 5H_2O$$

Aniline is formed in the form of dark brown oil on adding NaOH solution to anilinium chlorstanate.

Aniline is then separated by steam distillation and pure aniline is obtained by extracting it with ether followed by distillation.

(ii) Industrial method :

(a) $C_6H_5NO_2 \xrightarrow{Fe+HCl} C_6H_5NH_2$

$$Fe + 2HCl \longrightarrow FeCl_2 + 2H$$

$$C_6H_5NO_2 + 6H \longrightarrow C_6H_5NH_2 + 2H_2O$$

$$FeCl_2 + 2H_2O \longrightarrow Fe(OH)_2 + 2HCl$$

(regeneration)

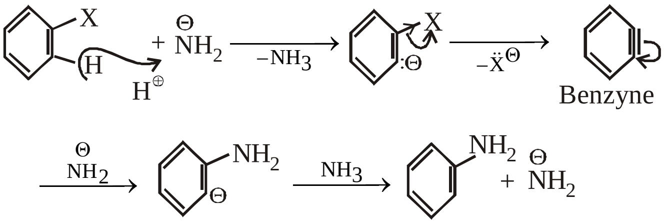
$$C_6H_5NO_2 + 6Fe(OH)_2 + 4H_2O \longrightarrow C_6H_5NH_2 + 6Fe(OH)_3$$

(b) $2C_6H_5Cl + 2NH_3 \xrightarrow[200°C]{Cu_2O} 2C_6H_5NH_2 + Cu_2Cl_2 + H_2O$

(c) $C_6H_5NO_2 + 2H_3 \xrightarrow[270°C]{Cu} C_6H_5NH_2 + 2H_2O$

(iii) $C_6H_5X + NaNH_2 \xrightarrow{liq.\ NH_3} C_6H_5NH_2$

Mechanism : Elimination addition or benzyne mechanism.



PHYSICAL PROPERTIES

(i) Freshly prepared aniline is colourless, poisonous oily liquid with characteristic smell.

(ii) Partially soluble in water, completely soluble in organic solvents like alcohol, ether, benzene, etc.

(iii) Becomes pink then brown and finally black on coming into contact with air and light.

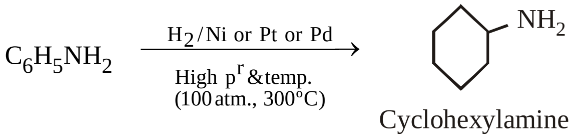
(iv) Boiling point is 184°C

(v) Steam volatile liquid.

CHEMICAL REACTIONS

(A) Reactions due to benzene ring :

(i) Catalytic hydrogenation :

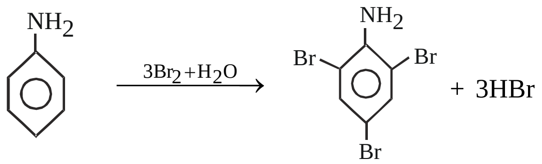


Cyclohexylamine

Note : Hybridisation state changes from sp^2 το sp^3.

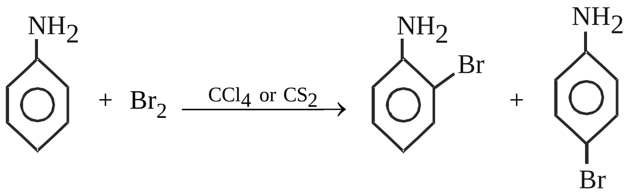
(ii) Halogenation :

(a) Polar medium :



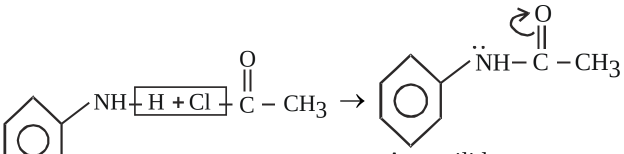
2,4,6-Tribromoaniline (white ppt.)

(b) Non polar medium :



(o- & p-Bromoaniline)

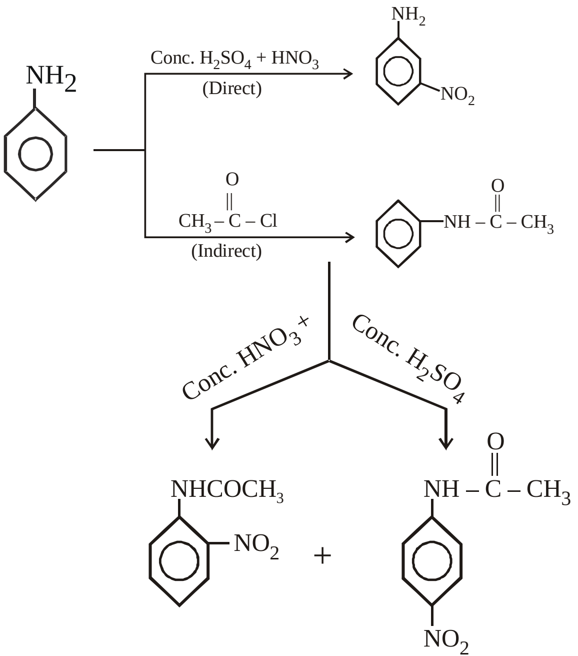
Cl_2 & Br_2 both have oxidising property. Ar – NH_2 group highly activates benzene, due to oxidising property this activated benzene ring can be decomposed. Therefore reactivity of benzene ring is decreased by its acetylation. This process is called protection of aniline.



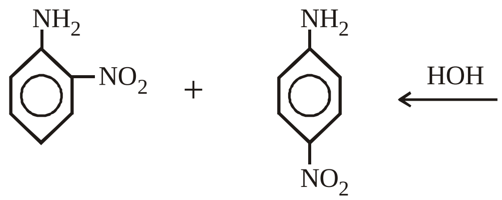
Acetanilide

Electron attracting group (>C=O) present in acetanilide decreases availability of lone pair on nitrogen atom and hence therefore decreases +M effect of $–NH_2$ group.

(iii) Nitration :



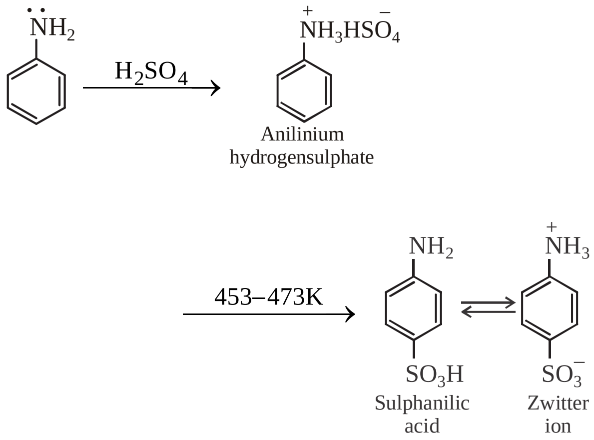
o- & p- Nitroacetanilide



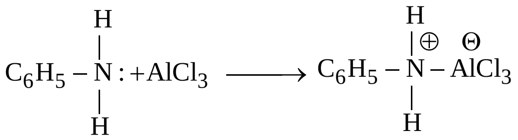
o-Nitroaniline (minor product)

p-Nitroaniline (major product)

(iv) Sulphonation :

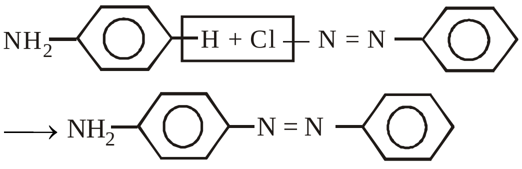


Note : Aniline does not give friedel craft reaction. Because aniline is base and $AlCl_3$ (Catalyst) is lewis acid. The Aluminium atom of acid attracts the lone pair of electrons present on the nitrogen atom and thus restricts the effect of $–NH_2$ group.



$$C_6H_5 - \overset{H}{\underset{H}{N}}: + AlCl_3 \longrightarrow C_6H_5 - \overset{H\,\oplus}{\underset{H}{N}} - \overset{\ominus}{AlCl_3}$$

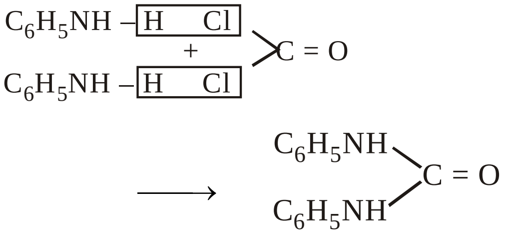
(v) Coupling reaction :



p-Amino azobenezene (Aniline yellow, a azo dye)

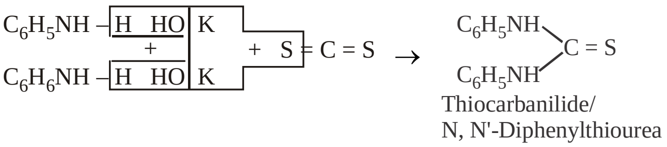
(B) Reactions differ from aliphatic amines :

(1) With phosgene :

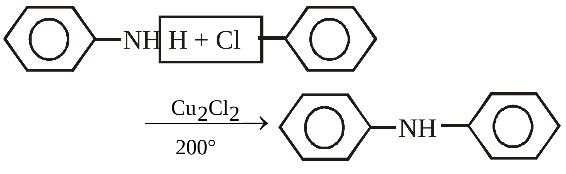


N, N'-Diphenylurea

(2) With CS_2 + Solid KOH :



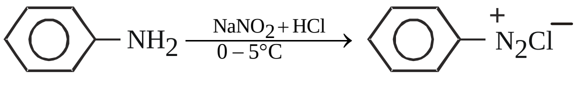
(3) Arylation :



Diphenyl amine

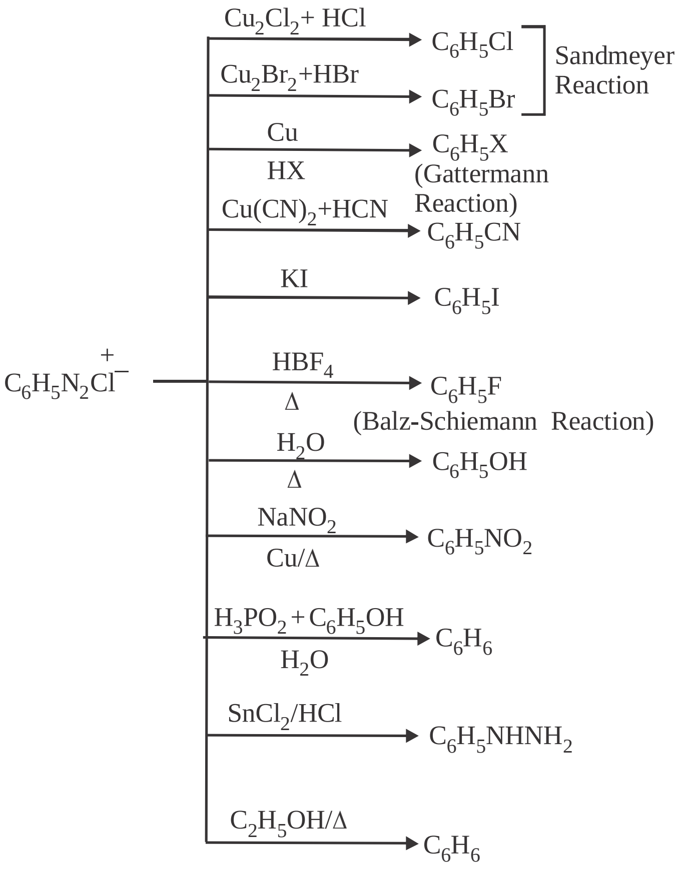
(4) Diazotization : The process of converting a primary aromatic amine into its diazonium salt by treatment with nitrous acid is called diazotisation.

Benzenediazonium chloride is obtained by treating aniline with nitrous acid (HNO_2) at 0 - 5° C (icebath temperature).

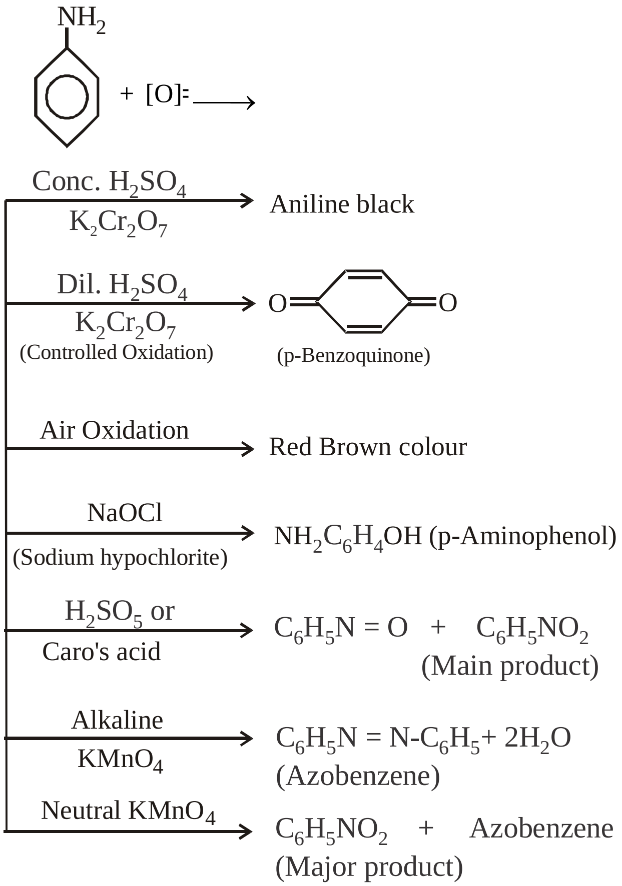


Aniline Benzenediazonium chloride

Benzenediazonium chloride is extremely useful synthetically. It is used in the preparation of many organic compounds.



(C) Oxidation :



Test for Aniline :

(i) Isocyanide test C_6H_5NC

(ii) Bromine water test White ppt. (2,4,6-Tribromoaniline)

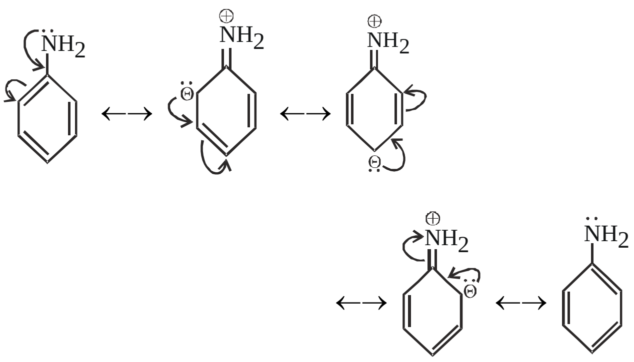
(iii) Aqueous NaOCl test : A violet colour instantly appears, which rapidly fades.

(iv) Dye test : A bright red orange azo dye is formed on reaction of benzene diazonium chloride with 10% NaOH solution of β-Naphthol.

USES :

(i) In manufacturing dyes.
(ii) As a rocket fuel
(iii) In manufacturing of explosive, plastics, medicines, etc.

RESONANCE IN ANILINE AND RELATED POINTS



1. The group ($-\ddot{N}H_2$) present in Aniline exert +M effect i.e. it increases electron density in benzene ring by giving lone pair of e^-.
2. $-\ddot{N}H_2$ is ortho (o–) and para (p-) directing because it increases e^- density on o- and p-locations, due to which the attacking electrophile effects on o- and p- position.
3. Aniline is weaker base as compared to aliphatic amines because availability of e^- on N atom is less due to resonance. So order of basicity.

   $R \rightarrow \ddot{N}H_2 > H-\ddot{N}H_2 > Ar-NH_2$

   (+I effect of R) (Resonance)
4. **Order of basicity of substituted Aniline :**

   p-Toluedine > Aniline

   (More availability of e^- pair)

   > m-Nitroaniline > p-Nitroaniline

   (less availability of e^- pair) (Very less availability of e^- pairs)

   Electron donating groups increase the basic strength while electron with drawing groups decrease the basic strength.

CYANIDES AND ISOCYANIDES

These are alkyl derivatives of hydrogen cyanide which exists in two tautomeric forms.

$H-C\equiv N \rightleftharpoons H-N\overset{\rightarrow}{\equiv}C$

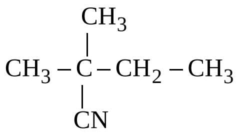
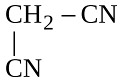
$R-C\equiv N \rightleftharpoons R-N\overset{\rightarrow}{\equiv}C$

Alkyl cyanide Alkyl isocyanide

NOMENCLATURE

(i) **In common system :** Alkyl cyanide

(ii) **IUPAC system :** Alkanenitrile.

Formula	Common name	IUPAC name
CH_3CN	Methyl cyanide	Ethanenitrile
C_2H_5CN	Ethyl cyanide	Propanenitrile
$\overset{4}{C}H_3-\overset{3}{C}H_2-\overset{2}{C}H_2-\overset{1}{C}N$	n-Propyl cyanide	1-Butanenitrile
 $CH_3-C(CH_3)(CN)-CH_2-CH_3$	t-Pentyl cyanide	2,2-Dimethyl-1-butanenitrile
 $CH_2(CN)-CN$	Methylene cyanide	1,3-Propanedinitrile
$(CH_2)_2(CN)_2$	Ethylene cyanide	1,4-Butanedinitrile

PREPARATION

(i) **From alkyl halides :**

$R-X + KCN \text{ (or NaCN)} \xrightarrow[(-KX)]{\Delta} R-CN + R-N\overset{\rightarrow}{\equiv}C$

Alkane Nitrile Alkyl isocyanide (in small amount)

$C_2H_5Br + KCN \xrightarrow[(-KBr)]{\Delta} C_2H_5CN + C_2H_5NC$

Main product

(ii) **From acid amides :**

$R-CONH_2 \xrightarrow[\Delta]{P_2O_5} R-C\equiv N + H_2O$

$CH_3CONH_2 \xrightarrow{P_2O_5} CH_3-C\equiv N + H_2O$

Ethanamide Ethanenitrile

(iii) **From Grignard's reagents :**

$RMgCl + ClCN \longrightarrow R-C\equiv N + MgCl_2$

Cyanogen chloride

$CH_3MgBr + ClCN \longrightarrow CH_3-C\equiv N + MgBrCl$

This is the best method of preparing tertiary alkyl cyanides.

$(CH_3)_3CMgCl + ClCN \longrightarrow (CH_3)_3CCN + MgCl_2$

t-Butyl cyanide

(iv) **By the dehydration of aldoximes :**

$R-CH=NOH \xrightarrow[\text{acetic anhydride}]{\Delta,\ P_2O_5 \text{ or}} R-C\equiv N + H_2O$

Alkanenitrile

(v) **From Primary amines :**

$R-CH_2NH_2 \xrightarrow[500^\circ C]{\text{Cu or Ni}} R-C\equiv N + 2H_2$

$CH_3CH_2NH_2 \xrightarrow[500^\circ C]{\text{Cu or Ni}} CH_3-C\equiv N + 2H_2$

PHYSICAL PROPERTIES

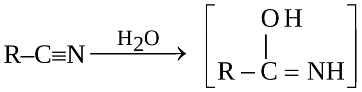
(i) Alkyl cyanides are sweet smelling, fairly stable liquids.

(ii) Lower alkyl cyanides are soluble in water with which they can form H-bonds, but solubility diminishes with rise in molecular mass. They are readily miscible with organic solvents.

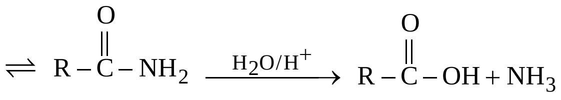
(iii) They are poisonous but less than HCN.

CHEMICAL PROPERTIES

(i) **Hydrolysis :**



$R-C\equiv N \xrightarrow{H_2O} \left[R-C(OH)=NH\right]$



$\rightleftharpoons R-C(=O)-NH_2 \xrightarrow{H_2O/H^+} R-C(=O)-OH + NH_3$

$R-C\equiv N + 2H_2O \xrightarrow{NaOH} R-COONa + NH_3$

Alkanenitrile Sodium salt

(ii) **Reduction :**

(a) With $LiAlH_4$ or $H_2 | Ni$, RCN gives 1°-amine

$R-CN \xrightarrow[H_2/\text{Ni or Pt}]{LiAlH_4} R-CH_2-NH_2$ 1°-amine

(b) Stephen's reaction :

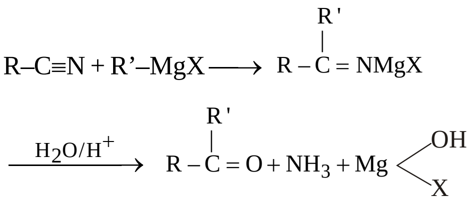
$$R{-}C{\equiv}N \xrightarrow{SnCl_2/HCl} R{-}CH{=}NH.HCl \ \text{(Aldimine)}$$

$$\xrightarrow{H_2O} \underset{\text{Aldehyde}}{R{-}CHO} + \underset{\text{hydrochloride}}{NH_4Cl}$$

(c) Mendius reaction : It involves reduction of RCN with Na and alcohol.

$$\underset{\text{Alkyl cyanide}}{R{-}C{\equiv}N + 4[H]} \xrightarrow{Na+alcohol} \underset{\text{Primary amine}}{R{-}CH_2{-}NH_2}$$

(iii) Reaction with GR : Ketones are obtained.



$$R{-}C{\equiv}N + R'{-}MgX \longrightarrow R-\overset{\displaystyle R'}{\overset{|}{C}}=NMgX$$

$$\xrightarrow{H_2O/H^+} R-\overset{\displaystyle R'}{\overset{|}{C}}=O + NH_3 + Mg\begin{smallmatrix}OH\\X\end{smallmatrix}$$

(iv) Ethanolysis :

$$R{-}C{\equiv}N + R'{-}OH + H_2O \longrightarrow RCOOR' + NH_3$$

$$CH_3CN + C_2H_5OH + H_2O \longrightarrow \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + NH_3$$

USES :

Alkyl cyanides are important intermediates in the laboratory preparation of organic compounds such as amides, amines, acids, ester, etc.

ISOCYANIDES

NOMENCLATURE

(i) Common system : Alkyl isocyanide or alkyl carbylamine.

(ii) In IUPAC system : Alkane isonitrile.

Formula	**Common system**	**IUPAC system**
$CH_3{-}NC$	Methyl isocyanide or Methyl carbylamine	Methane isonitrile
C_2H_5-NC	Ethyl isocyanide or Ethyl carbylamine	Ethane isonitrile

PREPARATION

(i) From alkyl halides :

$$\underset{\text{Alkyl halide}}{R{-}X} + AgCN \xrightarrow[\Delta]{alcohol} \underset{\text{Alkyl isocyanide}}{R{-}NC} + AgX$$

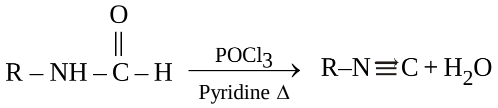
$$CH_3CH_2Br + \underset{\text{Silver cyanide}}{AgCN} \longrightarrow \underset{\text{Ethyl isocyanide}}{CH_3CH_2{-}NC} + AgX$$

(ii) From primary amines (carbylamine reaction) :

By heating primary amine with chloroform and alc. KOH.

$$R{-}NH_2 + CHCl_3 + 3KOH \xrightarrow{warm} \underset{\text{(Alkyl isocyanide)}}{R{-}N{\equiv}C} + 3KCl + 3H_2O$$

(iii) From N-alkyl formamide :



$$\underset{\text{(N-alkyl formamide)}}{R-NH-\overset{\displaystyle O}{\overset{\|}{C}}-H} \xrightarrow[Pyridine\ \Delta]{POCl_3} \underset{\text{(Alkylisocyanide)}}{R{-}N{\equiv}C + H_2O}$$

PHYSICAL PROPERTIES

(i) Alkyl isocyanides are colourless, most unpleasant smelling liquids with lower b.p. than the isomeric alkyl cyanides.

