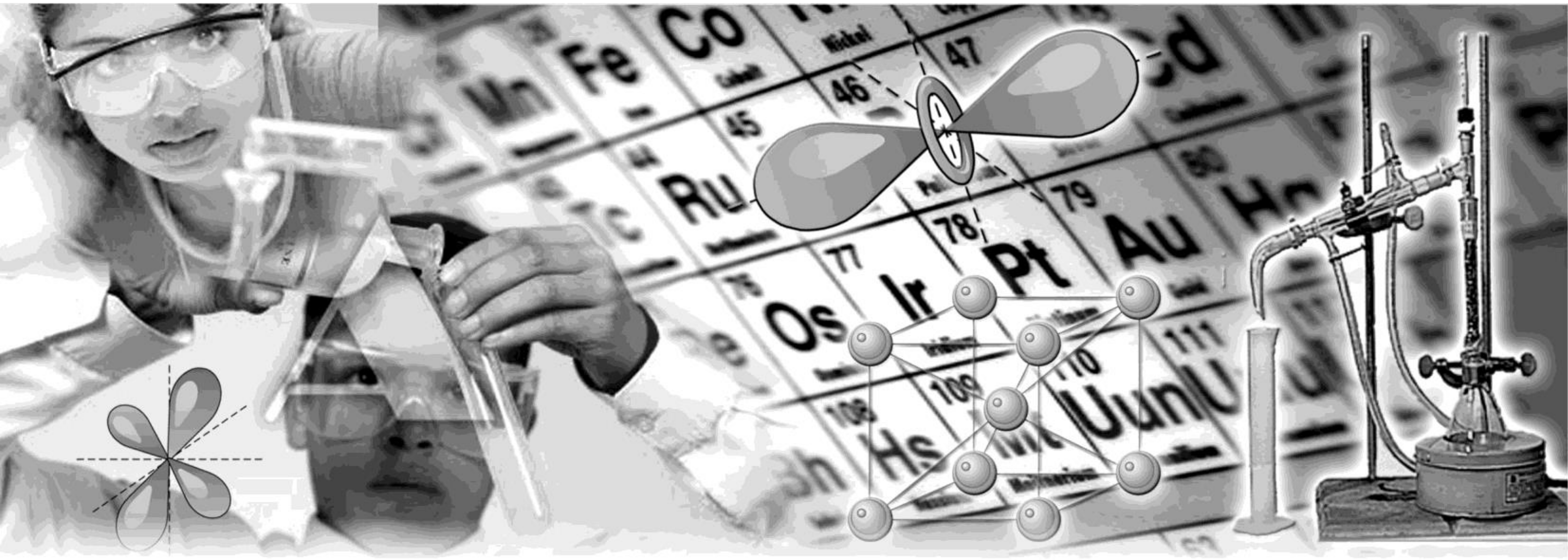


Chapter

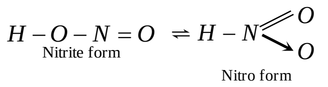
29

Nitrogen Containing Compounds

The important nitrogen containing organic compounds are alkyl nitrites (*RONO*), nitro-alkanes (*RNO₂*), aromatic nitro compounds (*ArNO₂*), alkyl cyanides (*RCN*), alkyl iso cyanides (*RNC*), amines (–*NH₂*), aryl diazonium salts (*ArN₂Cl*), amides (–*CONH₂*) and oximes (>*C* = *N OH*).

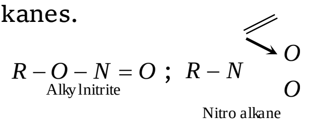
Alkyl nitrites and nitro alkanes

Nitrous acid exists in two tautomeric forms.



$$\underset{\text{Nitrite form}}{H-O-N=O} \rightleftharpoons \underset{\text{Nitro form}}{H-N\overset{\nearrow O}{\underset{\searrow O}{}}}$$

Corresponding to these two forms, nitrous acid gives two types of derivatives, i.e., alkyl nitrites and nitro alkanes.



$$\underset{\text{Alkyl nitrite}}{R-O-N=O}\ ;\ \underset{\text{Nitro alkane}}{R-N\overset{O}{\underset{O}{}}}$$

It is important to note that nitro alkanes are better regarded as nitro derivatives of alkanes, while alkyl nitrites are regarded as alkyl esters of nitrous acid.

(1) **Alkyl nitrites :** The most important alkyl nitrite is ethyl nitrite.