(ii) They are not very soluble in water because the nitrogen atom does not have a lone pair of electrons for H-bond formation with H_2O molecules.

(iii) Isocyanides are much more poisonous than isomeric cyanides.

CHEMICAL PROPERTIES

(i) Hydrolysis : These are hydrolysed by dil. acids (not by alkalis) to give primary amines and formic acid.

$$\underset{\text{Alkyl isocyanide}}{R{-}N{\equiv}C + H_2O} \xrightarrow{H^+} R{-}NH_2 + HCOOH$$

(ii) Reduction : Alkyl isocyanides are reduced to secondary amines either by dissolving metals or by catalytic reduction.

$$R{-}N{\equiv}C + 4[H] \xrightarrow[H_2/Ni\ or\ Na/alc.]{Metal/acid\ or} \underset{\substack{2^o\text{-amine}\\ \text{(Methyl alkylamine)}}}{R{-}NH{-}CH_3}$$

(iii) Action of heat :

$$R{-}N{\equiv}C \xrightarrow[time]{\Delta\ for\ a\ long} R{-}C{\equiv}N$$

(iv) Addition reactions : Alkyl isocyanides give addition reactions due to the presence of unshared electrons pair on carbon atom.

(a) $CH_3{-}N{\equiv}C + Cl_2 \longrightarrow CH_3{-}N{=}CCl_2$
(Methyl imino carbonyl chloride)

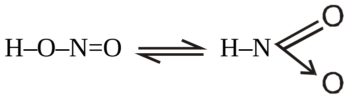
(b) $CH_3{-}N{\equiv}C + S \longrightarrow CH_3{-}N{=}C{=}S$
Mehtyl iso thiocyanate

(c) $CH_3{-}N{\equiv}C + HgO \longrightarrow CH_3{-}N{=}C{=}O + Hg$
Methyl isocynate **(MIC)**

Note : The famous Bhopal tregedy in Dec. 1984 was caused by MIC.

ALKYL NITRITES AND NITROALKANES

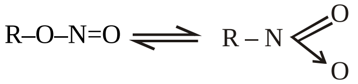
Nitrous acid exists in two tautomeric forms :



$$H{-}O{-}N{=}O \rightleftharpoons H{-}N\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix}$$

Nitrite form Nitro form

Thus, nitrous acid gives two types of alkyl derivatives.



$$R{-}O{-}N{=}O \rightleftharpoons R-N\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix}$$

Alkyl nitrite Nitroalkane

Alkyl nitrite is an ester of nitrous acid as it gives back the parent acid (HNO_2) on hydrolysis.

Nitroalkanes may not be regarded as the esters of nitrous acid, as they are not hydrolysed to HNO_2. They are better regarded as nitro derivatives of alkanes.

ETHYL NITRITE (C_2H_5–O–N=O)

PREPARATION

(i) By adding conc. HCl or sulphuric acid to an aqueous solution of sodium nitrite and ethyl alcohol at very low temp. (0°C)

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

$$C_2H_5OH + HNO_2 \longrightarrow C_2H_5\text{–O–N=O} + H_2O$$

(ii) By the action of N_2O_3 on ethanol :

$$2C_2H_5OH + N_2O_3 \longrightarrow \underset{\text{Ethyl nitrite}}{2C_2H_5\text{O–N=O}} + H_2O$$

(iii) By the reaction between ethyl iodide and potassium nitrite.

$$C_2H_5I + KNO_2 \longrightarrow \underset{\text{Ethyl nitrite}}{C_2H_5\text{O–N=O}} + KI$$

PROPERTIES

(i) Ethyl nitrite is a gas at ordinary temperature. It can be liquefied to a colourless liquid (b.p. 17ºC). It has a characteristic smell of apples. It is insoluble in water, but soluble in alcohol and ether.

(ii) Hydrolysis : It is readily hydrolysed by water, dilute alkali or dilute acid forming ethyl alcohol and nitrous acid.

$$C_2H_5ONO + H_2O \longrightarrow C_2H_5OH + HNO_2$$

(iii) Reduction :

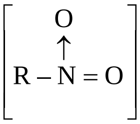
$$C_2H_5\text{–O–N=O} + 6[H] \xrightarrow{Sn/HCl} C_2H_5OH + NH_3 + H_2O$$

$$C_2H_5\text{–O–N=O} + 4[H] \xrightarrow{Sn/HCl} C_2H_5OH + NH_2OH$$

USES :

It dilates blood vessels and lowers blood pressure, so it used in medicine for the treatment of asthma and heart diseases. Its 4% alcoholic solution is known as sweet spirit of nitre and is used as a diuretic.

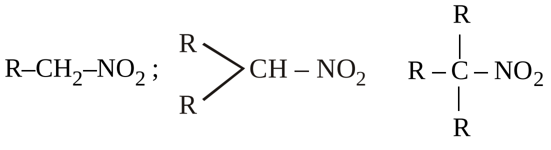
NITRO ALKANE



$$\left[\begin{array}{c} O \\ \uparrow \\ R-N=O \end{array}\right]$$

INTRODUCTION

These are classified as primary, secondary and tertiary depending upon the nature of carbon atom to which nitro group is attached.



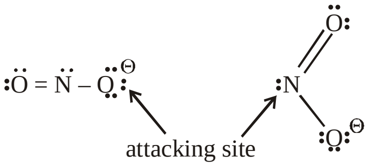
1°-Nitroalkane 2°-nitroalkane 3°-nitroalkane

PREPARATION

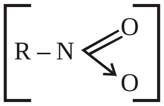
(i) From alkyl halides :

$$\underset{\text{Alkyl halide}}{R\text{–}X} + \underset{\text{(alc.)}}{AgNO_2} \xrightarrow[(-AgX)]{\Delta} \underset{\text{Nitro alkane}}{R\text{–}NO_2} + \underset{\substack{\text{Alkyl nitrite}\\\text{(a small amount)}}}{R\text{–O–N=O}}$$

The reaction of nitrite ion with alkyl halide is an example of nucleophilic substitution reaction. Nitrite ion $\left(\overset{\Theta}{O}-\ddot{N}=O\right)$ behaves like an ambident nucleophile because it can attack the alkyl halide through either 'O' or 'N' atom.



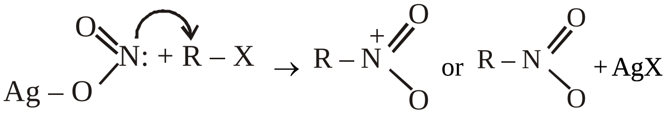
When the electron pair donor is N atom, nitroalkanes



are obtained as major product while the attack of alkyl halide through 'O' atom forms alkyl nitrite (R – O – N = O). Sodium or potassium nitrites are ionic compounds.

These contain the nitrite ion, $\overset{\Theta}{O}-N=O$. Therefore both N and O are available for attack at R – X molecule. However, the attack mainly takes place through 'O' because C – O bond is relatively stronger. So, alkyl nitrites are the main products of the reaction between R – X and KNO_2 or $NaNO_2$. On the other hand, silver nitrite is a covalent compound. In this molecule, only N is available for attack at R – X molecule. Consequently reaction between R – X and $AgNO_2$ gives mainly $\begin{array}{c} O \\ \uparrow \\ R-N=O \end{array}$

$$\underset{\text{Sodium nitrite}}{O\text{=N–}O^{-}Na^{+}} + R\text{–}X \rightarrow \underset{\text{Alkyl nitrite}}{R\text{–O–N=O}} + NaX$$



Silver nitrite Nitroalkane

A mixture of nitroalkane and alkyl nitrite can be separated by fractional distillation.

(ii) By direct nitration of alkanes :

$$\underset{\text{Alkane}}{R\text{–}H} + HONO_2 \xrightarrow[\text{(Vapour phase nitration)}]{400°C} \underset{\text{Nitroalkane}}{R\text{–}NO_2} + H_2O$$

PROPERTIES

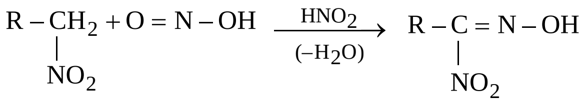
(i) Nitroalkanes are colourless, pleasant smelling liquids. They have much higher b.p. than isomeric alkyl nitrites. They are sparingly soluble in water, but soluble in organic solvents.

(ii) Reduction :

(i) $R\text{–}NO_2 + 6[H] \xrightarrow[LiAlH_4 \text{ or } H_2/Ni]{Sn/HCl,\ Fe/HCl} R\text{–}NH_2 + 2H_2O$

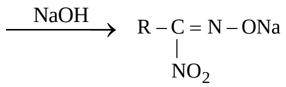
(ii) $R\text{–}NO_2 + 4[H] \xrightarrow{Zn/NH_4Cl} \underset{\text{N-alkyl hydroxyl amine}}{R\text{–NHOH}} + H_2O$

(iii) Action of nitrous acid : Different products are formed from 1°, 2° and 3°-nitroalkanes.



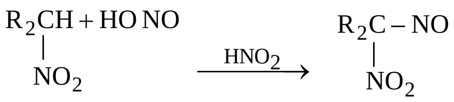
$$\underset{NO_2}{R-CH_2}+O=N-OH\xrightarrow[(-H_2O)]{HNO_2}\underset{NO_2}{R-C}=N-OH$$

Primary nitro alkane Nitrolic acid



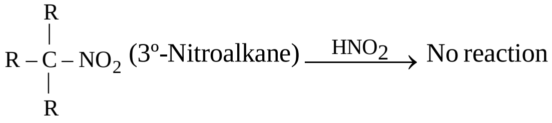
$$\xrightarrow{NaOH}\underset{NO_2}{R-C}=N-ONa$$

Red. colour (Sodium salt)



$$\underset{NO_2}{R_2CH}+HO\,NO\xrightarrow{HNO_2}\underset{NO_2}{R_2C}-NO$$

2°-Nitroalkane Pseudo nitrol (Blue colour)



$$R-\overset{R}{\underset{R}{C}}-NO_2\text{ (3°-Nitroalkane)}\xrightarrow{HNO_2}\text{No reaction}$$

This reaction can be used to distinguish between 1°, 2°, and 3°-nitroalkanes.

(iv) Thermal decomposition : Upon rapid heating nitroalkanes decompose with great violence.

$$CH_3NO_2\xrightarrow{Heat}CO_2+(1/2)\,N_2+(3/2)\,H_2$$

(v) Halogenation : Nitromethane reacts with halogen in presence of alkali to form trihalogen derivative. (e.g.,) with chlorine it forms chloropicrin, CCl_3NO_2 which is used as soil sterilizing agent.

$$CH_3NO_2+3Cl_2\xrightarrow{NaOH}CCl_3NO_2+3HCl$$

Chloro picrin (trichloro nitro methane)

(vi) Hydrolysis : 1°-nitroalkanes are hydrolysed by boiling hydrochloric acid or by 85% H_2SO_4 to a carboxylic acid and hydroxyl amine.

$$R–CH_2NO_2+H_2O\xrightarrow[boil]{HCl}RCOOH+NH_2OH$$

$$CH_3CH_2CH_2NO_2\text{ (1°-Nitropropane)}+H_2O\xrightarrow[boil]{H_2SO_4(85\%)}CH_3CH_2COOH+NH_2OH$$

2°-nitroalkanes on hydrolysis with boiling HCl give ketones and nitrous oxide.

$$\underset{\text{2°-Nitroalkane}}{2R_2CHNO_2}\xrightarrow[boil]{HCl}2R_2CO+N_2O+H_2O$$

3°-nitroalkanes are generally unaffected by HCl.

USES :

(i) As powerful explosives.

(ii) As solvent for cellulose acetate, synthetic rubber, etc.

(iii) For preparing amines, hydroxyl amines, etc.

NITROBENZENE

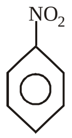
Introduction :

(i) Aromatic nitro compounds are obtained when hydrogen atom or atoms of aromatic compound are replaced by $-NO_2$ (nitro) group

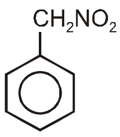
(ii) Aromatic nitro compound are of two types.

(a) Those compounds, in which nitro group is attached directly to the benzene ring e.g. nitrobenzene.

(b) Those compounds, in which nitrogroup is attached to a side chain.



(I)
(nitro benzene)



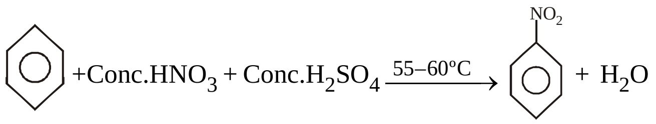
(II)
(phenyl nitromethane)

(iii) Nitrobenzene is also called as 'oil of mirbane' or 'artificial oil of bitter almond's.

(iv) It has a smell similar to benzaldehyde.

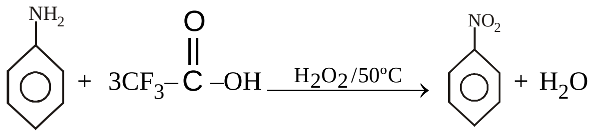
METHODS OF PREPARATIONS

1. By Nitration of Benzene [Laboratory method]



$$C_6H_6+Conc.HNO_3+Conc.H_2SO_4\xrightarrow{55–60°C}C_6H_5NO_2+H_2O$$

2. By Oxidation of Aniline :



$$C_6H_5NH_2+3CF_3–\overset{O}{\overset{\|}{C}}–OH\xrightarrow{H_2O_2/50°C}C_6H_5NO_2+H_2O$$

PHYSICAL PROPERTIES

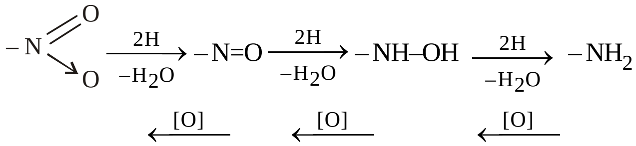
1. Pale yellow, poisonous, volatile oily liquid.
2. Heavier than water, very sparingly soluble in water, but miscible with organic solvents like alcohol, ether, benzene, etc.
3. B.P. = 211°C

CHEMICAL REACTIONS

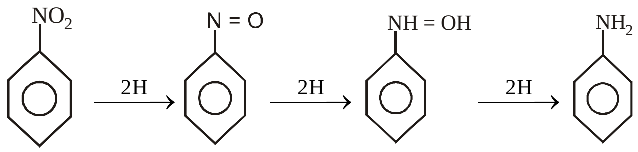
1. Reactions due to nitro group
2. Electrophilic substitution reaction due to benzene ring. The attack is at meta position where it gets least repulsions.
3. Nucleophilic substitution reaction due to benzene ring.

(1) Reactions due to Nitro group :

Reduction of nitrobenzene takes place due to nitro $(-NO_2)$ group.



$$-NO_2\underset{[O]}{\overset{2H,\,-H_2O}{\rightleftharpoons}}-N=O\underset{[O]}{\overset{2H,\,-H_2O}{\rightleftharpoons}}-NH–OH\underset{[O]}{\overset{2H,\,-H_2O}{\rightleftharpoons}}-NH_2$$



Nitro benzene Nitroso benzene (I) N-Phenyl hydroxylamine (II) Aniline (III)

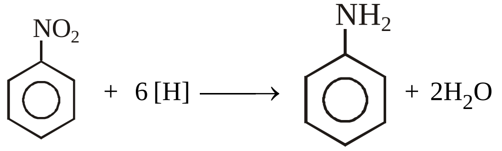
Note : Products (I), (II) & (III) are primary reduction products of Nitrobenzene the products obtained from further reduction of primary reaction product are called secondary reduction product of nitrobenzene such as.

S.R.P. = Hydrozobenzene, Azobenzene, Azoxybenzene.

(a) Reduction in acidic medium :

Acidic medium = Zn + HCl,

Zn + CH_3COOH, Fe + HCl, etc. Sn + HCl,



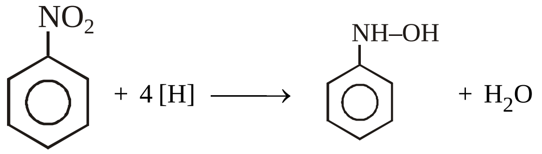
Note : Low pH and high temperature increases the rate of reduction.

(b) Neutral medium :

Neutral medium = Zn + NH_4Cl, Zn + $CaCl_2$,

Zn + CH_3COONa etc.

Al – Hg + NH_4Cl,



N-Phenylhydroxylamine

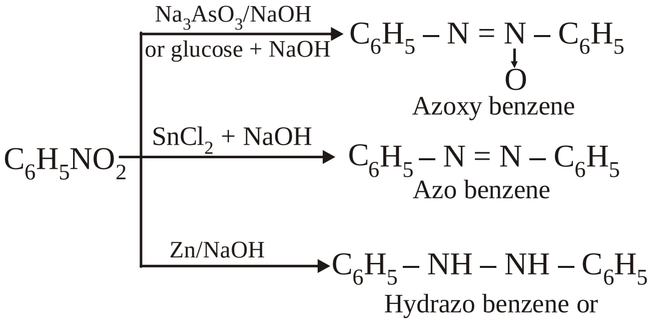
(c) Alkaline medium :

Alkaline medium : Zn + NaOH , CH_3OH + NaOH

Sn + NaOH , Glucose + NaOH

$SnCl_2$ + NaOH , As_2O_3 + NaOH

Nitrosobenzene and N-phenylhydroxylamine are formed.

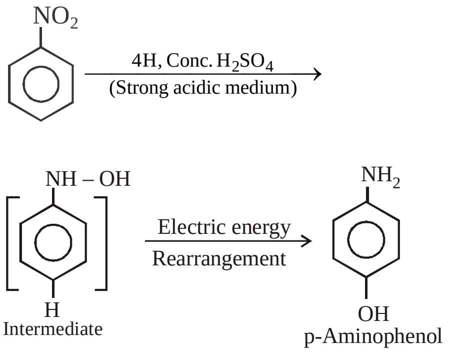


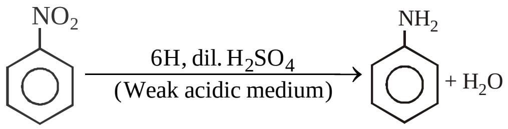
Azoxy benzene

Azo benzene

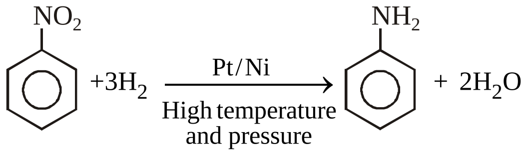
Hydrazo benzene or
(N, N' - Diphenyl hydrazine)

(d) Electrolytic reduction :

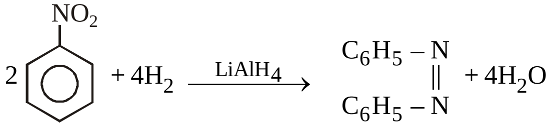




(e) Catalytic reduction :

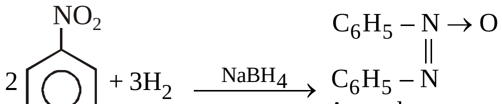


(f) Reduction by Lithiumalluminium hydride ($LiAlH_4$) :



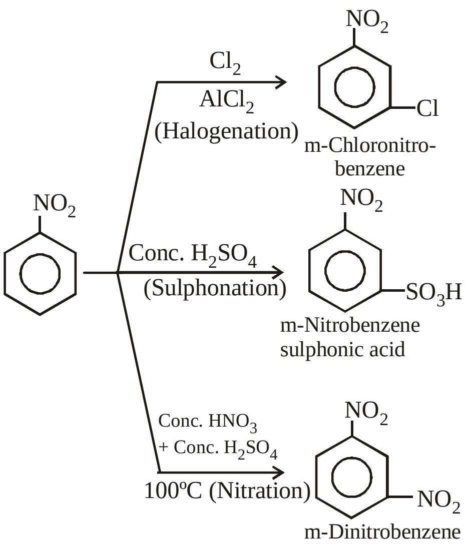
Azobenzene

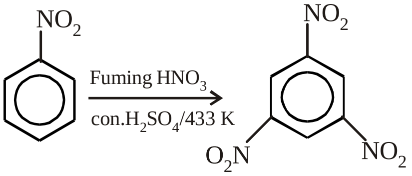
(g) Reduction by sodium borohydride ($NaBH_4$) :



Azoxybenzene

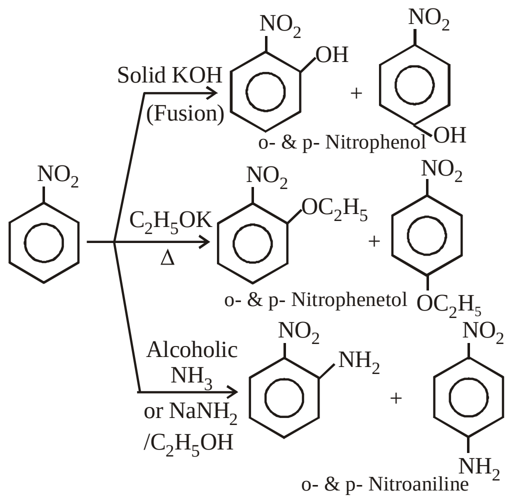
(2) Electrophilic substitution reaction due to benzene ring :





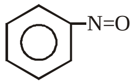
1,3,5-Trinitro benzene

(3) Nucleophilic substitution reactions :



Test of Nitrobenzene : (Mulliken and Barker test)

$C_6H_5NO_2$ + Zn + $CaCl_2$
(alcoholic) (dust) (Anhyd.)

$\xrightarrow[4H]{\text{Reduction}} C_6H_5NHOH \xrightarrow[AgNO_3]{NH_4OH}$  $+ Ag\downarrow$

Blackgrey (ppt.)

Oxidation of N-Phenyl hydroxyl amine and reaction of ammoniacal silver nitrate takes place.

USES

(i) As an industrial solvent
(ii) Used as intermediate in the production of on explosive 1, 3, 5-Trinitrobenzene (T.N.B.)
(iii) In the preparation of shoe polish, floorpotshes, etc.
(iv) In manufacturing of aniline.

GOLDEN TIPS

* On reduction with Na_2SO_3, the benzene diazonium chloride gives phenyl hydrazine. On reduction with Zn + HCl, $C_6H_5N_2Cl$ forms aniline as the main product. On catalytic reduction with H_2/Ni, benzene diazonium chloride forms aniline.

* Some derivatives of ammonia arranged in order of decreasing basic nature are $(CH_3)_4N^+OH^-$, $(CH_3)_2NH$, CH_3NH_2, $(CH_3)_3N$, NH_3, $C_6H_5CH_2NH_2$, $C_6H_5NHCH_3$, $C_6H_5NH_2$, $(C_6H_5)_2NH$,CH_3CONH_2.

* Secondary amines (aliphatic as well as aromatic) react with nitrous acid to form N-nitrosoamines.

* Nitrosoamines are water-insoluble yellow oils and when warmed with a crystal of phenol and a few drops of conc. H_2SO_4 produce a green solution which turns blue on adding alkali. This reaciton is known as Libermann's nitroso reaction and may be used as a test for secondary amines.

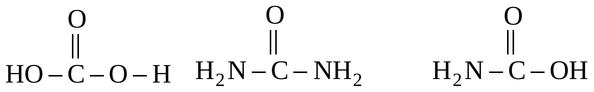
* Nitrosoamines when heated with conc. HCl regenerate the secondary amines.

* Aliphatic tertiary amines dissolve in cold nitrous acid to form unstable nitrites which decompose on warming to give nitrosoamine and alcohol.

UREA

INTRODUCTION :

(i) IUPAC name of urea is 'Aminomethanamide'.
(ii) It is also called CARBAMIDE.
(iii) It was first discovered in 1773 in urine by Roulle.
(iv) Wohler, a scientist first synthesied it in laboratory.
(v) Urea is diamide of carbonic acid and monoamide of carbamic acid.



$HO-\overset{\overset{O}{\|}}{C}-O-H \qquad H_2N-\overset{\overset{O}{\|}}{C}-NH_2 \qquad H_2N-\overset{\overset{O}{\|}}{C}-OH$

Carbonic acid Urea Carbamic acid

(vi) Carbon in urea is sp² hybridised and N is in sp³ hybridisation state.

METHODS OF PREPARATION

(i) Extraction from Urine :

$(NH_2CONH_2)_2\, H_2C_2O_4 + CaCO_3$
$\longrightarrow 2NH_2CONH_2 + CaC_2O_4 + CO_2 + H_2O$

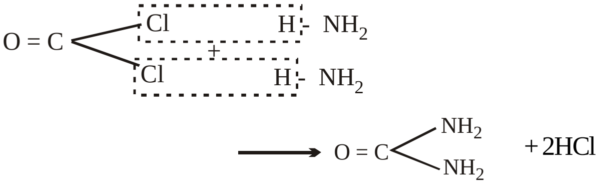
(ii) Wohler's method : In this method Urea is obtained by rearrangement of ammonium cyanate

$2KCNO + (NH_4)_2SO_4 \longrightarrow 2NH_4CNO + K_2SO_4$

$\Delta \downarrow$ rearangement

NH_2CONH_2

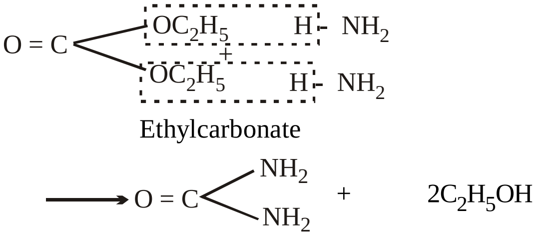
(iii) From phosgene gas :



$O=C(Cl)_2 + 2H-NH_2 \longrightarrow O=C(NH_2)_2 + 2HCl$

Urea

(iv) From Ethyl carbonate :

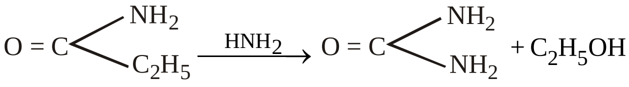


$O=C(OC_2H_5)_2 + 2H-NH_2 \longrightarrow O=C(NH_2)_2 + 2C_2H_5OH$

Ethylcarbonate

Urea

(v) From Ethyl carbamate or urethane :

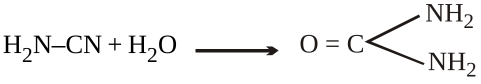


$O=C(NH_2)(C_2H_5) \xrightarrow{HNH_2} O=C(NH_2)_2 + C_2H_5OH$

Urethane Urea

(vi) Hydrolysis of Cyanamide :

$CaCN_2 + 2H_2O \longrightarrow Ca(OH)_2 + H_2N-CN$
Calcium Cyanamide



$H_2N\text{–}CN + H_2O \longrightarrow O=C(NH_2)_2$

urea

PHYSICAL PROPERTIES

Urea is a white, odourless crystalline solid (melting point 132.7º) having cold salty taste. It is soluble in water, alcohol and benzene, but sparingly soluble in ether and almost insolulbe in chloroform. It undergoes decomposition before its boiling point.

(i) Structure of Urea : Urea is represented by the formula NH_2CONH_2 for convenience. But this formula does not explain all properties of ureas correctly. For example, the following properties cannot be justified by the above formula.

(a) High Melting Point : Compounds having molecular weight almost equal to urea have low boiling point and are volatile liquids. Urea is a high melting solid (132.7º). Therefore, urea should be a compound having very high polarity.

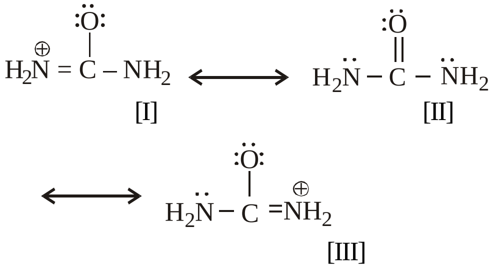
(b) Very Low Solubility in Ether : Low solubility in ether also confirms high polarity of urea.

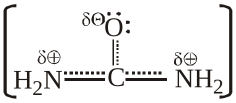
(c) Monoacid Base Nature : Due to the presence of two NH_2 groups in the above structural formula of urea, two protons should be able to attack it and it should be a diacid base. But urea is invariably a monoacid base.

Above three properties can be explained on the basis of resonance in urea.

(d) Bond Lengths : On measuring both C – N bond distances this point came out that the value of this distance is 1.37 Å. In other compounds value of C–N single bond distance is 1.47 Å and C–N double bond distance is 1.28 Å. Occurrence of C–N bond distance value of urea between both values shows that there is resonance in urea.

(ii) Resonance in Urea : Urea molecule shows resonance and is regarded as the resonance hybrid of canonical structures [I], [II] and [III].





Resonance hybrid

Urea actually exists in the form of resonance hybrid formula. It is clear that urea is a strongly polar compound and due to this it is a compound having high melting point and is almost insoluble in ether. Due to the presence of partial positive charge on nitrogen atoms, attack by a proton is not possible on them. But, due to the presence of partial negative charge on oxygen atom, only one proton can attack here. Therefore, urea behaves as a monoacid base.

CHEMICAL PROPERTIES :

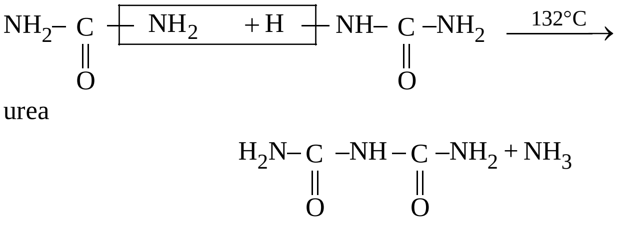
(i) Hydrolysis : Hydrolysis of urea takes place under all conditions, i.e., ammonium compounds are formed in neutral, acidic as well as alkaline mediums.

$$NH_2–CO–NH_2 + 2H_2O$$
$$\downarrow$$
$$2NH_4Cl + CO_2 \xleftarrow[\text{Acidic medium}]{HCl} [2NH_3 + H_2CO_3] \xrightarrow[\text{Alkaline medium}]{NaOH} Na_2CO_3 + NH_3$$
$$\text{Neutral medium}\downarrow$$
$$(NH_4)_2CO_3$$

The enzyme urease, present in soyabeans and some bacteria bring about enzymic hydrolysis of urea in very small amount of water (humidity) to give ammonia and carbon dioxide (or ammonium carbonate in larger amounts of water). This reaction is rapid and complete. Therefore, it is used in the estimation of urea in blood and urine.

$$NH_2CONH_2 + H_2O \xrightarrow{\text{Urease}} 2NH_3 + CO_2 \longrightarrow (NH_4)_2CO_3$$

(ii) Effect of heat :



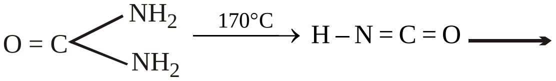
urea

Biuret

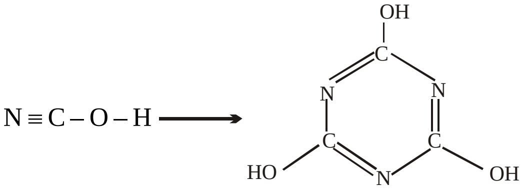
Note :

(a) When an aqueous solution of biuret is heated with sodium hydroxide solution and a drop of copper sulphate solution, a violet colour is produced which is characteristic of all compounds containing –CO–NH– group. This test is called Buret test.

(b) If heated strongly first cyanic acid is formed which polymerises to trimer called cyanuric acid.



urea Isocyanic acid



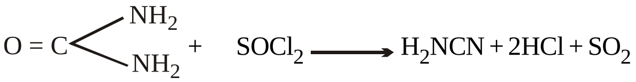
cyanic acid cyanuric acid

(iii) Salt Formation : It forms salts due to it's weak basic nature. Urea is a weak monoacid base. It reacts with cold conc. nitric acid and oxalic acid to form salts.

$$\underset{\text{urea}}{NH_2CONH_2} + HNO_3 \longrightarrow \underset{\text{urea nitrate}}{[H_2N–CO–NH_2].HNO_3}$$

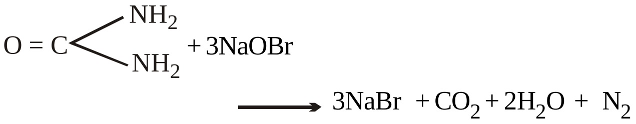
$2NH_2CONH_2 + (COOH)_2 \longrightarrow [H_2N\text{–}CO\text{–}NH_2]_2.(COOH)_2$
urea urea oxalate

(iv) Reaction with : $SOCl_2$



Cyanamide

(v) Reaction with Hypobromite solution :

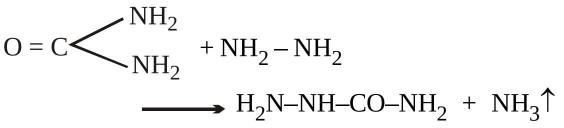


(vi) Acetylation : Form Acetyl urea.

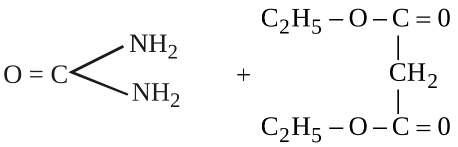
$CH_3COCl + H_2NCONH_2 \longrightarrow CH_3CONHCONH_2 + HCl$

$(CH_3CO)_2O + H_2NCONH_2 \longrightarrow CH_3CONHCONH_2 + CH_3COOH$

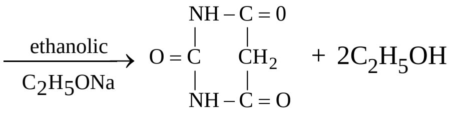
(vii) Reaction with Hydrazine : Gives semicarbazide,



(viii) Reaction with Malonic ester :



Melonic ester



Barbituric acid or mallonyl urea

Note : Barbituric acid is used as sedatives and hypnotics.

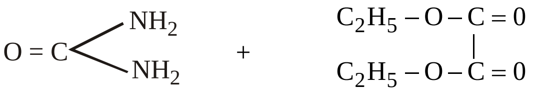
(ix) Reaction with Oleum :

Sulphamic acid is formed by the reaction of urea and oleum, i.e., fuming sulphuric acid ($H_2SO_4 + SO_3$).

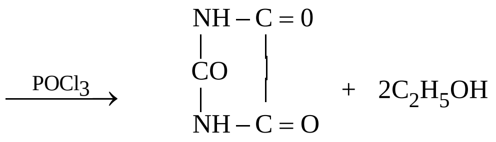
$NH_2CONH-H + H_2SO_4 \longrightarrow NH_2CONH\text{–}SO_3H + H_2O$
Sulphamic acid

$H_2O + SO_3 \longrightarrow H_2SO_4$

(x) Reaction with ester :



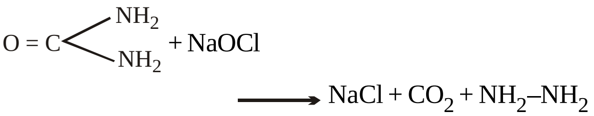
Oxalic ester (parabanic acid)



Oxalyl urea

Note : Parabanic acid (Oxalyl urea) can also be produced when urea reacts with oxalic acid in presence of $POCl_3$

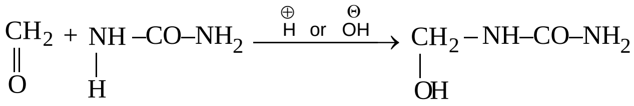
(xi) Reaction with NaOCl



(Hydrozine)

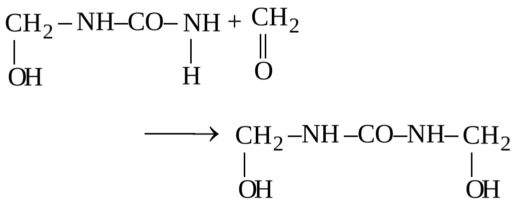
(xii) With formaldehyde

Methylourea is formed on addition of urea on formaldehyde in the presence of an acid or low amount f an alkali.Methylolurea adds on one more formaldehyde molecule to form dimethylourea.



$$\underset{\underset{O}{\|}}{CH_2} + \underset{\underset{H}{|}}{NH}\text{–}CO\text{–}NH_2 \xrightarrow{\overset{\oplus}{H}\ \text{or}\ \overset{\ominus}{OH}} \underset{\underset{OH}{|}}{CH_2}-NH\text{–}CO\text{–}NH_2$$

Methylolurea



$$\underset{\underset{OH}{|}}{CH_2}-NH\text{–}CO\text{–}\underset{\underset{H}{|}}{NH} + \underset{\underset{O}{\|}}{CH_2} \longrightarrow \underset{\underset{OH}{|}}{CH_2}\text{–}NH\text{–}CO\text{–}NH\text{–}\underset{\underset{OH}{|}}{CH_2}$$

Dimethylolurea

A polymer urea-formaldehyde resin is formed on addition polymerisation of dimethylourea. This polymer plastic is used as an electrical insulator.

$nHOCH_2NHCONH_2CH_2OH$

$\longrightarrow [\text{–}CH_2NHCONH_2CH_2O\text{–}]_n$
Urea-formaldehyde resin

(xiii) With Nitrous Acid :

Nitrogen. carbon dioxide and watyer are formed on reaction of urea with nitrous acid.

$NH_2CONH_2 + 2HNO_2 \longrightarrow 2N_2 + CO_2 + 3H_2O$

Estimation of urea can be done by finding out the volume of nitrogen liberated in this reaction.

USES :

(i) Urea used chiefly as a fertilizer.

(ii) It can also be used for manufacturing urea formaldehyde resins and stabiliser for explosive (nitrocellulose)

(iii) In the formation of semi carbazide, barbituric acid, sulphamic acid, parabomic acid etc.

USEFUL TIPS

* Amines less acidic than alcohols of comparable molecular masses because $C_2H_5O^{\Theta}$ is more stable than $C_2H_5NH^{\Theta}$ because oxygen is more electronegative than nitrogen.

* Primary amines have higher boiling point than tertiary amines due to the presence of two H-atoms on N-atoms of primary amines, they undergo extensive intermolecular H-bonding while tertiary amines due to absence of a H-atom on the N-atom do not undergo H-bonding.

* Aliphatic amines stronger bases than aromatic amines because there is electron with drawing C_6H_5 group in aromatic amines which makes them less basic than aliphatic amines in which alkyl group is electron releasing.

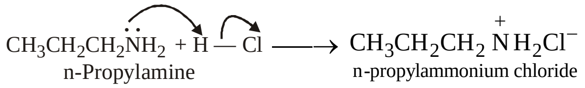
* Order of basic strengths :

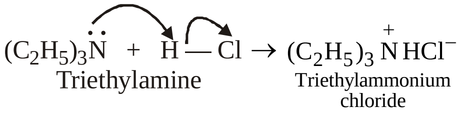
$$C_6H_5NH_2 < NH_3 < C_6H_5CH_2NH_2 < C_2H_5NH_2 < (C_2H_5)_2NH$$

* Nitro ethane is soluble in NaOH solution because it can exhibits tautomerism of nitroform and aciform. Aciform is acidic and soluble in NaOH.

* $CH_3CH_2NO_2$ has two α-hydrogen and that reacts with HNO_2.

* 2-methyl-2-nitro propane is neither soluble in NaOH nor reacts with nitrous acid because it has no α-hydrogen.

* 

* 

* Amide which gives propanamine by Hoffmann bromamide reaction : Butanamide.

* $$\underset{\text{Chloroethane}}{CH_3CH_2-Cl}\xrightarrow[\text{NaCN}]{\text{Ethanolic}}\underset{\text{Propanenitrile}}{CH_3CH_2-C\equiv N}$$

$$\xrightarrow{\text{reduction}}\underset{\text{Propan-1-amine}}{CH_3-CH_2-CH_2-NH_2}$$

TRY IT YOURSELF

Q.1 Which of the following can be detected by carbylamine reaction

(A) Urea (B) CH_3CONH_2
(C) $C_2H_5NH_2$ (D) All the above

Q.2 How many isomeric amines can have the formula $C_4H_{11}N$

(A) Five (B) Six
(C) Seven (D) Eight

Q.3 Which of the following is produced by reducing RCN in sodium and alcohol ?

(A) $RCONH_2$ (B) $RCOONH_4$
(C) RCH_2CH_2 (D) $(RCH_2)_3N$

Q.4 When a solution of aliphatic amine is treated with $NaNO_2$, the effervescence occurs due to the formation of –

(A) CO_2 (B) NO_2
(C) N_2 (D) H_2

Q.5 Butanenitrile may be prepared by heating –

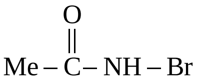
(A) propyl alcohol with KCN
(B) butyl alcohol with KCN
(C) butyl chloride with KCN
(D) propyl chloride with KCN

Q.6 Determine the end product of the following reactions

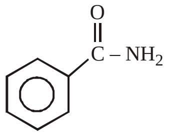
$$C_2H_5NH_2 \xrightarrow{HNO_2} A \xrightarrow{PCl_5} B \xrightarrow{NH_3} C$$

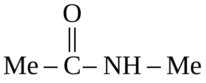
(A) ethyl cyanide (B) methyl amine
(C) ethyl amine (D) acetamide

Q.7 Which of the following cannot give Hoffmann's bromamide reaction –

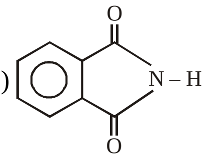
(A) 

$$Me-\overset{\overset{\large O}{||}}{C}-NH-Br$$

(B) 

(C) 

$$Me-\overset{\overset{\large O}{||}}{C}-NH-Me$$

(D) 

Q.8 The correct order of basic strength of Toluedines is –

(A) o > m > p (B) p > m > o
(C) m > p > o (D) m > o > p

Q.9 CH_3-NH_2 and $(CH_3)_2NH$ can be distinguished by –

(A) Carbylamine test (B) Libermann nitroso test
(C) Hoffmann musturd test (D) All of these

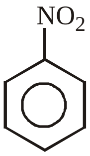
Q.10 Which of the following is not possible directly in nitrobenzene?

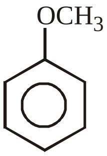
(A) Halogenation (B) Sulphonation
(C) Nitration (D) Alkylation

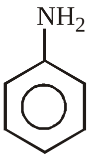
Q.11 Which of the following is most acidic molecule ?

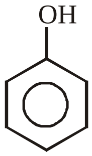
(A) CH_3-NO_2 (B) $(CH_3)_2CH-NO_2$
(C) $(NO_2)_3C-H$ (D) $CH_3-CH_2-NO_2$

Q.12 The compound which is most reactive towards diazocoupling with benzene diazonium chloride is –

(A) 

(B) 

(C) 

(D) 

Q.13 Coupling of diazo salt with phenol is most favourable in

(A) Acidic solution (B) Neutral solution
(C) Basic medium (D) Same in all

ANSWERS

(1) (C) **(2)** (D) **(3)** (C)
(4) (C) **(5)** (D) **(6)** (C)
(7) (C) **(8)** (B) **(9)** (D)
(10) (D) **(11)** (C) **(12)** (C)
(13) (C)

QUESTION BANK

CHAPTER 12 : ORGANIC COMPOUNDS CONTAINING NITROGEN

EXERCISE - 1 [LEVEL-1]

Choose one correct response for each question.

PART - 1 : STRUCTURE AND CLASSIFICATION OF AMINES

Q.1 Triaminobenzene is a –
(A) 2° amine (B) 3° amine
(C) 1° amine (D) Quarternary salt

Q.2 C_3H_9N represents
(A) Primary amine (B) Secondary amine
(C) Tertiary amine (D) All of these

Q.3 Select the quaternary ammonium compound from the given options.
(A) Trimethylphenyl ammonium bromide
(B) Tribenzylamine
(C) Dibenzylamine
(D) None of the above

Q.4 The shape of $(CH_3)_3N$ is pyramidal because –
(A) nitrogen forms three sp^3 hybridised sigma bonds with carbon atoms of methyl groups and there is one non-bonding electron pair.
(B) nitrogen forms three sp^2 hybridised sigma bonds with carbon atoms of methyl groups and fourth orbital forms pi bond.
(C) nitrogen has five valencies which are arranged in pyramidal shape.
(D) the unpaired electron present on nitrogen is delocalised.

Q.5 Which of the following is a 3° amine?
(A) 1-Methylcyclohexylamine (B) Triethylamine
(C) tert-Butylamine (D) N-Methylaniline

Q.6 Which of the following statement(s) is/are true about amines?
(A) Amines are derived by replacing one or more hydrogen atoms of ammonia molecule by alkyl/aryl group(s).
(B) In nature, they occur among proteins, vitamins, alkaloids and hormones.
(C) Synthetic examples of amines are polymers, dyestuffs and drugs.
(D) All of the above

Q.7 If one hydrogen atom of NH_3 is replaced by R, ___ is obtained and if two hydrogen atoms are replaced, then ____ is obtained.
(A) 1° amine; 2° amine (B) 1° amine; 3° amine
(C) 2° amine; 1° amine (D) 2° amine; 3° amine

Q.8 What is the hybridisation and the geometry of the amines?
(A) sp^2 hybridised and pyramidal geometry.
(B) sp^3 hybridised and planar geometry.
(C) sp^2 hybridised and planar geometry.
(D) sp^3 hybridised and pyramidal geometry.