Ethyl nitrite (*C₂H₅ONO*)

(i) ***General methods of preparation*** **:** It is prepared

(a) By adding concentrated *HCl* or *H₂SO₄* to aqueous solution of sodium nitrite and ethyl alcohol at very low temperature (0°*C*).

$$NaNO_2 + HCl \rightarrow NaCl + HNO_2$$

$$C_2H_5OH + HNO_2 \rightarrow \underset{\text{Ethyl nitrite}}{C_2H_5ONO} + H_2O$$

(b) From Ethyl iodide

$$\underset{\text{Ethyl iodide}}{C_2H_5I} + \underset{\text{Pot. nitrite}}{KONO} \rightarrow \underset{\text{Ethyl nitrite}}{C_2H_5ONO} + KI$$

(c) By the action of N_2O_3 on ethyl alcohol.

$$2C_2H_5OH + N_2O_3 \rightarrow 2C_2H_5ONO + H_2O$$

(ii) ***Physical properties***

(a) At ordinary temperature it is a gas which can be liquified on cooling to a colourless liquid, *(boiling point 17°C) having characteristic smell of apples.*

(b) It is insoluble in water but soluble in alcohol and ether.

(iii) ***Chemical properties***

(a) *Hydrolysis* : It is hydrolysed by aqueous alkalies or acids into ethyl alcohol.

$$C_2H_5ONO + H_2O \xrightarrow{NaOH} C_2H_5OH + HNO_2$$

(b) *Reduction* :

$$C_2H_5ONO + 6H \xrightarrow[HCl]{Sn} C_2H_5OH + NH_3 + H_2O$$

Small amount of hydroxylamine is also formed.

$$C_2H_5ONO + 4H \rightarrow C_2H_5OH + NH_2OH$$

(iv) ***Uses***

(a) Ethyl nitrite dialates the blood vessels and thus accelerates pulse rate and lowers blood pressure, *so it is used as a medicine for the treatment of asthma and heart diseases* (angina pectoris).

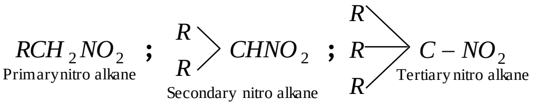
(b) Its 4% alcoholic solution (known as ***sweet spirit of nitre***) is used in medicine as a diuretic.

(c) Since it is easily hydrolysed to form nitrous acids, it is used as a source of nitrous acid in organic synthesis.

❑ ***Isoamyl nitrite** is used as an antispasmodic in angina pectoris and as a restorative in cardiac failure.*

(2) **Nitro alkanes or Nitroparaffins :** Nitro alkanes are regarded as nitro derivatives of hydrocarbons.

(i) ***Classification*** **:** They are classified as primary, secondary and tertiary depending on the nature of carbon atom to which nitro groups is linked.



RCH_2NO_2 ; R_2CHNO_2 ; R_3C-NO_2

Primary nitro alkane; Secondary nitro alkane; Tertiary nitro alkane

(ii) ***General methods of preparation***

(a) By heating an alkyl halide with aqueous alcoholic solution of silver nitrite

$$C_2H_5Br + AgNO_2 \rightarrow C_2H_5NO_2 + AgBr$$

Some quantity of alkyl nitrite is also formed in this reaction. It can be removed by fractional distillation since alkyl nitrites have much lower boiling points as compared to nitro alkanes.

(b) By the direct nitration of paraffins (Vapour phase nitration)

$$CH_3CH_3 + HONO_2(\text{fuming}) \xrightarrow{400°C} CH_3CH_2NO_2 + H_2O$$

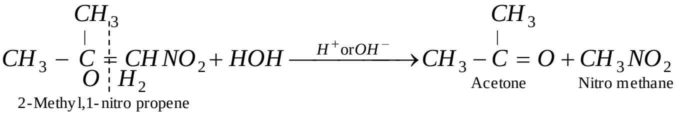
With higher alkanes, a mixture of different nitro alkanes is formed which can be separated by ***fractional distillation.***

(c) By the action of sodium nitrite on α-halo carboxylic acids

$$\underset{\alpha-\text{Chloro acetic acid}}{CH_2ClOOH} \xrightarrow[-NaCl]{NaNO_2} \underset{\alpha-\text{Nitro acetic acid}}{CH_2NO_2COOH}$$

$$\xrightarrow{\text{heat}} \underset{\text{Nitro methane}}{CH_3NO_2} + CO_2$$

(d) By the hydrolysis of α–nitro alkene with water or acid or alkali (Recent method)



$$\underset{\text{2-Methyl,1-nitro propene}}{CH_3-\overset{CH_3}{\overset{|}{C}}=CHNO_2} + HOH \xrightarrow{H^+ \text{or} OH^-} \underset{\text{Acetone}}{CH_3-\overset{CH_3}{\overset{|}{C}}=O} + \underset{\text{Nitro methane}}{CH_3NO_2}$$

(e) Tertiary nitro alkanes are obtained by the oxidation of *t*-alkyl amines with $KMnO_4$.

$$R_3CNH_2 \xrightarrow{KMnO_4} R_3CNO_2 + H_2O$$

(iii) ***Physical properties***

(a) Nitro alkanes are colourless, pleasant smelling liquids.