PART - 2 : NOMENCLATURE OF AMINES

Q.9 I. An aliphatic amine is named by prefixing alkyl group to amine in the common system.
II. In secondary and tertiary amines, when two or more groups are the same, the prefix di or tri is appended before the name of alkyl group.
III. If more than one amino group is present at different positions in the parent chain then suitable prefix such as di, tri is attached to the amine. The letter 'e' of the suffix of the hydrocarbon part is retained.
Select the incorrect statement(s) from the above statements and choose the appropriate option.
(A) Only I (B) Only II
(C) Only III (D) All of these

Q.10 The correct IUPAC name for $CH_2 = CHCH_2NHCH_3$ is –
(A) allyl methylamine
(B) 2-amino-4-pentene
(C) 4-aminopent -1-ene
(D) N-methylprop-2-en-1-amine

Q.11 Identify the incorrect IUPAC name.
(A) $(CH_3CH_2)_2NCH_3$ = N-Ethyl-N-methylethanamine
(B) $(CH_3)_3CNH_2$ = 2-Methylpropan-2-amine
(C) $CH_3NHCH(CH_3)_2$ = N-Methylpropan-2-amine
(D) $(CH_3)_2CHNH_2$ = 2, 2-Dimethyl-N-propanamine

Q.12 IUPAC name of $H_2N - CH_2 - CH_2 - NH_2$ is
(A) ethan-1, 2-diamine (Bethane-1, 2-diamine
(C) ethane-1-2, diamine (D) ethan-1-2, diamine

PART - 3 : PREPARATION OF AMINES

Q.13 Ethylamine can be obtained by the –
(A) Action of NH_3 on ethyl iodide
(B) Action of NH_3 on ethyl alcohol
(C) Both (A) and (B)
(D) None of the above

Q.14 Reduction of nitroalkanes yields
(A) Acid (B) Alcohol
(C) Amine (D) Diazo compounds

Q.15 Which one of the following compound gives a secondary amine on reduction
(A) Nitromethane (B) Nitrobenzene
(C) Methyl isocyanide (D) Methyl cyanide

Q.16 When ethanol is mixed with ammonia and passed over alumina the compound formed is
(A) $C_2H_5NH_2$ (B) C_2H_4
(C) $C_2H_5OC_2H_5$ (D) CH_3OCH_3

Q.17 Which of the following reactions does not yield an amine

(A) $RX + NH_3 \longrightarrow$ (B) $RCH = NOH + [H] \xrightarrow[C_2H_5OH]{Na}$

(C) $RCN + H_2O \xrightarrow{H^+}$ (D) $RCONH_2 + 4H \xrightarrow{LiAlH_4}$

Q.18 Which of the following reactions will not give primary amine

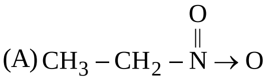
(A) $CH_3CONH_2 \xrightarrow{KOH.Br_2}$ (B) $CH_3CN \xrightarrow{LiAlH_4}$

(C) $CH_3NC \xrightarrow{LiAlH_4}$ (D) $CH_3CONH_2 \xrightarrow{LiAlH_4}$

Q.19 When methyl iodide is heated with ammonia, the product obtained is

(A) Methylamine
(B) Dimethylamine
(C) Trimethylamine
(D) A mixture of the above three amines

Q.20 Which of the following gives primary amine on reduction



(A) $CH_3-CH_2-\overset{\overset{O}{\|}}{N}\rightarrow O$ (B) $CH_3-CH_2-O-N=O$

(C) $CH_3CH_2NO_3$ (D) None of these

Q.21 A primary amine is formed from an amide by the treatment of bromine and alkali. The primary amine has –

(A) 1 carbon atom less than amide
(B) 1 carbon atom more than amide
(C) 1 hydrogen atom less than amide
(D) 1 hydrogen atom more than amide

Q.22 Which of the following amines can be prepared by Gabriel synthesis?

I. Isobutyl amine II. 2-phenylethylamine
III. N-methylbenzylamine IV. Aniline
(A) Only I and II (B) Only II and III
(C) Only III and IV (D) Only I and IV

Q.23 The most convenient method to prepare an amine containing one carbon atom less is –

(A) Gabriel phthalimide synthesis
(B) Reductive amination of aldehydes
(C) Hofmann bromamide reaction
(D) Reduction of isonitriles.

Q.24 In order to prepare a 1° amine from an alkyl halide with simultaneous addition of one CH_2 group in the carbon chain, the reagent used as source of nitrogen is –

(A) sodium amide, $NaNH_2$
(B) sodium azide, NaN_3
(C) potassium cyanide, KCN
(D) potassium phthalimide, $C_6H_4(CO)_2N^-K^+$

Q.25 What is the product formed in the given reaction?

$$R\text{-}CONH_2 \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4}$$

(A) RNH_2 (B) RCH_2NH_2
(C) $RCH_2CH_2NH_2$ (D) RCN

Q.26 Reduction of CH_3CH_2NC with hydrogen in presence of Ni or Pt as catalyst gives

(A) $CH_3CH_2NH_2$ (B) $CH_3CH_2NHCH_3$
(C) $CH_3CH_2NHCH_2CH_3$ (D) $(CH_3)_3N$

Q.27 Which of the following statement(s) is/are true about Hofmann bromamide reaction?

(A) In this reaction, migration of an alkyl or aryl group takes place from nitrogen atom of amide to the carbonyl carbon.
(B) The amine so formed contains one carbon more than that present in the amide.
(C) It is the degradation reaction.
(D) None of the above.

Q.28 Which of the following amides will give ethylamine on reaction with sodium hypobromide?

(A) Butanamide (B) Propanamite
(C) Acetamide (D) Benzamide

PART - 4 : PHYSICAL AND CHEMICAL PROPERTIES OF AMINES

Q.29 Ethyl amine on heating with CS_2 in presence of $HgCl_2$ forms

(A) C_2H_5NCS (B) $(C_2H_5)_2S$
(C) $(C_2H_5)_2CS$ (D) $C_2H_5(CS)_2$

Q.30 Which of the following reacts with $NaNO_2 + HCl$ to give phenol

(A) $C_6H_5CH_2NHCH_3$ (B) $(CH_3)_2NH$
(C) CH_3NH_2 (D) $C_6H_5NH_2$

Q.31 When aniline is treated with sodium nitrite and hydrochloric acid at $0^{o}C$, it gives

(A) Phenol and N_2 (B) Diazonium salt
(C) Hydrazo compound (D) No reaction takes place

Q.32 Reaction of primary amines with aldehyde yields

(A) Amides (B) Aldimines
(C) Nitriles (D) Nitro compounds

Q.33 When primary amines are treated with HCl, the product obtained is

(A) An alcohol (B) A cyanide
(C) An amide (D) Ammonium salt

Q.34 Which one is weakest base

(A) Ammonia (B) Methylamine
(C) Dimethylamine (D) Trimethylamine

Q.35 Ethyl amine undergoes oxidation in the presence of $KMnO_4$ to form

(A) An acid (B) An alcohol
(C) An aldehyde (D) A nitrogen oxide

Q.36 Among the following compounds nitrobenzene, benzene, aniline and phenol, the strongest basic behaviour in acid medium is exhibited by

(A) Phenol (B) Aniline
(C) Nitrobenzene (D) Benzene

Q.37 The correct order of basicity of amines in water is :

(A) $(CH_3)_2NH > (CH_3)_3N > CH_3NH_2$
(B) $CH_3NH_2 > (CH_3)_2NH > (CH_3)_3N$
(C) $(CH_3)_3N > (CH_3)_2NH > CH_3NH_2$
(D) $(CH_3)_3N > CH_3NH_2 > (CH_3)_2NH$

Q.38 Product obtained by electrolytic reduction of nitrobenzene in presence of H_2SO_4 is

(A) o-amino phenol (B) m-amino phenol
(C) p-amino phenol (D) None of these

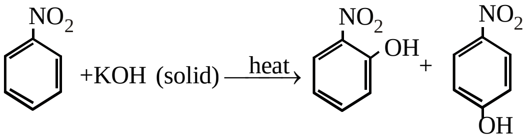
Q.39 The correct order of basicity in amines

(i) $C_4H_5NH_2$ (ii) CH_3NH_2
(iii) $(CH_3)_2NH$ (iv) $(CH_3)_3NH$
(A) (i) < (iv) < (ii) < (iii) (B) (iv)< (iii) < (ii) < (i)
(C) (i) < (ii) < (iii) < (iv) (D) (ii)< (iii) < (iv) < (i)

Q.40 Which of the following would be most reactive towards nitration

(A) Benzene (B) Nitro benzene
(C) Toluene (D) Chloro benzene

Q.41 The following reaction is



(A) Nucleophilic substitution
(B) Electrophilic substitution
(C) Free radical substitution
(D) None of these

Q.42 Which of the following reactions is not correctly matched?

(A) Hofmann bromamide reaction : Reaction used to convert amide into primary amine with one carbon atom less
(B) Carbylamine reaction : Reaction used to convert primary amines into isocyanides.
(C) Hinsberg's reaction : Reaction used to distinguish primary, secondary and tertiary amines.
(D) Victor Meyer's synthesis : Preparation of primary amines using phthalimide.

Q.43 Aniline is more stable than anilinium ion because aniline has _____ resonating structure.

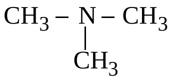
(A) 2 (B) 4
(C) 5 (D) 6

Q.44 Tertiary amines have lowest boiling points amongst isomeric amines because –

(A) they have highest molecular mass.
(B) they do not form hydrogen bonds.
(C) they are more polar in nature.
(D) they are most basic in nature.

Q.45 Which of the following is amphoteric in nature?

(A) CH_3NH_2 (B) CH_3NHCH_3
(C) CH_3CONH_2 (D)



$CH_3-\underset{\displaystyle CH_3}{\underset{|}{N}}-CH_3$

Q.46 Amines are reactive because –

(A) of the difference in the electronegativity between nitrogen and hydrogen atoms.
(B) of the presence of unshared pair of electrons over the nitrogen atom.
(C) Both (A) and (B)
(D) None of the above

Q.47 Which of the following reaction(s) is/are electrophilic substitution?

(A) Bromination of aniline (B) Nitration of aniline
(C) Sulphonation of aniline (D) All of the above

Q.48 n-Butylamine (I), diethylamine (II) and N, N-dimethylethyl amine (III) have the same molar mass. The increasing order of their boiling point is

(A) III < II < I (B) I < II < III
(C) II < III < I (D) II < I < III

Q.49 Primary amines react with benzoyl chloride to give –

(A) benzamides (B) ethanamides
(C) imides (D) imines

Q.50 Which of the following is used as Hinsberg's reagent?

(A) $C_6H_5SO_2Cl$ (B) $C_6H_5SO_3H$
(C) $C_6H_5NHCH_3$ (D) $C_6H_5COCH_3$

Q.51 Which of the following factor(s) affect the basic strength of amines?

(A) Solvation effect (B) Inductive effect
(C) Steric hindrance (D) All of these

Q.52 Which of the following statement(s) is/are true about amines?

(A) Amine salts are soluble in ether but insoluble in water.
(B) Amines have an unshared pair of electrons on nitrogen atom due to which they behave as Lewis acid.
(C) Basic character of amines can be understood in terms of their K_b and pK_b values.
(D) All of the above

Q.53 The decreasing order of boiling points of ethyldimethylamine, n-butylamine and diethylamine is n-Butylamine > Diethylamine > Ethyldimethylamine. This trend of boiling point can be explained as

(A) boiling point increases with increase in molecular mass.
(B) tertiary amines have highest boiling point due to highest basicity.
(C) intermolecular hydrogen bonding is maximum in primary amines and absent in tertiary amines.
(D) intramolecular hydrogen bonding is present in tertiary amines.

Q.54 Which of the following compounds reacts with $NaNO_2$ & HCl at 0-4°C to give alcohol/phenol?

(A) $C_6H_5NH_2$ (B) $C_2H_5NH_2$
(C) CH_3NHCH_3 (D) $C_6H_5NHCH_3$

Q.55 For nitration of aniline, which of the following steps is followed?

(A) Direct nitration using nitrating mixture (conc. HNO_3 + conc. H_2SO_4) followed by oxidation.
(B) Using fuming HNO_3 carrying out reaction at 273 K followed by hydrolysis.
(C) Using $NaNO_2$ and HCl followed by reaction with conc. HNO_3 followed by hydrolysis.
(D) Acetylation followed by nitration and hydrolysis.

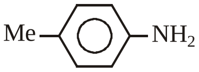
Q.56 Which of the following statement(s) is/are true?

(A) Primary and secondary amines react with acid chlorides anhydrides and esters by nucleophilic substitution reaction. This reaction is known as acylation.
(B) In the acylation reaction of amines there is replacement of hydrogen atom of NH_2 or NH group by the acyl group.
(C) The products obtained by acylation reaction in amines are known as amides.
(D) All of the above

PART - 5 : IDENTIFICATION OF AMINES

Q.57 Primary amines can be distinguished from secondary and tertiary amines by reacting with
(A) Chloroform and alcoholic KOH (B) Methyl iodide
(C) Chloroform alone (D) Zinc dust

Q.58 p-chloro aniline and anilinium hydrogen chloride can be distinguished by
(A) Sandmaeyer reaction (B) Carbyl amine reaction
(C) Hinsberg's reaction (D) $AgNO_3$

Q.59 Which amine amongst the following will answer positively the carbylamine test (i.e., heating with $CHCl_3$ and KOH) ?
(A) $C_6H_5-NH-CH_3$
(B) 

(C) $C_6H_5-NH-C_4H_9$ (D) $C_6H_5-N(C_2H_5)_2$

Q.60 Which of the following compounds cannot be identified by carbylamine test?
(A) $CH_3CH_2NH_2$ (B) $(CH_3)_2CHNH_2$
(C) $C_6H_5NH_2$ (D) $C_6H_5NHC_6H_5$

PART - 6 : CYANIDES AND ISOCYANIDES

Q.61 Allyl isocyanide has –
(A) 9 sigma bonds and 4 pi bonds.
(B) 8 sigma bonds and 5 pi bonds.
(C)8 sigma bonds, 3pi bonds & 4 non-bonding electrons.
(D)9 sigma bonds, 3 pi bonds & 2 non-bonding electrons.

Q.62 KCN reacts readily to give a cyanide with
(A) Ethyl alcohol (B) Ethyl bromide
(C) Bromobenzene (D) Chlorobenzene

Q.63 The alkyl cyanides when hydrolysed to the corresponding acid, the gas evolved is–
(A) N_2 (B) O_2
(C) NH_3 (D) CO_2

Q.64 Which one of the following will give a primary amine on hydrolysis
(A) Nitroparaffin (B) Alkyl cyanide
(C) Oxime (D) Alkyl isocyanide

Q.65 Reduction of methyl isocyanide gives
(A) Ethylamine (B) Methylamine
(C) Dimethylamine (D) Trimethylamine

Q.66 An isocyanide on hydrolysis gives
(A) An amide
(B) A carboxylic acid and ammonia
(C) A N-substituted amide
(D) A 1°-amine and formic acid

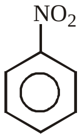
Q.67 Which of the following compound reacts with chloroform and a base to form phenyl isocyanide?
(A) Phenol (B) Aniline
(C) Benzene (D) Nitro benzene

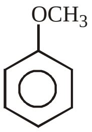
PART - 7 : DIAZONIUM SALTS

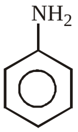
Q.68 The colour of p-amino azobenzene is
(A) Orange (B) Congo red
(C) Bismark brown (D) Indigo

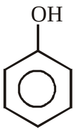
Q.69 Diazo-coupling is useful to prepare some
(A) Dyes (B) Proteins
(C) Pesticides (D) Vitamins

Q.70 The compound which is most reactive towards diazocoupling with benzene diazonium chloride is

(A) 

(B) 

(C) 

(D) 

Q.71 Coupling of diazo salt with phenol is most favourable in
(A) Acidic solution (B) Neutral solution
(C) Basic medium (D) Same in all

Q.72 Benzenediazonium chloride is a name of
(A) $C_6H_5Cl^-$ (B) $C_6H_5N_2^+Cl^-$
(C) $C_6H_5N_2^+$ (D) $C_6H_5NH_2$

Q.73 "Diazonium salts also form the complexes with metallic salts such as zinc chloride".
What is the correct structure of the complex?
(A) $(ArN_2^+)_2ZnCl_4$ (B) $ArN_2^+ZnCl_4^-$
(C) $(ArN_2^+)_2ZnCl_4^{2-}$ (D) $ArN_2^+ZnCl_2^-$

Q.74 Benzenediazonium chloride cannot be stored and is used immediately after its preparation because
(A) it slowly evaporates on storage.
(B) it is very unstable and dissociates to give nitrogen.
(C) it gets oxidised in air hence cannot be stored
(D) it reacts with all the containers in which it is stored.

Q.75 The diazotisation of two feebly basic aromatic amines is achieved by using
(A) sulphuric acid (B) nitrosyl-sulphuric acid
(C) nitrous acid (D) nitrosyl-hydrochloric acid

Q.76 The coupling reaction of aryldiazonium chloride with aniline are carried out in
(A) strongly acidic medium. (B)strongly basic medium.
(C) mild basic medium. (D) mild acidic medium.

Q.77 The reaction,

$$ArN_2^{\oplus}X^- \xrightarrow{CuCN/KCN} ArCN + N_2 \text{ is named as}$$

(A) Sandmeyer reaction (B) Gattermann reaction
(C) Claisen reaction (D) Carbylamine reaction

PART - 8 : USES OF AMINES

Q.78 Diazonium salts are intermediates in the preparation of a variety of aromatic compounds including __.
(A) oils (B) dye
(C) Fats (D) All of these

Q.79 I. Diazonium salts are very good intermediates for the introduction of F, Cl, Br, I, CN, OH, NO_2 groups into the aromatic ring.
II. Aryl fluorides and iodides can be prepared by direct halogenation.
III. Cyano group can be introduced by nucleophilic substitution of chlorine in chlorobenzene.
IV. The replacement of diazo group by other groups is helpful in preparing those substituted aromatic compounds which cannot be prepared by direct substitution in benzene or substituted benzene.
Select the correct statements.
(A) Only I and II (B) Only II and III
(C) Only III and IV (D) Only I and IV

EXERCISE - 2 [LEVEL-2]

Choose one correct response for each question.

Q.1 The amines are basic in nature, hence they form salts with hydrochloric acid. Which of the following will be insoluble in dil. HCl ?

(A) $C_6H_5NH_2$ (B) $(C_6H_5)_3N$
(C) $C_2H_5NH_2$ (D) CH_3NHCH_3

Q.2 Identify X, Y and Z in the given reaction:

$$CH_2 = CH_2 \xrightarrow[CCl_4]{Br_2} X \xrightarrow[(2\text{ moles})]{NaCN} Y \xrightarrow{LiAlH_4} Z$$

(A) $X = CH_2Br–CH_2Br$, $Y = CH_3CH_2CH_2CN$
$Z = CH_3CH_2CH_2CH_2NH_2$
(B) $X = CH_2Br – CH_2Br$, $Y = CH_3CH_2CN$
$Z = CH_3CH_2CH_2NH_2$
(C) $X = CH_3CH_2Br$, $Y = CH_3CH_2CN$, $Z = CH_3CH_2CH_2NH_2$
(D) $X = CH_2Br – CH_2Br$, $Y = NCCH_2CH_2CN$
$Z = H_2NCH_2CH_2CH_2CH_2NH_2$

Q.3 Which of the following reagents would not be a good choice for reducing an aryl nitro compound to an amine?

(A) $H_{2(excess)}$ / Pt (B) $LiAlH_4$ in ether
(C) Fe and HCl (D) Sn and HCl

Q.4 Which of the following methods of preparation of amines will not give same number of carbon atoms in the chain of amines as in the reactant?

(A) Reaction of nitrite with $LiAlH_4$.
(B) Reaction of amide with $LiAlH_4$ followed by treatment with water.
(C) Heating alkyl halide with potassium salt of phthalimide followed by hydrolysis.
(D) Treatment of amide with bromine in aqueous solution of sodium hydroxide.

Q.5 Which of the following amines will give carbylamine reaction?

(A) $(C_2H_5)_3N$ (B) $(C_2H_5)_2NH$
(C) $C_2H_5NH_2$ (D) $C_3H_7NHC_2H_5$

Q.6 Acetylation of a secondary amine in alkaline medium yields

(A) N, N-dialkyl acetamide (B) N, N-dialkyl amine
(C) N, N-dialkyl amide (D) acetyl dialkyl amine

Q.7 Aniline can be converted into benzylamine by which of the following processes in sequence?

(A) $NaNO_2 + HCl$, CuCN, H_2/Ni
(B) Br_2/CCl_4, KCN, $LiAlH_4$
(C) HNO_2, $K_2Cr_2O_7/H^+$, Sn + HCl
(D) CH_3OH, $KMnO_4$, $OH^–$, H_3O^+

Q.8 Name the product(s) formed during the reactions of primary aliphatic amines with nitrous acid at room temperature?

(A) $RN_2^+Cl^–$ (B) ROH
(C) Both (A) and (B) (D) None of these

Q.9 The reactions of diazonium salts can be divided into the categories based on the –

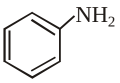
(A) reactions involving displacement of nitrogen.
(B) reactions involving retention of diazo group.
(C) Both (A) and (B)
(D) None of the above

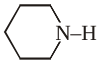
Q.10 Identify the correct pathway to convert propanoic acid to ethylamine. The reagent represented by A, B & C are

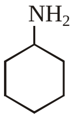
$$CH_3CH_2COOH \xrightarrow{A} X \xrightarrow{B} Y \xrightarrow{C} CH_3CH_2NH_2$$

(A) A-$Ca(OH)_2$, B-Heat, C-Pt/H_2
(B) A-$SOCl_2$, B-NH_3, C-Br_2/KOH
(C) A-HNO_2, B-P + I_2, C-$LiAlH_4$
(D) A-HCN, B-NH_3, C-Br_2/KOH

Q.11 Which of the following is the weakest Bronsted base?

(A) 

(B) 

(C) 

(D) CH_3NH_2

Q.12 What would be the side products formed with primary amine in the Hoffmann bromamide degradation reaction?

(A) $Na_2CO_3 + NaBr$ (B) $NaBr + H_2O + NaOH$
(C) $NaBr + H_2O + Na_2CO_3$ (D) $Br_2 + H_2O + Na_2CO_3$

Q.13 Electrophilic substitution of aniline with bromine water at room temperature gives

(A) 2-bromoaniline (B) 3-bromoaniline
(C) 2,4, 6-tribromoaniline (D) 3,5, 6-tribromoaniline.

Q.14 The Hinsberg test of a compound, $C_5H_{14}N_2$ produces a solid that is insoluble in 10% aq. NaOH. This solid derivative dissolves in 10% aqueous sulphuric acid. Which of the following would best describe these facts?

(A) $NH_2CH_2CH_2N(CH_3)_2$
(B) $(CH_3)_2NCH_2CH_2NHCH_3$
(C) $NH_2CH_2C(CH_3)_2CH_2NH_2$
(D) $(CH_3)_2NCH_2N(CH_3)_2$

Q.15 Secondary amines can be prepared by

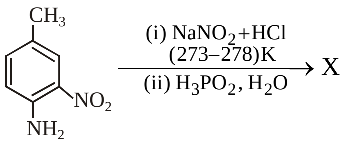
(A) Reduction of nitro compounds
(B) Reduction of amides
(C) Reduction of isonitriles
(D) Reduction of nitriles.

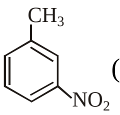
Q.16 The correct decreasing order of basic strength of the following species is –

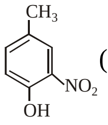
H_2O, NH_3, $OH^–$, $NH_2^–$

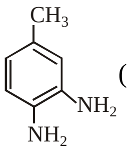
(A) $NH_2^– > OH^– > NH_3 > H_2O$
(B) $OH^– > NH_2^– > H_2O > NH_3$
(C) $NH_3 > H_2O > NH_2^– > OH^–$
(D) $H_2O > NH_3 > OH^– > NH_2^–$

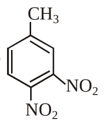
Q.17 The structure of product X in the following reaction is



(A) 

(B) 

(C) 

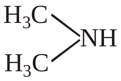
(D) 

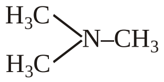
Q.18 The correct order of increasing boiling points for the bases, CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$ is –

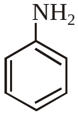
(A) $CH_3NH_2 < (CH_3)_2NH < (CH_3)_3N$
(B) $CH_3NH_2 < (CH_3)_3N < (CH_3)_2NH$
(C) $(CH_3)_3N < (CH_3)_2NH < CH_3NH_2$
(D) $(CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$

Q.19 The most reactive amine towards dilute hydrochloric acid is –

(A) CH_3-NH_2

(B)


(C)


(D)


Q.20 Benzenediazonium chloride decomposes easily in the –

(A) cold state
(B) warm state
(C) dry state
(D) humid state

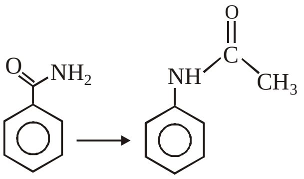
Q.21 Choose the incorrect statement.

(A) Primary amines show intermolecular hydrogen bonds.
(B) tert-Butylamine is a primary amine.
(C) Tertiary amines do not show intermolecular hydrogen bonds.
(D) Isopropylamine is a secondary amine.

Q.22 Primary, secondary and tertiary amines may be separated by using

(A) iodoform
(B) diethyloxalate
(C) benzene sulphonyl chloride
(D) acetyl chloride

Q.23 The reagent required to convert



(A) KOH/Br_2, $LiAlH_4$
(B) KOH/Br_2, CH_3COCl
(C) HNO_2, $(CH_3CO)_2O$
(D) KOH/Br_2, CH_3OH/Na

Q.24 Reduction of aromatic nitro compounds using Sn and HCl gives

(A) aromatic primary amines
(B) aromatic secondary amines
(C) aromatic tertiary amines
(D) aromatic amides.

Q.25 When excess of ethyl iodide is treated with ammonia, the product is –

(A) ethylamine
(B) diethylamine
(C) triethylamine
(D) tetraethylammonium iodide

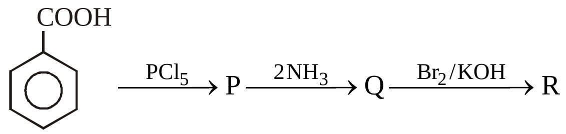
Q.26 The order of basic strength among the following amines in benzene solution is

(A) $CH_3NH_2 > (CH_3)_3N > (CH_3)_2NH$
(B) $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N$
(C) $CH_3NH_2 > (CH_3)_2NH > (CH_3)_3N$
(D) $(CH_3)_3N > CH_3NH_2 > (CH_3)_2NH$

Q.27 The gas evolved when methylamine reacts with nitrous acid is –

(A) NH_3
(B) N_2
(C) H_2
(D) C_2H_6

Q.28 What is the end product in the following sequence of reactions?



(A) Aniline
(B) Phenol
(C) Benzene
(D) Benzenediazonium chloride

Q.29 How the nitrous acid is produced?

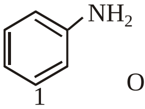
(A) It is produced by the reaction of sodium nitrite with HCl.
(B) It is produced by the reaction of sodium nitrate with HCl.
(C) It is produced by the reaction of sodium nitrite with HCN.
(D) None of the above.

Q.30 Which of the following species are involved in the carbylamine test?

(i) RNC
(ii) $CHCl_3$
(iii) $COCl_2$
(iv) $NaNO_2 + HCl$

(A) (i) and (iv)
(B) (i) and (ii)
(C) (ii) and (iv)
(D) (ii) and (iii)

Q.31 The correct order of increasing basic nature of the following bases is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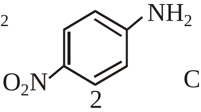
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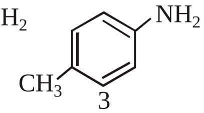
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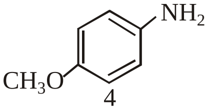
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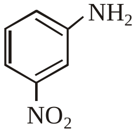
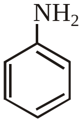
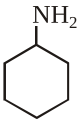
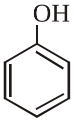

5

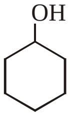
(A) $2 < 5 < 1 < 3 < 4$
(B) $5 < 2 < 1 < 3 < 4$
(C) $2 < 5 < 1 < 4 < 3$
(D) $5 < 2 < 1 < 4 < 3$

Q.32 Which of the following compounds is the weakest Bronsted base?

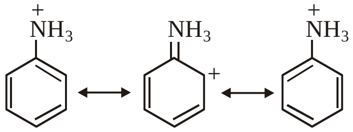
(A)


(B)


(C)


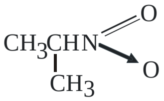
(D)


Q.33 Canonical structures of anilinium ion obtained by accepting a proton are given below. Choose the correct statements.



I II III

(A) Anilinium ion has two stable canonical structures I and III.
(B) II is not an acceptable structure because carbonium ion is less stable.
(C) Only I and III are acceptable aromatic canonical structures since II is non-aromatic.
(D) Anilinium ion has three stable canonical structures I, II and III.

Q.34 Which of the following is not a nitro-derivative
(A) $C_6H_5NO_2$ (B) CH_3CH_2ONO
(C)  $CH_3\underset{CH_3}{CH}N(=O)\rightarrow O$ (D) $C_6H_4(OH)NO_2$

Q.35 Acetonitrile is –
(A) C_2H_5CN (B) CH_3CN
(C) CH_3COCN (D) $C_6H_5CH_2CN$

Q.36 Number of isomeric primary amines obtained from $C_4H_{11}N$ are –
(A) 3 (B) 4
(C) 5 (D) 6

Q.37 Reaction $CH_3CONH_2 \xrightarrow{NaOBr}$ gives
(A) CH_3Br (B) CH_4
(C) CH_3COBr (D) CH_3NH_2

Q.38 Acetamide is treated separately with the following reagents. Which would give methyl amine –
(A) PCl_5 (B) $NaOH + Br_2$
(C) Sodalime (D) Hot conc. H_2SO_4

Q.39 Chloropicrin is manufactured by the reaction between Cl_2, NaOH and
(A) Nitromethane (B) Nitroethane
(C) Nitrophenol (D) Nitrostyrene

Q.40 $CH_3NO_2 \xrightarrow{Sn+HCl} CH_3X$, the 'X' contain
(A) $-NH_2$ (B) $-COOH$
(C) $-CHO$ (D) $(CH_3CO)_2O$

Q.41 For the preparation of p-nitroiodobenzene from p-nitroaniline, the best method is –
(A) $NaNO_2$/HCl followed by KI
(B) $NaNO_2$/HCl followed by CuCN
(C) $LiAlH_4$ followed by I_2
(D) $NaBH_4$ followed by I_2

Q.42 Aniline when treated with HNO_2 and HCl at 0°C gives
(A) Phenol (B) Nitrobenzene
(C) A diazo compound (D) None of these

Q.43 Which amines would undergo diazotisation
(A) Primary aliphatic amines
(B) Primary aromatic amines
(C) Both (A) and (B)
(D) None of these

Q.44 The maximum number of $-NO_2$ groups that can be introduced by nitration in benzene is usually
(A) 4 (B) 2
(C) 3 (D) 6

Q.45 The compound which on reaction with aqueous nitrous acid on HNO_2 at low temperature produces an oily nitrosoamine is
(A) Diethylamine (B) Ethylamine
(C) Aniline (D) Methylamine

Q.46 Which of the following is not used as an explosive
(A) Trinitrotoluene (B) Trinitrobenzene
(C) Picric acid (D) Nitrobenzene

Q.47 Nitrobenzene on further excessive nitration gives
(A) Trinitrobenzene (B) m-dinitrobenzene
(C) p-dinitrobenzene (D) All of these

Q.48 Amides may be converted into amines by reaction
(A) Perkin (B) Claisen
(C) Hoffmann (D) Kolbe

Q.49 $CH_3CN \xrightarrow{Na+C_2H_5OH} X$. The compound X is
(A) CH_3CONH_2 (B) $CH_3CH_2NH_2$
(C) C_2H_6 (D) CH_3NHCH_3

Q.50 In the reaction

$$CH_3COOH \xrightarrow{PCl_5} (A) \xrightarrow{NH_3} (B) \xrightarrow{NaBrO} (C).$$

the final product (C) is
(A) Ammonium acetate (B) Acetamide
(C) Amino methane (D) Ethanal

Q.51 Nitrobenzene combines with hydrogen in the presence of platinum to produce –
(A) Toluene (B) Benzene
(C) Aniline (D) Azobenzene

Q.52 Secondary nitro compounds when react with HNO_2 forms crystalline solids which one on treatment with NaOH gives
(A) Red solution (B) Blue solution
(C) White precipitate (D) Yellow colouration

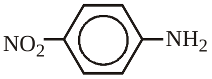
Q.53 The end product of the reactions is

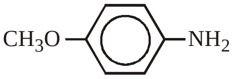
$$C_2H_5NH_2 \xrightarrow{HNO_2} A \xrightarrow{PCl_5} B \xrightarrow{H.NH_2} C$$

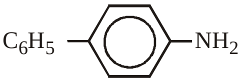
(A) Ethyl cyanide (B) Ethyl amine
(C) Methyl amine (D) Acetamide

Q.54 The reaction of HNO_2 with 'A' gives quaternary ammonium salt. A is
(A) Methyl amine (B) Dimethyl amine
(C) Trimethyl amine (D) Aniline

Q.55 Which one is less alkaline

(A) 

(B) 

(C) 

(D) All of these

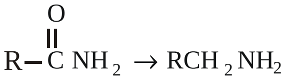
Q.56 Ethyl amine on acetylation gives
(A) N-ethyl acetamide (B) Acetamide
(C) Methyl acetamide (D) None

Q.57 When acetamide reacts with Br_2 and caustic soda, then we get :
(A) Acetic acid (B) Bromoacetic acid
(C) Methyl amine (D) Ethyl amine

Q.58 A positive carbylamine test is given by
(A) N, N-dimethylaniline (B) 2, 4-dimethylaniline
(C) N-methyl-o-methylaniline (D) p-methylbenzylamine

Q.59 The refluxing of $(CH_3)_2NCOCH_3$ with acid gives
(A) $2CH_3NH_2 + CH_3COOH$
(B) $2CH_3OH + CH_3COOH$
(C) $(CH_3)_2NH + CH_3COOH$
(D) $(CH_3)_2NCOOH + CH_4$

Q.60 Which reducing agents is likely to be the most effective in bringing about the following change

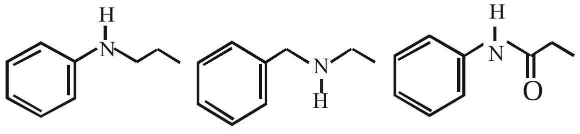


$$R-\overset{\overset{O}{\|}}{C}NH_2 \rightarrow RCH_2NH_2$$

(A) H_2–Ni (B) $NaBH_4$
(C) $LiAlH_4$ (D) Na-alcohol

Q.61 Nitroso amines ($R_2N-N=O$) are soluble in water. On heating them with concentrated H_2SO_4 they give secondary amines. The reaction is called
(A) Perkin's reaction
(B) Fittig's reaction
(C) Sandmeyer's reaction
(D) Liebermann's nitroso reaction

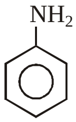
Q.62 Which of the following compound is most basic



(a) (b) (c)
(A) (a) (B) (b)
(C) (c) (D) All are equally basic

Q.63 $R-NH-COH \xrightarrow[\text{pyridine}]{POCl_3}$ product

In the given reaction what will be the product
(A) $R-N=C=O$ (B) $R-\overset{+}{N}\equiv C^{-}$
(C) $R-C\equiv N$ (D) None of these.

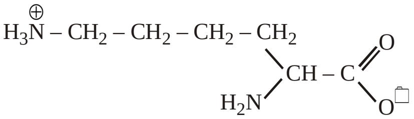
Q.64  $+ CHCl_3 + KOH \rightarrow ?$

(A) Phenyl isocyanide (B) Benzyl amine
(C) Benzyl chloride (D) None of these

EXERCISE - 3 (NUMERICAL VALUE BASED QUESTIONS)

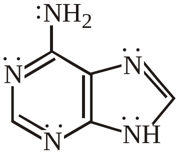
NOTE : The answer to each question is a NUMERICAL VALUE.

Q.1 The total number of basic groups in the following form of lysine is :



Q.2 The total number of lone-pairs of electrons in melamine is

Q.3 Active basic sites are available in purine is,



Q.4 If a molecule R – CN is reduced to $RCH_2 - NH_2$, the percentage of s-character change in the hybrid orbital of carbon is –

Q.5 Find the total number of correct statements.

(a) 1° Amines are formed on heating carbonyl compounds with ammonia formate or formamide. The reaction involve reductive amination.

(b) Isocyanates are formed by dehydrative rearrangement of hydroxamic acids. Hydrolysis of Isocyanate then gives 1° amines.

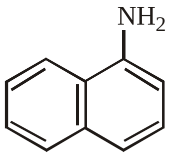
(c) b.p. of 1° amine < 2° amine < 3° amine

(d) Primary aliphatic amine on oxidation with $KMnO_4$ followed by hydrolysis give aldehydes and ketones.

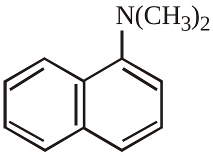
(e) Secondary aliphatic amines on oxidation with $KMnO_4$ give tetra alkyl hydrazine.

Q.6 Number of primary amines in the structures are –

(i)



(ii)



(iii) $(C_2H_5)_2CHNH_2$

(iv) $(C_2H_5)_2NH$

Q.7 Write the number of correct order in given statements :

(a) Decreasing order of the pK_b values :
$C_6H_5NH_2 < C_6H_5NHCH_3 < C_2H_5NH_2 < (C_2H_5)_2NH$

(b) Increasing order of basic strength :
$(C_2H_5)_2NH > CH_3NH_2 > C_6H_5NH(CH_3)_2 > C_6H_5NH_2$

(c) Increasing order of basic strength :
Aniline < p-nitroaniline < p-toluidine

(d) Increasing order of basic strength :
$C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$

(e) Decreasing order of the basic strength in gas phase
$(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$

(f) Increasing order of boiling point :
$C_2H_5OH < C_2H_5NH_2 < (CH_3)_2NH$

(g) Increasing order of solubility in water :
$C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2$

EXERCISE - 4 [PREVIOUS YEARS JEE MAIN QUESTIONS]

Q.1 Reaction : Primary amine + $CHCl_3$ + KOH → product, here product will be - **[AIEEE-2002]**

(A) Cyanide (B) Isocyanide
(C) Amine (D) Alcohol

Q.2 The compound formed in the positive test for nitrogen with the Lassaigne solution of an organic compound is **[AIEEE-2004]**

(A) $Fe_4[Fe(CN)_6]_3$ (B) $Na_3[Fe(CN)_6]$
(C) $Fe(CN)_3$ (D) $Na_4[Fe(CN)_5NOS]$

Q.3 Which one of the following methods is neither meant for the synthesis nor for separation of amines **[AIEEE-2005]**

(A) Hofmann method (B) Hinsberg method
(C) Curtius reaction (D) Wurtz reaction

Q.4 Reaction of cyclohexanone with dimethylamine in the presence of catalytic amount of an acid forms a compound if water during the reaction is continuously removed. The compound formed is generally known as **[AIEEE-2005]**

(A) an enamine (B) a Schiff's base
(C) an amine (D)an imine

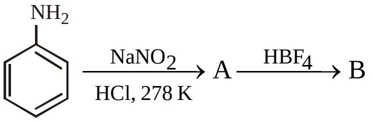
Q.5 In the chemical reaction,
$CH_3CH_2NH_2 + CHCl_3 + 3KOH \rightarrow A + B + 3H_2O$,
the compounds A and B are respectively **[AIEEE-2007]**

(A) C_2H_5CN and 3KCl (B) $CH_3CH_2CONH_2$ and 3KCl
(C) C_2H_5NC and K_2CO_3 (D) C_2H_5NC and 3KCl

Q.6 Toluene is nitrated and the resulting product is reduced with tin and hydrochloric acid. The product so obtained is diazotised and then heated with cuprous bromide. The reaction mixture so formed contains **[AIEEE-2008]**

(A) mixture of o– and p-dibromobenzenes
(B) mixture of o- and p-bromoanilines
(C) mixture of o- and m-bromotoluenes
(D) mixture of o- and p-bromotoluenes

Q.7 In the chemical reactions,



[AIEEE 2010]

the compounds 'A' and 'B' respectively are
(A) nitrobenzene and fluorobenzene
(B) phenol and benzene
(C) benzene diazonium chloride and fluorobenzene
(D) nitrobenzene and chlorobenzene

Q.8 A compound with molecular mass 180 is acylated with CH_3COCl to get a compound with molecular mass 390. The number of amino groups present per molecule of the former compound is – **[JEE MAIN 2013]**

(A) 2 (B) 5 (C) 4 (D) 6

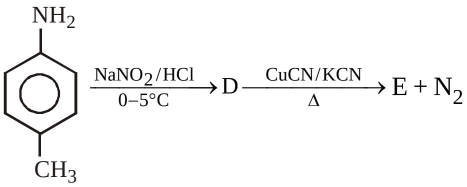
Q.9 On heating an aliphatic primary amine with chloroform and ethanolic potassium hydroxide, the organic compound formed is – **[JEE MAIN 2014]**

(A) an alkyl cyanide (B) an alkyl isocyanide
(C) an alkanol (D) an alkanediol

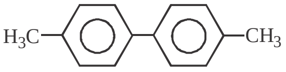
Q.10 Considering the basic strength of amines in aqueous solution, which one has the smallest pK_b value? **[JEE MAIN 2014]**

(A) $(CH_3)_3N$ (B) $C_6H_5NH_2$
(C) $(CH_3)_2NH$ (D) CH_3NH_2

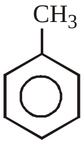
Q.11 In the reaction

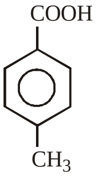


the product E is **[JEE MAIN 2015]**

(A) 

(B) 

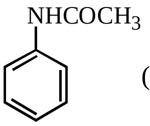
(C) 

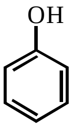
(D) 

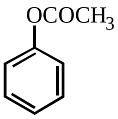
Q.12 In the Hofmann bromamide degradation reaction, the number of moles of NaOH and Br_2 used per mole of amine produced are: **[JEE MAIN 2016]**

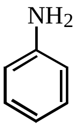
(A) Four moles of NaOH and two moles of Br_2
(B) Two moles of NaOH and two moles of Br_2
(C) Four moles of NaOH and one mole of Br_2
(D) One mole of NaOH and one mole of Br_2

Q.13 Which of the following compounds will form significant amount of meta product during mono-nitration reaction? **[JEE MAIN 2017]**

(A) 

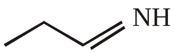
(B) 

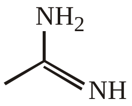
(C) 

(D) 

Q.14 The increasing order of basicity of the following compounds is: **[JEE MAIN 2018]**

(a) 

(b) 

(c) 

(d) 

(A) (b) < (a) < (d) < (c) (B) (d) < (b) < (a) < (c)
(C) (a) < (b) < (c) < (d) (D) (b) < (a) < (c) < (d)

Q.15 The major product of following reaction is :

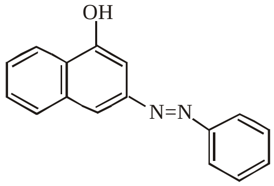
$R-C\equiv N \xrightarrow[\text{(ii) } H_2O]{\text{(i) } AlH(i-Bu_2)} ?$ **[JEE MAIN 2019 (Jan)]**

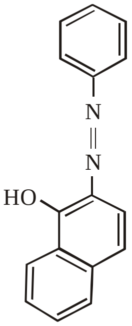
(A) RCHO (B) RCOOH
(C) RCH_2NH_2 (D) $RCONH_2$

Q.16 In the following compounds, the decreasing order of basic strength will be - **[JEE MAIN 2019 (April)]**

(A) $(C_2H_5)_2NH > C_2H_5NH_2 > NH_3$
(B) $(C_2H_5)_2NH > NH_3 > C_2H_5NH_2$
(C) $NH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$
(D) $C_2H_5NH_2 > NH_3 > (C_2H_5)_2NH$

Q.17 Coupling of benzene diazonium chloride with 1-napthol in alkaline medium will give **[JEE MAIN 2019 (April)]**

(A)


(B)


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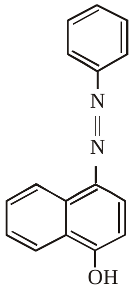

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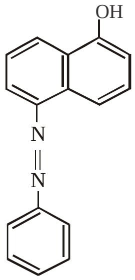
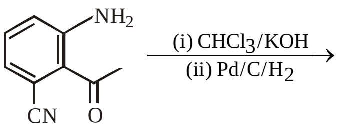


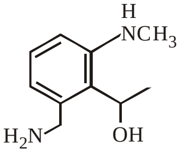
Q.18 Which of the following amines can be prepared by Gabriel phthalimide reaction ? **[JEE MAIN 2019 (April)]**

(A) Neo-pentylamine (B) n-butylamine
(C) triethylamine (D) t-butylamine

Q.19 The major product obtained in the following reaction is



[JEE MAIN 2019 (APRIL)]

(A)


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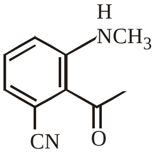

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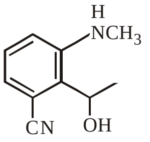
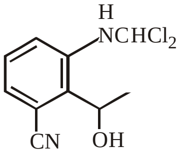
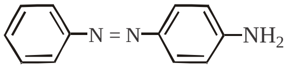
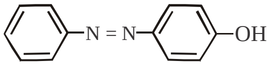


(D)


Q.20 Aniline dissolved in dilute HCl is reacted with sodium nitrite at 0°C. This solution was added dropwise to a solution containing equimolar mixture of aniline and phenol in dil. HCl. The structure of the major product is **[JEE MAIN 2019 (APRIL)]**

(A)


(B)


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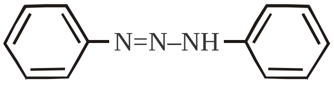

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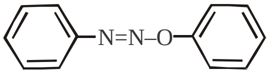
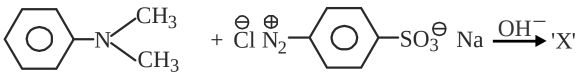


Q.21 Ethylamine ($C_2H_5NH_2$) can be obtained from N-ethylphthalimide on treatment with : **[JEE MAIN 2019 (APRIL)]**

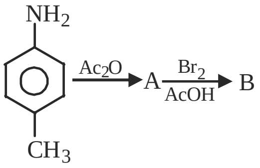
(A) $NaBH_4$ (B) CaH_2
(C) H_2O (D) NH_2NH_2

Q.22


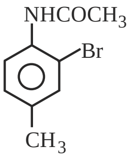
formed product 'X' is used as: **[JEE MAIN 2020 (JAN)]**

(A) Lab test of Phenol
(B) Acid base titration indicator
(C) Food colouring
(D) It can be used as an alternative to detect amino acid in place of ninhydrin.

Q.23 A and B are in the given reaction ?



[JEE MAIN 2020 (JAN)]

(A)


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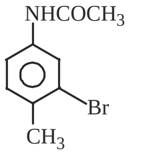
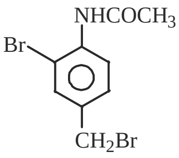
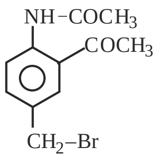
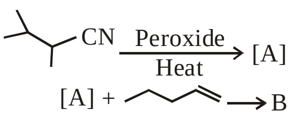


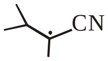
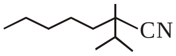
(C)


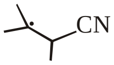
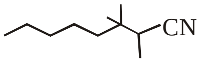
(D)


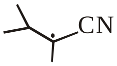
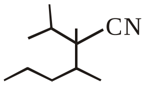
Q.24 The major products A and B in the following reactions are

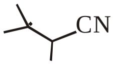
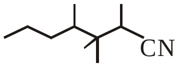


[JEE MAIN 2020 (JAN)]

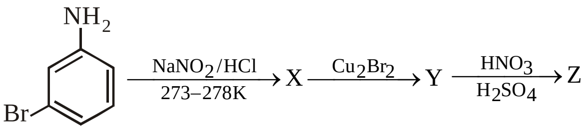
(A) A =  and B = 

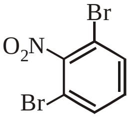
(B) A =  and B = 

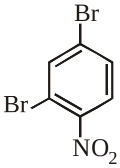
(C) A =  and B = 

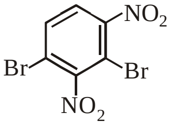
(D) A =  and B = 

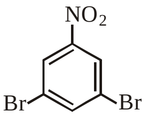
Q.25 The major product Z obtained in the following reaction scheme is : **[JEE MAIN 2020 (JAN)]**



(A) 

(B) 

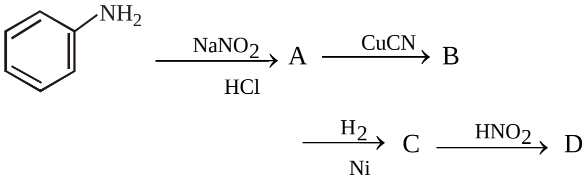
(C) 

(D) 

EXERCISE - 5 [PREVIOUS YEARS AIPMT / NEET QUESTIONS]

Q.1 Electrolytic reduction of nitrobenzene in weakly acidic medium gives – **[AIPMT 2005]**
(A) N-phenylhydroxylamine (B) Nitrosobenzene
(C) Aniline (D) p-Hydroxyaniline

Q.2 Aniline in a set of reactions yield a product D.

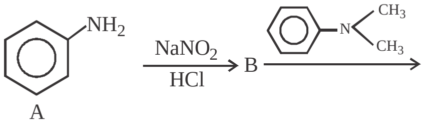


The structure of the product D would be **[AIPMT 2005]**
(A) C_6H_5NHOH (B) $C_6H_5NHCH_2CH_3$
(C) $C_6H_5CH_2NH_2$ (D) $C_6H_5CH_2OH$

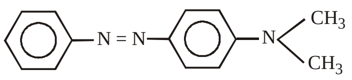
Q.3 Which of the following is more basic than aniline **[AIPMT 2006]**
(A) Triphenylamine (B) p-Nitroaniline
(C) Benzylamine (D) Diphenylamine

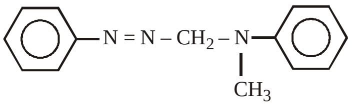
Q.4 Which one of the following on reduction with lithium aluminium hydride yields a secondary amine **[AIPMT 2007]**
(A) Methyl isocyanide (B) Acetamide
(C) Methyl cyanide (D) Nitroethane

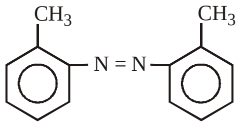
Q.5 In a reaction of aniline a coloured product C was obtained

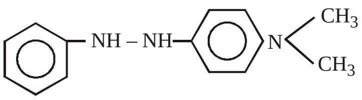


The structure of C would be **[AIPMT 2008, 10]**

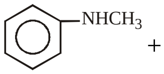
(A) 

(B) 

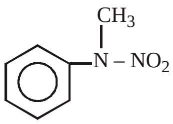
(C) 

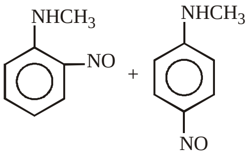
(D) 

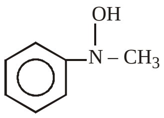
Q.6 Predict the product :

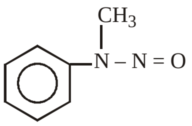


$+ NaNO_2 + HCl \rightarrow$ Product **[AIPMT 2009]**

(A) 

(B) 

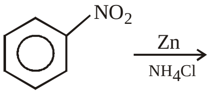
(C) 

(D) 

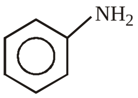
Q.7 Nitrobenzene can be prepared from benzene by using a mixture of conc. HNO_3 and conc. H_2SO_4 in the mixture, nitric acid acts as a/an: **[AIPMT 2009]**
(A) acid (B) base
(C) catalyst (D) reducing agent

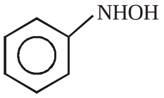
Q.8 Which of the following statements about primary amines is 'False'? **[AIPMT [PRE] 2010]**
(A) Alkyl amines are stronger bases than aryl amines.
(B) Alkyl amines react with nitrous acid to produce alcohols.
(C) Aryl amines react with nitrous acid to produce phenols.
(D) Alkyl amines are stronger bases than ammonia.

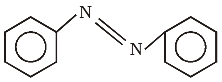
Q.9 What is the product obtained in the following reaction

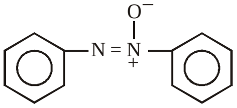


.... ? **[AIPMT [PRE] 2011]**

(A) 

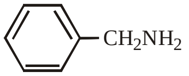
(B) 

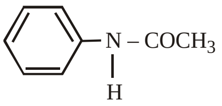
(C) 

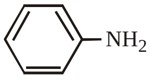
(D) 

Q.10 Which of the following compounds is most basic **[AIPMT [MAINS] 2011]**

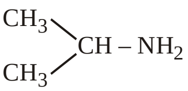
(A) 

(B) 

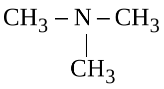
(C) 

(D) 

Q.11 An organic compound (C_3H_9N) 'A', when treated with nitrous acid, gave an alcohol and N_2 gas was evolved. 'A' on warming with $CHCl_3$ and caustic potash gave 'C' which on reduction gave isopropylmethylamine. Predict the structure of 'A'. **[AIPMT [MAINS] 2012]**

(A) 
$(CH_3)_2CH-NH_2$

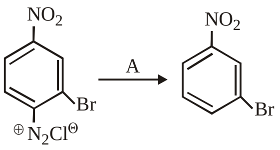
(B) $CH_3CH_2-NH-CH_3$

(C) 
$CH_3-N(CH_3)-CH_3$

(D) $CH_3CH_2\,CH_2-NH_2$

Q.12 Nitrobenzene on reaction with conc. HNO_3/H_2SO_4 at 80-100°C forms which one of the following products ? **[NEET 2013]**
(A) 1, 2, 4-Trinitrobenzene (B) 1, 2-Dinitrobenzene
(C) 1, 3-Dinitrobenzene (D) 1, 4-Dinitrobenzene

Q.13 In the reaction



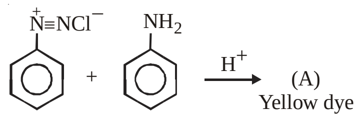
A is

[NEET 2013]

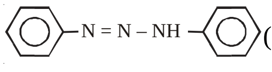
(A) H^+/H_2O (B) $HgSO_4/H_2SO_4$

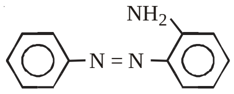
(C) Cu_2Cl_2 (D) H_3PO_2 and H_2O

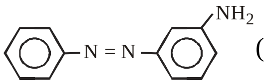
Q.14 In the following reaction, the product (A)

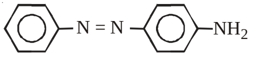


is **[AIPMT 2014]**

(A)


(B)


(C)


(D)


Q.15 Which of the following will be most stable diazonium salt $RN_2^+X^-$? **[AIPMT 2014]**

(A) $CH_3N_2^+X^-$ (B) $C_6H_5N_2^+X^-$

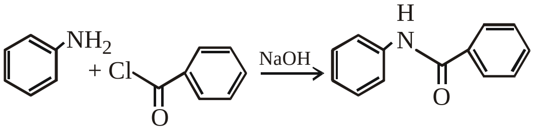
(C) $CH_3CH_2N_2^+X^-$ (D) $C_6H_5CH_2N_2^+X^-$

Q.16 The electrolytic reduction of nitrobenzene in strongly acidic medium produces : **[AIPMT 2015]**

(A) Azoxybenzene (B) Azobenzene

(C) Aniline (D) p-Aminophenol

Q.17 The following reaction



is known by the name : **[RE-AIPMT 2015]**

(A) Acetylation reaction (B) Schotten-Bauman reaction

(C) Friedel Craft's reaction (D) Perkin's reaction

Q.18 Method by which aniline cannot be prepared is **[RE-AIPMT 2015]**

(A) Reduction of nitrobenzene with H_2/Pd in ethanol.

(B) Potassium salt of phthalimide treated with chlorobenzene followed by hydrolysis with aqueous NaOH solution.

(C) Hydrolysis of phenylisocyanide with acidic solution.

(D) Degradation of benzamide with bromine in alkaline solution.

Q.19 The number of structural isomers possible from the molecular formula C_3H_9N is : **[RE-AIPMT 2015]**

(A) 2 (B) 3

(C) 4 (D) 5

Q.20 The correct statement regarding the basicity of arylamines is **[NEET 2016 PHASE-1]**

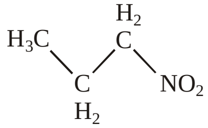
(A) Arylamines are generally less basic than alkylamines because the nitrogen lone-pair electrons are delocalized by interaction with the aromatic ring π electron system.

(B) Arylamines are generally more basic than alkylamines because the nitrogen lone-pair electrons are not delocalized by interaction with the aromatic π electron system.

(C) Arylamines are generally more basic than alkylamines because of aryl group.

(D) Arylamines are generally more basic than alkylamines, because the nitrogen atom in arylamines is sp-hybridized.

Q.21 Which one of the following nitro-compounds does not react with nitrous acid? **[NEET 2016 PHASE-2]**

(A)


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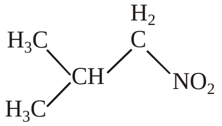

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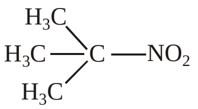

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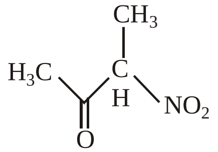
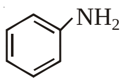


Q.22 A given nitrogen-containing aromatic compound A reacts with Sn/HCl, followed by HNO_2 to give an unstable compound B. B, on treatment with phenol, forms a beautiful coloured compound C with the molecular formula $C_{12}H_{10}N_2O$. The structure of compound A is – **[NEET 2016 PHASE-2]**

(A)


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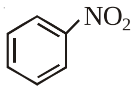

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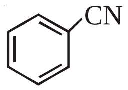
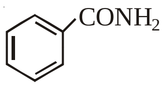
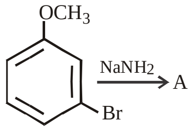
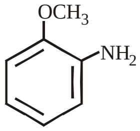


(D)


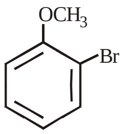
Q.23 Identify A and predict the type of reaction



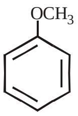
[NEET 2017]

(A)


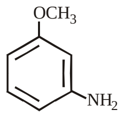
and elimination addition reaction

(B)


and cine substitution reaction

(C)


and cine substituion reaction

(D)


and substitution reaction

Q.24 Nitration of aniline in strong acidic medium also gives m-nitroaniline because **[NEET 2018]**

(A) In absence of substituents nitro group always goes to m-position.

(B) In electrophilic substitution reactions amino group is meta directive.

(C) Inspite of substituents nitro group always goes to only m-position.

(D) In acidic (strong) medium aniline is present as anilinium ion.

Q.25 The correct order of the basic strength of methyl substituted amines in aqueous solution is :**[NEET 2019]**

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

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

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

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

ANSWER KEY

EXERCISE - 1

Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
A	C	D	A	A	B	D	A	D	C	D	D	B	C	C	C	A	C	C	D	A	A	A	C	C	B	B	C	B	A	D
Q	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
A	B	B	D	A	C	B	A	C	A	B	A	D	C	B	C	C	D	A	A	A	D	C	C	B	D	D	A	D	B	D
Q	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79											
A	D	B	C	D	C	D	B	A	A	C	C	B	C	B	C	C	A	B	D											

EXERCISE - 2

Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
A	B	D	B	D	C	A	A	C	C	B	A	C	C	B	C	A	A	C	B	C	D	C	B	A	D	B	B	A	A	B
Q	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
A	A	C	A	B	B	B	D	B	A	A	A	C	B	C	A	D	B	C	B	C	C	B	B	C	A	A	C	B	C	A
Q	61	62	63	64																										
A	D	B	B	A																										

EXERCISE - 3

Q	1	2	3	4	5	6	7
A	2	6	3	50	4	2	5

EXERCISE - 4

Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
A	B	A	D	A	D	D	C	B	B	C	B	C	D	A	A	A	C	B	A	A	D	B	A	A	B

EXERCISE - 5

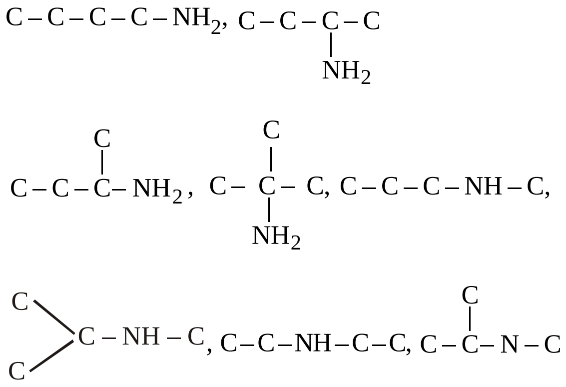
Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
A	C	D	C	A	A	D	B	C	B	B	A	C	D	D	B	D	B	B	C	A	C	B	D	D	A

ORGANIC COMPOUNDS CONTAINING NITROGEN

TRY IT YOURSELF

(1) **(C).** Primary amines give carbylamine test.

(2) **(D).**



$C-C-C-C-NH_2$, $C-C-\underset{NH_2}{C}-C$, $C-C-\overset{C}{C}-NH_2$, $C-\overset{C}{\underset{NH_2}{C}}-C$, $C-C-C-NH-C$, $(C)_2C-NH-C$, $C-C-NH-C-C$, $C-\overset{C}{C}-N-C$

(3) **(C).** $R-CN \xrightarrow{LiAlH_4} R-CH_2-NH_2$

(4) **(C).** $R-\ddot{N}H_2 \xrightarrow{HNO_2} R-OH+N_2+H_2O$

(5) **(D).** $CH_3-CH_2-CH_2-Cl \xrightarrow{KCN}$
$CH_3-CH_2-CH_2-CN+KCl$

(6) **(C).** $C_2H_5NH_2 \xrightarrow{HNO_2} \underset{(A)}{C_2H_5-OH}$

$\xrightarrow{PCl_5} \underset{(B)}{C_2H_5-Cl} \xrightarrow{NH_3} \underset{(C)}{C_2H_5-NH_2}$

(7) **(C).** Secondary amides do not give Haffmann's bromamide reaction.

(8) (B)

(9) **(D).** Only CH_3-NH_2 gives only carbyl amine and Hoffmann test and only $(CH_3)_2NH$ gives Libermann test.

(10) (D)

(11) (C)

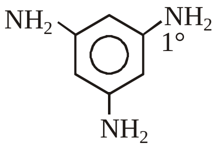
(12) **(C).** $-NH_2$ group increases electron density of benzene ring due to maximum + R effect.

(13) **(C).** Phenoxide is formed which is more reactive.

CHAPTER-12 : ORGANIC COMPOUNDS CONTAINING NITROGEN

EXERCISE-1

(1) **(C).**

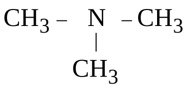


1° Amine

(2) **(D).** C_3H_9N can form all the 3 amines.

$\underset{1^o\ \text{amine}}{CH_3CH_2CH_2-NH_2}$,

$\underset{2^o\ \text{amine}}{CH_3-CH_2-NH-CH_3}$,



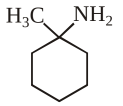
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{N}}-CH_3$

3^o amine

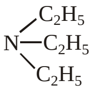
(3) **(A).** Trimethylphenyl ammonium bromide is a quaternary ammonium compound.

(4) **(A).** Nitrogen forms three sp^3 hybridised sigma bonds with carbon atoms of methyl groups and has a non-bonding electron pair in fourth sp^3 orbital. Thus, $(CH_3)_3N$ has pyramidal shape.

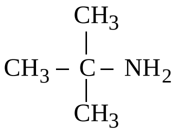
(5) **(B).**



1-Methyl cyclohexylamine (1° amine)

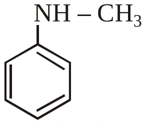


Triethylamine (3° amine)



$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}-NH_2$

tert-Butylamine (1° amine)



N-Methylaniline (2° amine)

(6) **(D).** Amines constitute an important class of organic compounds derived by replacing one or more hydrogen atoms of ammonia molecule by alkyl/aryl group(s). In nature, they occur among proteins, vitamins, alkaloids and hormones. Synthetic examples of amines are polymers, dyestuffs and drugs.

(7) **(A).** If one hydrogen atom of ammonia is replaced by R or Ar , we get RNH_2 or $ArNH_2$, a primary amine (1°). If two hydrogen atoms of ammonia or one hydrogen atom of R-NH_2 are replaced by another alkyl/aryl (R') group, we get
R-NHR', secondary amine. The second alkyl/aryl group may be same or different. Replacement of another hydrogen atom by alkyl/aryl group leads to the formation of tertiary amine.

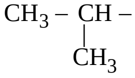
(8) **(D).** Nitrogen orbitals in amines are sp^3 hybridised and the geometry of amines is pyramidal.

(9) **(C).** In common system, an aliphatic amine is named by prefixing alkyl group to amine i.e., alkylamine as one word. In secondary and tertiary amines, when two or more groups are the same, the prefix di or tri is appended before the name of alkyl group. In case, more than one amino group is present at different positions in the parent chain, their positions are specified by given numbers to the carbon atoms bearing $-NH_2$ groups and suitable prefix such as di, tri is attached to the amine. The letter 'e' of the suffix of the hydrocarbon part is retained.

(10) **(D).** $\overset{3}{C}H_2=\overset{2}{C}H\overset{1}{C}H_2NHCH_3$

N-Methylprop-2-en-1-amine

(11) **(D).** $(CH_3)_2CHNH_2$:



$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-NH_2$ Propane-2-amine

(12) **(B).** $H_2N-CH_2CH_2NH_2$ is named as ethane-1, 2-diamine

(13) **(C).** $C_2H_5I+NH_3\rightarrow HI+C_2H_5-NH_2$

$C_2H_5OH+NH_3\rightarrow H_2O+C_2H_5-NH_2$

(14) **(C).**

$$\underset{\text{Nitroethane}}{CH_3-CH_2-NO_2}+6[H]\xrightarrow{Sn/HCl}\underset{\text{Ethyl amine}}{CH_3-CH_2-NH_2}+2H_2O$$

(15) **(C).** $CH_3-N\equiv C+4[H]\xrightarrow{\text{Reduction}}\underset{2^o\ \text{amine}}{CH_3-NH-CH_3}$

(16) **(A).** $C_2H_5OH+NH_3\xrightarrow{\text{alumina}}C_2H_5NH_2+H_2O$..

(17) **(C).** $R-CN+H_2O\xrightarrow{H_2O/H^+}RCOOH+NH_3$

It yield amine when reduced as –

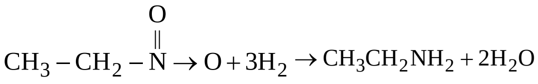
$R-CN+H_2\rightarrow R-CH_2-NH_2$

(18) **(C).** $CH_3-N\equiv C\xrightarrow{LiAlH_4}\underset{\text{sec. amine}}{CH_3-NH-CH_3}$

(19) **(D).** $CH_3I\xrightarrow[\Delta]{NH_3}\underset{\text{Methylamine}}{CH_3NH_2}$

$$\xrightarrow{CH_3I}\underset{\text{Dimethyl amine}}{(CH_3)_2NH}\xrightarrow{CH_3I}\underset{\text{Trimetyhl amine}}{(CH_3)_3N}$$

(20) **(A).**



$CH_3-CH_2-\overset{\displaystyle O}{\overset{\|}{N}}\rightarrow O+3H_2\rightarrow CH_3CH_2NH_2+2H_2O$

(21) **(A).** $\underset{\text{(Acetamide)}}{CH_3CONH_2}+Br_2+4KOH$

$$\xrightarrow[-2H_2O]{}\underset{\text{(Methyl amine)}}{CH_3NH_2}+2KBr+2K_2CO_3$$

(22) **(A).** Primary aliphatic amines can be prepared by Gabriel synthesis. 2° amines & aromatic 1° amines cannot be prepared.

(23) **(C).** Hofmann bromamide reaction is the best method to reduce one carbon atom in the amine from amide.

$$CH_3CH_2CONH_2 + Br_2 + 4KOH \xrightarrow{Heat} CH_3CH_2NH_2 + 2KBr + K_2CO_3 + 2H_2O$$

(24) **(C).** $R-X \xrightarrow{KCN} R-CN \xrightarrow{Na/C_2H_5OH} R-CH_2NH_2$

(25) **(B).** The amides on reduction with $LiAlH_4$ yield amine.

$$R\text{-}CONH_2 \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4} RCH_2NH_2$$

(26) **(B).** $CH_3CH_2NC \xrightarrow[Ni/Pt]{H_2} CH_3CH_2NHCH_3$

(27) **(C).** In this degradation reaction, migration of an alkyl or aryl group takes place from carbonyl carbon of the amide to the nitrogen atom. The amine so formed contains one carbon less than that present in the amide.

(28) **(B).** $CH_3CH_2CONH_2 \xrightarrow[(NaOBr)]{Br_2/NaOH}$

$$CH_3CH_2NH_2 + NaBr + Na_2CO_3 + H_2O$$

(29) **(A).** $C_2H_5NH_2 + CS_2 + HgCl_2 \rightarrow C_2H_5NCS + 2HCl + HgS$

(30) **(D).** $C_6H_5NH_2 \xrightarrow[HCl]{NaNO_2} C_6H_5N_2Cl$

$$\xrightarrow{H_2O} C_6H_5OH + N_2 + HCl$$

(31) **(B).** $C_6H_5NH_2 \xrightarrow{NaNO_2\ +\ HCl\ 0^oC} C_6H_5N_2Cl$

(32) **(B).** $\underset{1°\ amine}{R-CH_2-NH_2} + \underset{aldehyde}{O=CH-R} \rightarrow$

$$\underset{Aldimine}{R-CH_2-N=CH-R} + H_2O$$

(33) **(D).** $CH_3-CH_2-NH_2 + HCl \rightarrow \underset{Ethyl\ ammonium\ chloride}{CH_3CH_2-N\overset{+}{H_3}Cl^-}$

Amines are basic in nature they react with acid to form salt.

(34) **(A).** $\underset{2^o amine\ is\ most\ basic}{(CH_3)_2NH} > \underset{1^o amine}{CH_3NH_2} > \underset{3^o amine}{(CH_3)_3N} > \underset{Ammonia\ is\ least\ basic}{\ddot{N}H_3}$

(35) **(C).** $\underset{Ethylamine}{CH_3-CH_2-NH_2} \xrightarrow[[O]]{KMnO_4}$

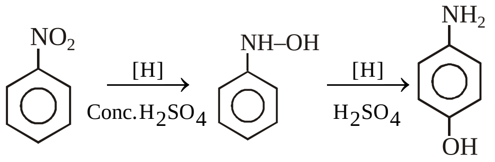
$$\underset{Aldimine}{CH_3-CH=NH} \xrightarrow{H_3O^+} \underset{Acetaldehyde}{CH_3-CHO}$$

(36) **(B).** Because the N atom in aniline has a lone pair to donate and also due to +I effect of $-NH_2$ group.

(37) **(A).** Basicity of amines increase with increase in number of $-CH_3$ groups (or any group which cause +I effect), due to increase in electron density on N atom. As a rule, the basicity of t-amine should be more than that of s-amine, but actually it is found to be lesser than s-amines. This is due to steric hinderance of bulkier alkyl groups, which decreases the availability of lone pair of electron on the N atom of the amino group. Hence the correct order of basicity is :

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

(38) **(C).**



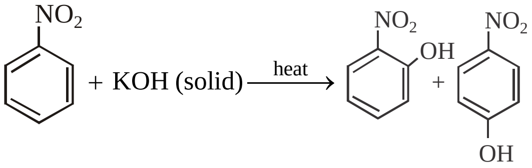
(39) **(A).** Basicity order is

$$C_4H_5NH_2 < (CH_3)_3NH < CH_3NH_2 < (CH_3)_2NH$$

$(CH_3)_3NH$ is less basic due to steric effect while $C_4H_5NH_2$ is less basic due to resonance.

(40) **(B).** The nitrogroup is very firmly linked to the benzene nucleus and does not undergo any displacement reaction. Nitro group deactivates the benzene nucleus.

(41) **(A).**



(42) **(D).** The synthesis of primary amines from phthalimide is known as Gabriel phthalimide synthesis.

(43) **(C).** Aniline is resonance hybrid of five structures and anilinium ion is obtained by accepting a proton can have only two resonating structures. Greater the number of resonating structures, greater is the stability.

(44) **(B).** Primary and secondary amines can form hydrogen bonds whereas tertiary amines fail to do so. Hence, their boiling points are lowest.

(45) **(C).** Amines are basic in nature while amides are amphoteric in nature.

(46) **(C).** Amines are reactive because of the difference in the electronegativity between nitrogen and hydrogen atoms. and also due to the presence of unshared pair of electrons over the nitrogen atom.

(47) **(D).** Electrophilic substitution reactions are

(a) Bromination of aniline

(b) Nitration of aniline

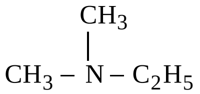
(c) Sulphonation of aniline

(48) **(A).** $H_3C-CH_2-CH_2-CH_2-NH_2$

n-Butylamine (Primary amine)

$CH_3CH_2-NH-CH_2-CH_3$

Diethylamine (Secondary amine)



$$CH_3-\overset{\overset{CH_3}{|}}{N}-C_2H_5$$

Ethyldimethylamine (Tertiary amine)

Primary amines have two hydrogen atoms available for hydrogen bond formation, while 2° amines have only one hydrogen atom for hydrogen bond formation.

3° amines do not have intermolecular association due to absence of hydrogen atom. Thus, order of boiling point of isomeric amines is as follows:
3° < 2° < 1° or III < II < I.

(49) **(A).** Primary amines react with benzoyl chloride to give benzamides and the reaction is known as benzoylation.

$$\underset{\text{Methanamine}}{CH_3NH_2} + \underset{\text{Benzoyl chloride}}{C_6H_5COCl} \rightarrow \underset{\text{N-Methylbenzamide}}{CH_3NHCOC_6H_5} + HCl$$

(50) **(A).** Benzenesulphonyl chloride ($C_6H_5SO_2Cl$) acts as Hinsberg's reagent.

(51) **(D).** Inductive effect, solvation effect, steric hindrance etc., affect the basic strength of amines.

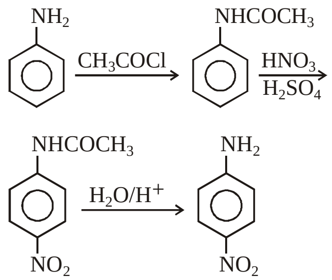
(52) **(C).** Amine salts are soluble in water but insoluble in organic solvents like ether. Amines have an unshared pair of electrons on nitrogen atom due to which they behave as Lewis base. Basic character of amines can be understood in terms of their K_b and pK_b values.

(53) **(C).** The trend in boiling point can be explained on the basis of intermolecular hydrogen bonding which is maximum in primary amines

(54) **(B).** Aliphatic primary amines react with $NaNO_2$ and HCl to yield alcohols.

$$C_2H_5NH_2 + HNO_2\,(NaNO_2 + HCl) \rightarrow C_2H_5OH + N_2 + H_2O$$

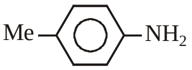
(55) **(D).** $-NH_2$ group is oxidised on direct nitration hence $-NH_2$ group is blocked by acetylation and then nitration is carried out.



(56) **(D).** Aliphatic and aromatic primary and secondary amines react with acid chlorides anhydrides and esters by nucleophilic substitution reaction. This reaction is known as acylation. In the acylation reaction of amines there is replacement of hydrogen atom of NH_2 or NH group by the acyl group. The products obtained by acylation reaction in amines are known as amides.

(57) **(A).** Primary amine reacts with $CHCl_3$ and alc. KOH to form isocyanide while secondary and tertiary amines do not react.

(58) **(D).** Anilinium hydrogen chloride produces chloride ion which gives white precipitate with $AgNO_3$. In fact anilium chloride is a part of aniline.

(59) **(B).** Only 1° amines (i.e.  in the present case) give positive carbylamine reaction.

(60) **(D).** Secondary amines do not give carbylamine test.

(61) **(D).** Allyl isocyanide.

$$CH_2 = CH - CH_2 - N \equiv C$$

(62) **(B).** $C_2H_5Br + KCN \xrightarrow{\text{alcohol}} C_2H_5CN + KBr$

(63) **(C).** $R - C \equiv N + 2H_2O \xrightarrow{\text{Hydrolysis}} R - COOH + NH_3$

(64) **(D).** $\underset{\text{Alkyl Isocyanide}}{RN \equiv C} + 2H_2O \xrightarrow{\text{Hydrolysis}} \underset{1^o\text{ amine}}{RNH_2} + \underset{\text{Formic acid}}{HCOOH}$

(65) **(C).** $CH_3NC + 4H \xrightarrow[\text{ether}]{LiAlH_4} (CH_3)_2NH.$

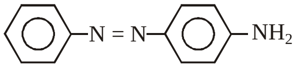
(66) **(D).** $R - NC + 2H_2O \rightarrow RNH_2 + HCOOH.$

(67) **(B).** $\underset{\text{Aniline}}{C_6H_5NH_2} + \underset{\text{Chloroform}}{CHCl_3} + 3KOH$

$$\rightarrow \underset{\text{phenyl isocyanide}}{C_6H_5NC} + 3KCl + 3H_2O$$

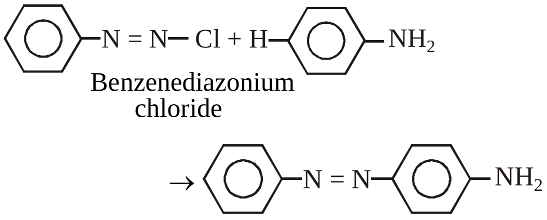
Thus in this reaction phenyl isocyanide is produced. This is called carbylamine reaction.

(68) **(A).**



Orange colour

(69) **(A).** Diazo-coupling is useful to prepare some dyes.



Amino azo benzene (yellow dye)

(70) **(C).** $-NH_2$ group increases electron density of benzene ring due to maximum + R effect.

(71) **(C).** Phenoxide is formed which is more reactive.

(72) **(B).** $C_6H_5N_2^+Cl^-$ is named as benzenediazonium chloride

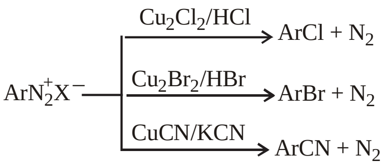
(73) **(C).** Diazonium salts also form the complexes with metallic salts such as zinc chloride i.e., $(ArN_2^+)_2ZnCl_4^{2-}$

(74) **(B).** Benzenediazonium chloride is very unstable and explodes on storage.

(75) **(C).** Diazotisation of aromatic amines is achieved by using nitrous acid.

(76) **(C).** Reaction is done in mild basic conditions.

(77) **(A).** The Cl^-, Br^- and CN^- nucleophiles can easily be introduced in the benzene ring in the presence of Cu(I) ion. This reaction is called Sandmeyer reaction.



(78) **(B).** Diazonium salts are intermediates in the preparation of a variety of aromatic compounds including dyes.

(79) **(D).** Diazonium salts are very good intermediates for the introduction of – F, Cl, Br, I, CN, OH, NO_2 groups into the aromatic ring.

Aryl fluorides and iodides cannot be introduced by nucleophilic substitution of chlorine in chlorobenzene but cyanobenzene can be easily obtained from diazonium salt. Replacement of diazo group by other groups is helpful in preparing those substituted aromatic compounds which cannot be prepared by direct substitution in benzene or substituted benzene.

EXERCISE-2

(1) **(B).** There is no free hydrogen in tertiary amines hence they do not form salts and are not soluble in acids.

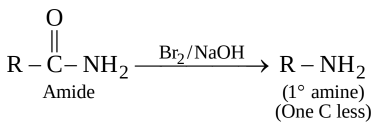
(2) **(D).** $\underset{}{CH_2=CH_2} \xrightarrow[CCl_4]{Br_2} \underset{(X)}{BrCH_2-CH_2Br} \xrightarrow{NaCN}$

$$\underset{(Y)}{NCCH_2CH_2CN} \xrightarrow{LiAlH_4} \underset{\substack{(1,4\text{-Diaminobutane})\\(Z)}}{H_2NCH_2CH_2CH_2CH_2NH_2}$$

(3) **(B).** $LiAlH_4$ in ether reduces aryl nitro compounds to azo compounds.

$$2C_6H_5NO_2 \xrightarrow[\text{ether}]{LiAlH_4/} C_6H_5\text{–}N=N\text{–}C_6H_5$$

Nitrobenzene Diazobenzene

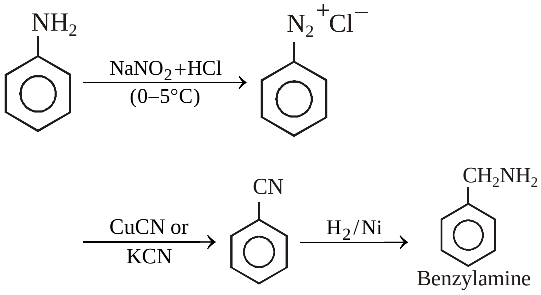
(4) **(D).** 

$$\underset{\text{Amide}}{R-\overset{\overset{O}{\|}}{C}-NH_2} \xrightarrow{Br_2/NaOH} \underset{\substack{(1°\text{ amine})\\(\text{One C less})}}{R-NH_2}$$

All other reactions give same number of C atoms in the chain of amines as in the reactants.

(5) **(C).** Only primary amines will give carbylamine reaction.

(6) **(A).** $$\underset{\substack{\text{Secondary}\\\text{amine}}}{R_2NH} + \underset{\substack{\text{Acetyl}\\\text{chloride}}}{CH_3COCl} \longrightarrow \underset{\substack{\text{N, N-dialkyl acetamide}\\\text{or dialkylethanamide}}}{RNCO.CH_3}$$

(7) **(A).** 

(8) **(C).** Primary aliphatic amines with nitrous acid to form aliphatic diazonium salts being unstable, liberate nitrogen gas quantitatively and alcohols.

$$R-NH_2 + HNO_2 \xrightarrow{NaNO_2+HCl}$$

$$[RN_2^+Cl^-] \xrightarrow{H_2O} ROH + N_2 + HCl$$

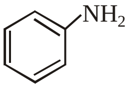
(9) **(C).** The reactions of diazonium salts can be broadly divided into the categories namely–

(a) reactions involving displacement of nitrogen.

(b) reactions involving retention of diazo group

(10) **(B).** $$CH_3CH_2COOH \xrightarrow[(A)]{SOCl_2} \underset{(X)}{CH_3CH_2COCl}$$

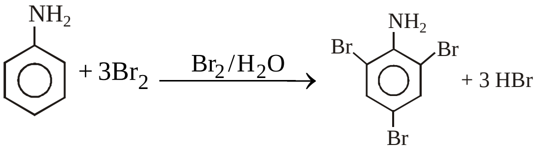
$$\xrightarrow[(B)]{NH_3} \underset{(Y)}{CH_3CH_2CONH_2} \xrightarrow[(C)]{Br_2/KOH} CH_3CH_2NH_2$$

(11) **(A).** 

is the weakest Bronsted base due to delocalisation of lone pair of electrons of N-atom into the benzene ring.

(12) **(C).** Hofmann developed a method for the preparation of primary amines by treating an amide with bromine in an aqueous or ethanolic solution of sodium hydroxide.

$$RCONH_2 + Br_2 + 4NaOH \rightarrow RNH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

(13) **(C).** 

2,4, 6-Tribromoaniline

(14) **(B).** 3° amine does not react with Hinsberg reagent, 2° amine reacts but is not soluble in alkali.

(15) **(C).** $RN\equiv C \xrightarrow{4H} RNHCH_3$

Other compounds give primary amines.

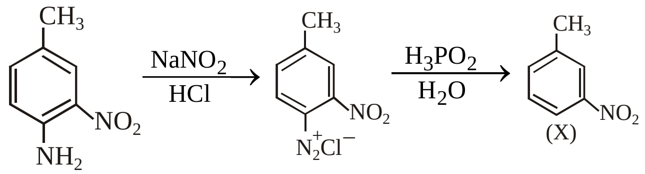
$$RNO_2 \xrightarrow{6H} RNH_2 + 2H_2O$$

$$RCONH_2 \xrightarrow{4H} RCH_2NH_2 + H_2O$$

$$RCN \xrightarrow{4H} RCH_2NH_2$$

(16) **(A).** NH_3 is more basic than H_2O, therefore NH_2^- (conjugate base of weak acid NH_3) is a stronger base than OH^-. Thus, decreasing order of basic strength is: $NH_2^- > OH^- > NH_3 > H_2O$.

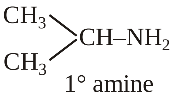
(17) **(A).**



(18) **(C).** The correct order of increasing boiling points for the bases $(CH_3)_3N < (CH_3)_2NH < CH_3NH_2$

(19) **(B).** In aqueous solution, the most basic amine is $(CH_3)_2NH$ and hence it is most reactive towards dilute hydrochloric acid.

(20) **(C).** Benzenediazonium chloride decomposes easily in the dry state.

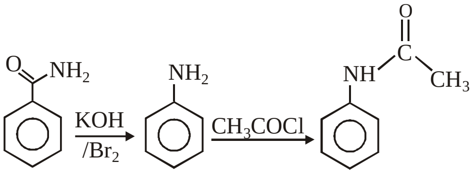
(21) **(D).** 

1° amine

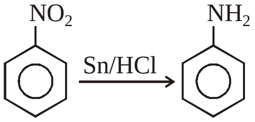
Isopropylamine is a primary amine.

(22) **(C).** Primary, secondary and tertiary amines can be separated by Hinsberg reagent which is benzenesulphonyl chloride.

(23) **(B).**



(24) **(A).**



(25) **(D).** $NH_3 + \underset{\text{(excess)}}{C_2H_5I} \rightarrow \underset{\text{Quaternary salt}}{[(C_2H_5)_4N^+]I^-}$

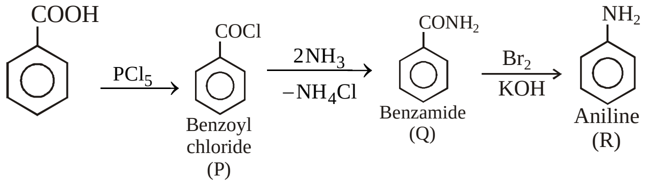
(26) **(B).**

$$\begin{array}{lccc} & (CH_3)_2NH > & CH_3NH_2 > & (CH_3)_3N \\ K_b = & 5.4\times10^{-4} & 4.5\times10^{-4} & 0.6\times10^{-4} \end{array}$$

(27) **(B).** $CH_3-NH_2 + HNO_2 \xrightarrow[+HCl]{NaNO_2}$

$[CH_3N_2^+\bar{C}l] \xrightarrow{H_2O} HCl + N_2 + CH_3OH$

(28) **(A).**



(29) **(A).** Nitrous acid is produced in the reaction mixture by the reaction of sodium nitrite with HCl.

(30) **(B).** $RNH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} RNC + 3KCl + 3H_2O$

Only RNC and $CHCl_3$ are involved in carbylamine reaction.

(31) **(A).** Presence of electron withdrawing (–I or –M group) like $-NO_2$ at p-position will decrease the basicity, so (2) will be the least basic, whereas presence of electron donating (+I or +M) group like $-OCH_3$ at p-position in (4) will increase the basicity so (4) will be the most basic. Hence correct order of increasing basic character is : $2 < 5 < 1 < 3 < 4$.

(32) **(C).** Amines are stronger Bronsted bases than alcohols and phenols as they have tendency to accept a proton.

Phenols are more acidic than alcohols, thus, phenol has least tendency to accept a proton hence, is the weakest Bronsted base.

(33) **(A).** II is not an acceptable canonical structure because nitrogen has 10 valence electrons in the structure. Anilinium ion exists in two canonical structures only which are I & III.

(34) **(B).** $CH_3CH_2-O-N=O$ is a nitrite derivative, hence it is not a nitro derivative.

(35) **(B).** CH_3CN is called acetonitrile.

(36) **(B).** Four 1° amines are possible

$CH_3CH_2CH_2CH_2NH_2, (CH_3)_2CHCH_2NH_2$

$CH_3CH(NH_2)CH_2CH_3, (CH_3)_3CNH_2$

(37) **(D).** $CH_3CONH_2 \xrightarrow{NaOBr} CH_3NH_2$.

(38) **(B).** $\underset{\text{Acetamide}}{CH_3CONH_2} + Br_2 + 4NaOH \rightarrow$

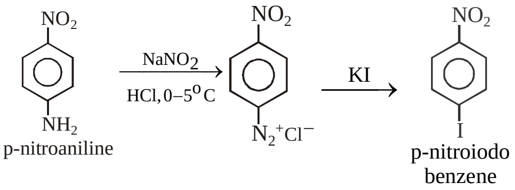
$\underset{\text{Methyl amine}}{CH_3NH_2} + Na_2CO_3 + 2NaBr + 2H_2O$

(39) **(A).**

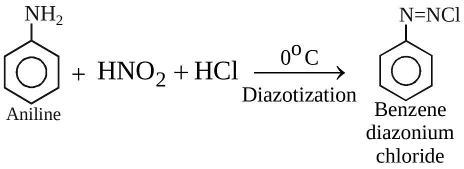
$\underset{\text{Nitromethane}}{CH_3NO_2} + 3Cl_2 + 3NaOH \rightarrow \underset{\text{(chloropicrin)}}{CCl_3-NO_2} + 3NaCl + 3H_2O.$

(40) **(A).** $CH_3NO_2 + 6H \xrightarrow[HCl]{Sn} CH_3NH_2 + 2H_2O$

(41) **(A).** p-nitroiodobenzene from p-nitroaniline

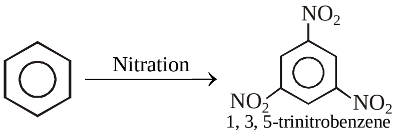


(42) **(C).**



(43) **(B).** Only primary aromatic amines can undergo diazotisation.

(44) **(C).**



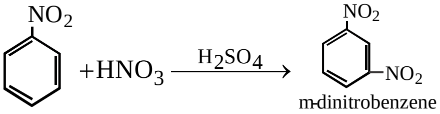
3- nitro group can be introduced.

(45) **(A).**

$(C_2H_5)_2NH + (aq.)HONO \rightarrow \underset{\text{Diethyl nitrosoamine}}{(C_2H_5)_2N-N=O} + H_2O$

(46) **(D).** Nitro compounds are not explosive but stable compound.

(47) **(B).**



(48) **(C).** Hofmann's bromamide reaction

$\underset{\text{Acetamide}}{CH_3-CO-NH_2} + Br_2 + 4KOH \xrightarrow{H_2O}$

$\underset{\text{Methyl amine}}{CH_3NH_2} + K_2CO_3 + 2KBr + 2H_2O$

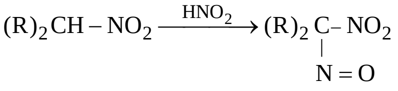
(49) **(B).** $CH_3C\equiv N + 4[H] \xrightarrow[\text{Reduction}]{Na+C_2H_5OH} CH_3CH_2NH_2$

(50) **(C).** $CH_3COOH \xrightarrow{PCl_5} CH_3COCl$

$\xrightarrow{NH_3} CH_3CONH_2 \xrightarrow{NaOBr} CH_3NH_2$

(51) **(C).** $\underset{\text{Nitrobenzene}}{C_6H_5NO_2} + 6H \xrightarrow{pt/H_2} \underset{\text{Aniline}}{C_6H_5NH_2} + 2H_2O$

(52) **(B).**



$(R)_2CH-NO_2 \xrightarrow{HNO_2} (R)_2\underset{\underset{N=O}{|}}{C}-NO_2$

$\xrightarrow{NaOH}$ Blue colour.

(53) **(B).** $\underset{\text{Ethyl amine}}{C_2H_5NH_2} \xrightarrow{HNO_2} \underset{\text{Ethyl alcohol}}{C_2H_5OH}$

$\xrightarrow{PCl_5} C_2H_5Cl \xrightarrow{NH_3} \underset{\text{Ethyl amine}}{C_2H_5NH_2}$

(54) **(C).** $R_3N + HONO \rightarrow R_3N.HONO$

called as Quaternary ammonium salt.

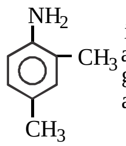
(55) **(A).** Because of presence of electron withdrawing group -NO_2.

(56) **(A).** $CH_3CH_2NH_2 + CH_3COCl$

$\rightarrow \underset{\text{N Ethyl acetamide}}{CH_3CH_2NHCOCH_3} + HCl$

(57) **(C).** This is Hoffman-bromide reaction. In this reaction one carbon less amines are formed from amides.

$CH_3CONH_2 \xrightarrow{Br_2/KOH} CH_3NH_2$

(58) **(B).** 

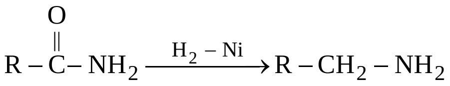
is a type of 1° amine and hence gives +ve carbyl amine test.

(59) **(C).** $(CH_3)_2NCOCH_3 + HCl/H_2O$

$\downarrow$

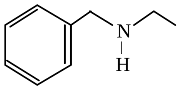
$(CH_3)_2NH + CH_3COOH$

(60) **(A).**



$R-\overset{\overset{O}{||}}{C}-NH_2 \xrightarrow{H_2-Ni} R-CH_2-NH_2$

(61) **(D).** Liebermann's Nitroso reaction.

(62) **(B).** 

is most basic

(63) **(B).** N-alkyl formamides when dehydrated with $POCl_3$ in presence of pyridine give isocyanides.

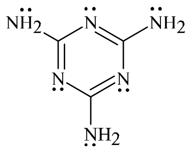
(64) **(A).** $C_6H_5-NH_2 + CHCl_3 + 3KOH$

$\rightarrow \underset{\text{Phenyl Isocyanide}}{C_6H_5NC} + 3KCl + 3H_2O$

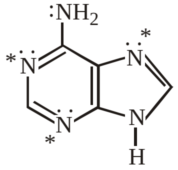
EXERCISE-3

(1) **2** $-NH_2$ and $-COO^{\ominus}$ are two basic groups.

(2) **6.** lone pair.



Melamine

(3) **3.** 

* Active basic sties

Lone pairs at * marked nitrogen are not involved in resonance hence available for reaction with acids.

(4) **50.** Hybridisation of carbon in $R-C\equiv N$ is sp while that of the carbon in RCH_2NH_2 is sp^3.

So, percentage change in s-character

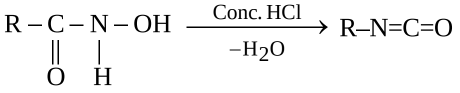
$$= \frac{\frac{1}{2}-\frac{1}{4}}{\frac{1}{2}} \times 100 = \frac{\frac{1}{4}}{\frac{1}{2}} \times 100 = 50\%$$

(5) **4.**

(a) $>C=O + HCOONH_4 \longrightarrow >CHNHCHO + H_2O + CO_2$

$\xrightarrow[\text{Hydrolysis}]{H^{\oplus}} HCHO + >CH_2-NH_2$

(b)



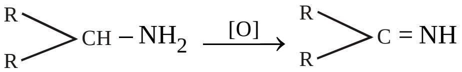
$R-\underset{\underset{O}{||}}{C}-\underset{\underset{H}{|}}{N}-OH \xrightarrow[-H_2O]{\text{Conc. HCl}} R-N=C=O$

$\xrightarrow{2KOH} R-NH_2 + K_2CO_3$

(c) b.p. of 1° amine > 2° amine > 3° amine

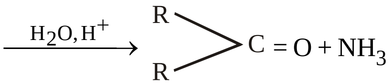
Primary and secondary amines form inter molecular H-bonds. While tertiary amines do not form inter molecular H-bonds. As a result, 1° & 2° amines show high B.P. than 3° amines.

(d) $\underset{\text{Alkyl amine}}{RCH_2NH_2} \xrightarrow{[O]} \underset{\text{Aldimine}}{R-CH=NH} \xrightarrow{H_2O, H^+} \underset{\text{Aldehyde}}{RCHO + NH_3}$



$\begin{matrix}R\\R\end{matrix}\!\!>CH-NH_2 \xrightarrow{[O]} \begin{matrix}R\\R\end{matrix}\!\!>C=NH$

Ketimine



$\xrightarrow{H_2O, H^+} \begin{matrix}R\\R\end{matrix}\!\!>C=O + NH_3$

Ketone

(e) $2R_2NH \xrightarrow[-H_2O]{[O]} R_2N-NR_2$

2°- amine Tetraalkylhydrazine

(6) **2.** Structures are : (i) 1° (ii) 3° (iii) 1° (iv) 2°

(7) **5.**

(a) Decreasing order of the pK_b values :
$C_6H_5NH_2 < C_6H_5NHCH_3 < C_2H_5NH_2 < (C_2H_5)_2NH$

(b) Increasing order of basic strength :
$(C_2H_5)_2NH > CH_3NH_2 > C_6H_5NH(CH_3)_2 > C_6H_5NH_2$

(c) Increasing order of basic strength :
p-nitroaniline < Aniline < p-toluidine

(d) Increasing order of basic strength :
$C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$

(e) Decreasing order of the basic strength in gas phase
$(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$

(f) Increasing order of boiling point :
$(CH_3)_2NH < C_2H_5NH_2 < C_2H_5OH$

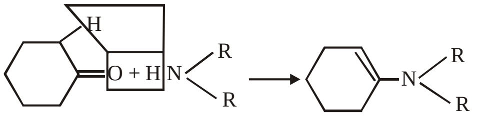
(g) Increasing order of solubility in water :
$C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2$

EXERCISE-4

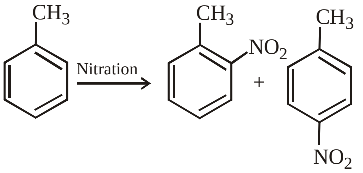
(1) **(B).** Isocynide

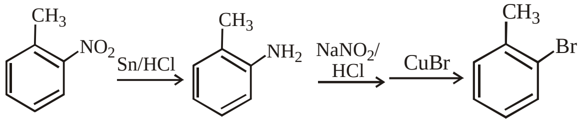
(2) **(A).**

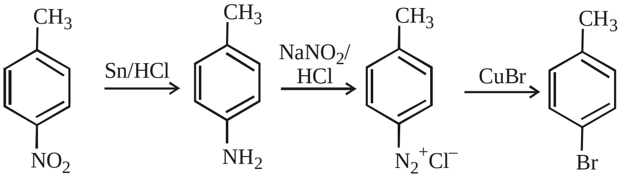
(3) **(D).** Wurtz reaction for alkanes.

(4) **(A).** 

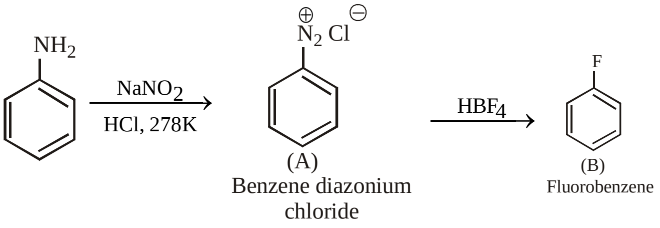
(5) **(D).** $CH_3-CH_2-NH_2+CHCl_3+3KOH \rightarrow C_2H_5NC+3KCl$

(6) **(D).** 



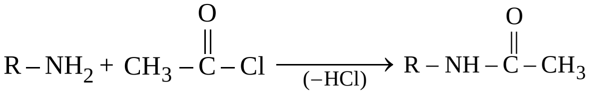


(7) **(C).**



$+ N_2 + BF_3 + HCl$

(8) **(B).** By reaction with one mole of $CH_3-\overset{O}{\overset{\|}{C}}-Cl$ with one $-NH_2$ group the molecular mass increases with 42 unit. Since the mass increases by (390 – 180) = 210 hence the number of $-NH_2$ groups is 5.



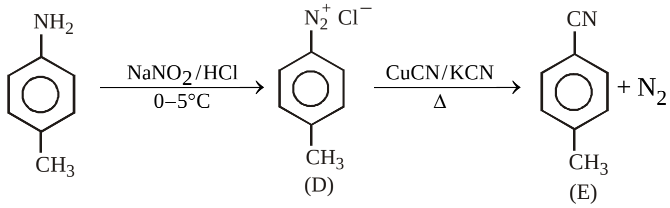
$$R-NH_2+CH_3-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[(-HCl)]{} R-NH-\overset{O}{\overset{\|}{C}}-CH_3$$

(9) **(B).** $RNH_2+CHCl_3+\underset{(alc.)}{3KOH}$

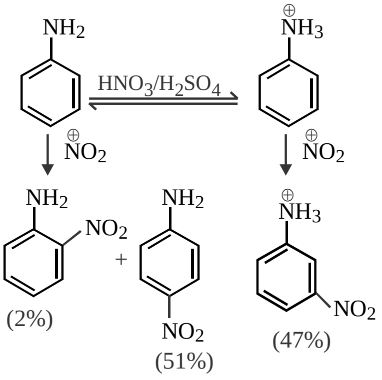
$$\longrightarrow \underset{\text{(alkyl isocyanide)}}{RNC\uparrow}+3KCl+3H_2O$$

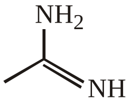
(10) **(C).** Aliphatic amines are more basic than aromatic amines.
$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N$
(among aliphatic amines in water).
Among $C_6H_5NH_2$, CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$, $C_6H_5NH_2$ is least basic due to resonance.
Out of $(CH_3)_3N$, CH_3NH_2, $(CH_3)_2NH$
$(CH_3)_2NH$ is most basic due to +I effect and hydrogen bonding in H_2O.

(11) **(B).**



(12) **(C).** $RCONH_2+4NaOH+Br_2 \rightarrow RNH_2+Na_2CO_3+2NaBr+2H_2O$

(13) **(D).** 

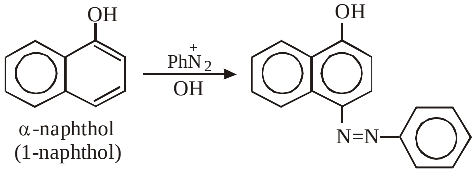
(14) **(A).** Amidines,  are stronger organic bases.

(15) **(A).** $R-C\equiv N \xrightarrow{AlH(i-Bu_2)} R-CH=N$

$$\xrightarrow{H_2O} R-CH=O$$

(16) **(A).** Basic strength order
$\underset{2^\circ\text{ amine}}{(CH_3CH_2)_2NH} > \underset{1^\circ\text{ amine}}{CH_3CH_2NH_2} > NH_3$

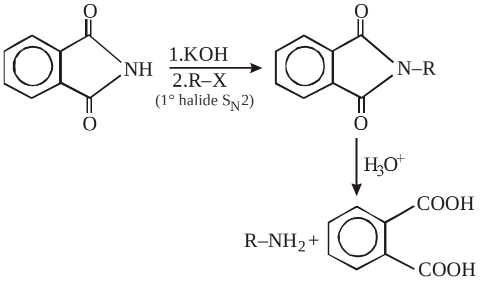
(17) **(C).**



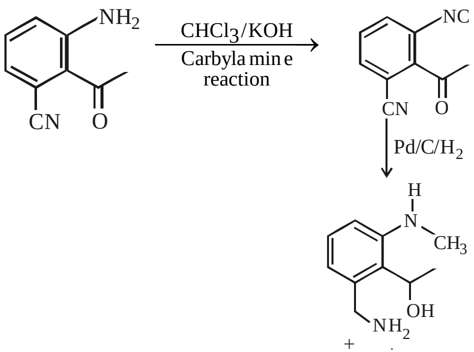
α-naphthol (1-naphthol)

orange red dye

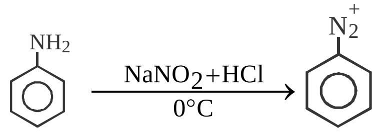
(18) **(B).** Gabriel phthalimide synthesis :



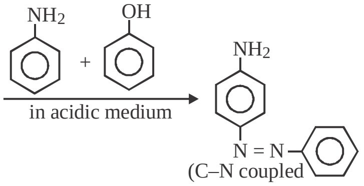
(19) **(A).**



(20) **(A).**



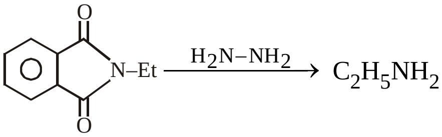
(Aniline)



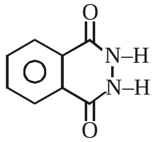
(C–N coupled product)

Aniline undergoes diazo coupling in acidic medium with $Ph\overset{+}{N}_2$.

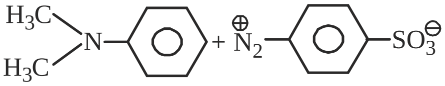
(231) **(D).**

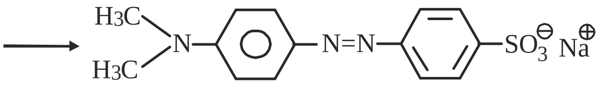


Reagent is NH_2-NH_2 by-product will be



(22) **(B).**

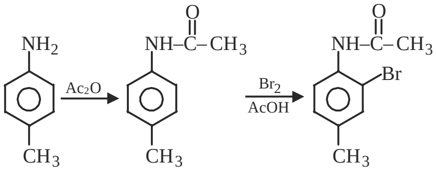




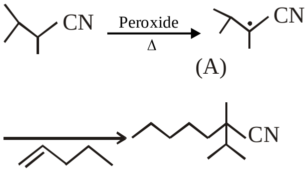
Methyl orange

Methyl orange is used as an indicator in acid base titration.

(23) **(A).**



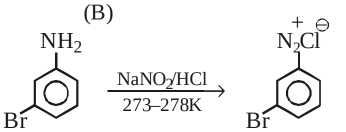
(24) **(A).**



(A)

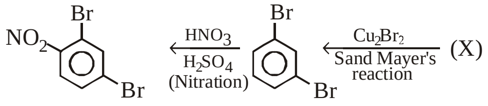
(B)

(25) **(B).**



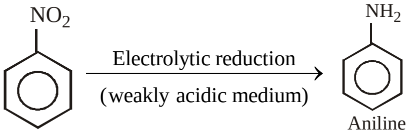
(Diazotisation)

(m-Bromo benzene diazonium chloride)



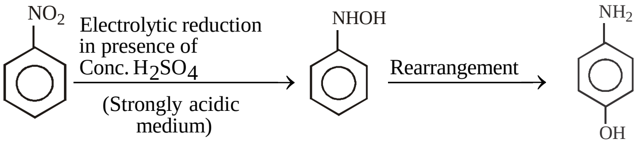
EXERCISE-5

(1) **(C).** Electrolytic reduction of Nitroalkane in weakly acidic medium give aniline.



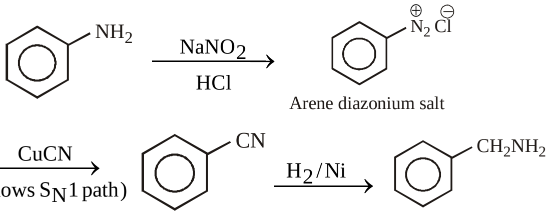
Aniline

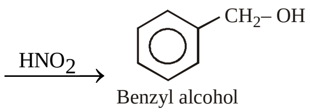
Whereas in strongly acidic medium it gives p-hydroxyaniline



p-Hydroxy aniline

(2) **(D).**





Benzyl alcohol

(3) **(C).** Benzylamine is more basic than aniline. The reason is that in aniline, the lone pair of nitrogen is conjugated with benzene ring so it is not available readily for others. On the other hand in Benzylamine, nitrogen is not directly attached with ring so lone pairs are not conjugated with ring.

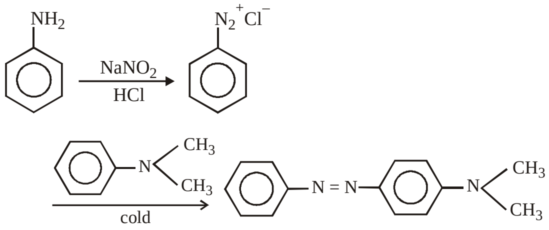
(4) **(A).** Reduction of alkyl isocyanides in presence of $LiAlH_4$ yields secondary amines containing methyl as one of the alkyl group.

$$R-N\equiv C+4[H]\xrightarrow{LiAlH_4}\underset{2^\circ\text{ amine}}{R-NH-CH_3}$$

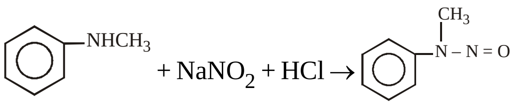
eg., $$CH_3-N\equiv C+4[H]\xrightarrow{LiAlH_4}\underset{\text{dimethyl amine}}{CH_3-NH-CH_3}$$

whereas, alkyl cyanides give 1° amine on reduction.

(5) **(A).**



(6) **(D).** 2° aliphatic and aromatic amines react with nitrous acid to form N-nitrosoamine.



N-nitroso-N-methylaniline

(7) **(B).** $HONO_2+H_2SO_4\rightarrow NO_2^{\,+}+H_2O+HSO_4^{\,-}$
Nitric acid acts as a base by accepting a proton.

(8) **(C).**

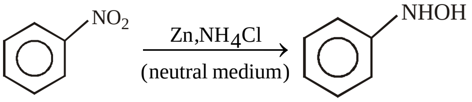
(i) Presence of electron withdrawing substiuent decreases the basicity while the presence of electron releasing substituent like, $-CH_3$, $-C_2H_5$ etc. increases the acidity.

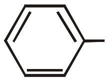
(ii) HNO_2 converts $-NH_2$ group of alphatic amine into –OH while that of aromatic amines into $-N=NCl$
Since, phenyl group is a electron withdrawing group, it decreases the basicity. Alkyl group, on the other hand, being electron releasing, increases the basicity. Thus, alkyl amines are more basic as compared to aryl amines as well as ammonia.

$$R-NH_2\xrightarrow{HNO_2}R-OH$$

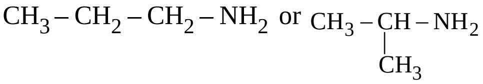
Thus, HNO_2 (nitrous acid) converts alkyl amines to alcohols. But $C_6H_5NH_2\xrightarrow{HNO_2}C_6H_5N=NCl$
benzene diazonium chloride
HNO_2 does not convert aryl amines into phenol.

(9) **(B).**



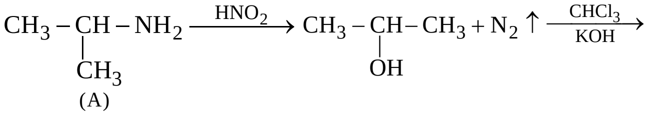
(10) **(B).**  CH_2NH_2 compound is most basic due to localized lone pair of electron on nitrogen atom while other compounds have delocalized lone pair of electron.

(11) **(A).** As (A) gives alcohol on treatment with nitrous acid thus it should be primary amine. C_3H_9N has two possible structures with $-NH_2$ group.

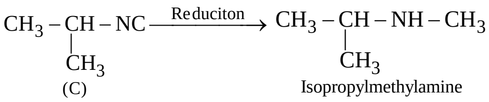


$$CH_3-CH_2-CH_2-NH_2\text{ or }CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-NH_2$$

As it gives isopropylmethylamine thus it should be isopropyl amine not n-propylamine.

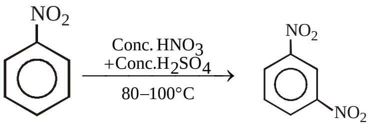


$$\underset{(A)}{CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-NH_2}\xrightarrow{HNO_2}CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3+N_2\uparrow\xrightarrow[KOH]{CHCl_3}$$



$$\underset{(C)}{CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-NC}\xrightarrow{\text{Reduciton}}\underset{\text{Isopropylmethylamine}}{CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-NH-CH_3}$$

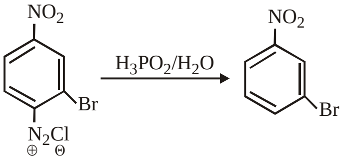
(12) **(C).**



1, 3-Dinitro benzene

Mixture of [Conc HNO_3 conc H_2SO_4] gives $\overset{\oplus}{N}O_2$ which acts as electrophile and in nitrobenzene $-NO_2$ group is m-directing group so $\overset{\oplus}{N}O_2$ attacks at m-position.

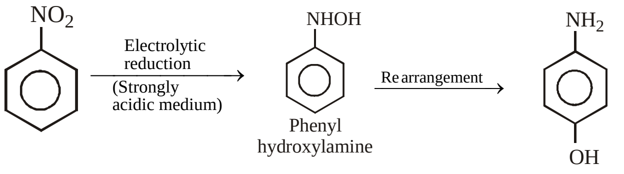
(13) **(D).**



(14) **(D).** Major product is formed by para attack.

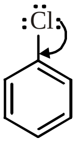
(15) **(B).** Aromatic diazonium salts are more stable due to dispersal of the positive charge in benzene ring.

(16) **(D).**

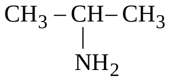


p-aminophenol

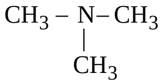
(17) **(B).** Benzoylation of aniline is an example of Schotten Bauman reaction.

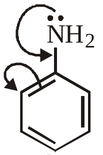
(18) **(B).**  due to resonance C – Cl bond acquires double bond character. Does not undergo nucleophilic substitution under normal conditions.

(19) **(C).** $C_3H_9N : CH_3 - CH_2 - CH_2 - NH_2,$


$CH_3 - \underset{NH_2}{\underset{|}{CH}} - CH_3$ 1° amine

$CH_3 - CH_2 - NH - CH_3$ 2° amine

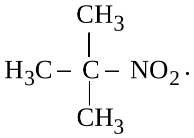

$CH_3 - \underset{CH_3}{\underset{|}{N}} - CH_3$ 2° amine

(20) **(A).** 

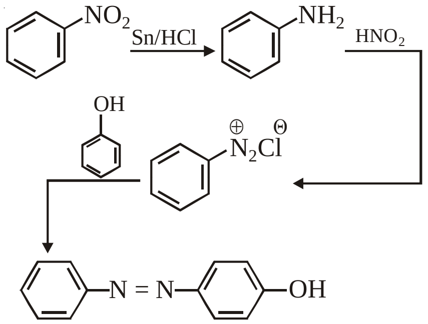
Arylamine
(less basic)

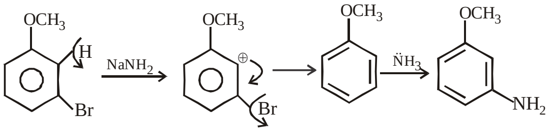
$R - \ddot{N}H_2$

Alkyl amine
(more basic)

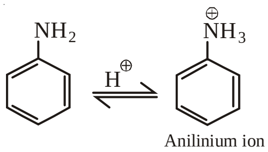
(21) **(C).** 
$H_3C - \underset{CH_3}{\underset{|}{\overset{\overset{CH_3}{|}}{C}}} - NO_2 \cdot$

No acidic H-atom on the carbon atom having NO_2-group.

(22) **(B).** 

(23) **(D).** 

Example of substitution reaction.

(24) **(D).** 

$-\overset{\Theta}{N}H_3$ is m-directing, hence besides para (51%) and ortho (2%), meta product (47%) is also formed in significant yield.

(25) **(A).** In aqueous solution, electron donating inductive effect, solvation effect (H-bonding) and steric hindrance all together affect basic strength of substituted amines.

Basic character :

$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N$
2° 1° 3°