(b) These are sparingly soluble in water but readily soluble in organic solvents.

(c) *Their boiling points are much higher than isomeric alkyl nitrites* due to polar nature.

(d) Again due to polar nature, nitro alkanes are excellent solvents for polar and ionic compounds.

❑ *1° and 2° - Nitro alkanes are known to exist as tautomeric mixture of nitro-form and aci-form.*

$$\underset{(nitro\text{-form})}{CH_3-\overset{}{\underset{\overset{\downarrow}{O}}{N}}=O} \qquad \underset{(aci\text{-form})}{CH_2=\underset{\overset{\downarrow}{O}}{N}-OH}$$

(iv) ***Chemical properties***

(a) *Reduction* : Nitro alkanes are reduced to corresponding primary amines with *Sn* and *HCl* or *Fe* and *HCl* or catalytic hydrogenation using nickel as catalyst.

$$RNO_2 + 6H \rightarrow RNH_2 + 2H_2O$$

However, when reduced with a neutral reducing agent **(*Zinc dust + NH₄Cl*)**, nitro alkanes form ***substituted hydroxylamines.***

$$R-NO_2 + 4H \xrightarrow{Zn+NH_4Cl} R-NHOH + H_2O$$

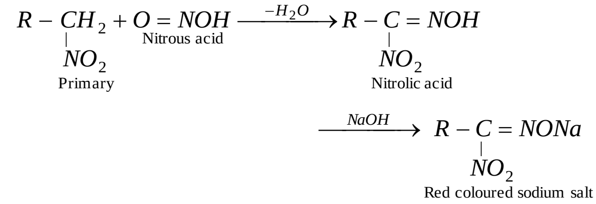
(b) *Hydrolysis* : Primary nitro alkanes on hydrolysis form hydroxylamine and carboxylic acid.

$$RCH_2NO_2 + H_2O \xrightarrow{HCl \text{ or } 80\% H_2SO_4} RCOOH + NH_2OH$$

secondary nitro alkanes on hydrolysis form ketones.

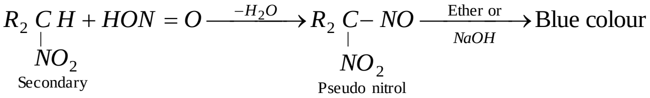
$$2R_2CHNO_2 \xrightarrow{HCl} \underset{Ketone}{2R_2CO} + N_2O + H_2O$$

(c) *Action of nitrous acid* : Nitrous acid reacts with primary, secondary and tertiary nitro alkanes differently.



$$\underset{\text{Primary}}{R-\underset{NO_2}{\underset{|}{CH_2}}} + \underset{\text{Nitrous acid}}{O=NOH} \xrightarrow{-H_2O} \underset{\text{Nitrolic acid}}{R-\underset{NO_2}{\underset{|}{C}}=NOH}$$

$$\xrightarrow{NaOH} \underset{\text{Red coloured sodium salt}}{R-\underset{NO_2}{\underset{|}{C}}=NONa}$$



$$\underset{\text{Secondary}}{R_2\underset{NO_2}{\underset{|}{C}}H} + HON=O \xrightarrow{-H_2O} \underset{\text{Pseudo nitrol}}{R_2\underset{NO_2}{\underset{|}{C}}-NO} \xrightarrow[NaOH]{\text{Ether or}} \text{Blue colour}$$

Tertiary nitro alkanes do not react with nitrous acid.

(d) *Thermal decomposition* : .

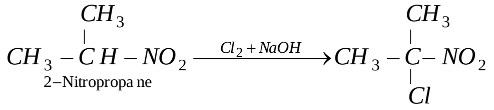
$$R.CH_2.CH_2NO_2 \xrightarrow[\text{moderately}]{>300°C} R.CH=CH_2 + HNO_2$$

On rapid heating nitro alkanes decompose with great violence.

$$CH_3NO_2 \xrightarrow{\text{heat, Rapidly}} \frac{1}{2}N_2 + CO_2 + \frac{3}{2}H_2$$

(e) *Halogenation* : Primary and secondary nitro alkanes are readily halogenated in the α-position by treatment with chlorine or bromine.

$$CH_3-NO_2 \xrightarrow[NaOH]{Cl_2} \underset{\text{Chloropicrin or nitro chloroform (insecticide)}}{CCl_3NO_2}$$

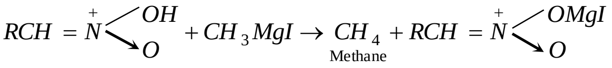


$$\underset{\text{2-Nitropropane}}{CH_3-\overset{\displaystyle CH_3 \atop |}{C}H-NO_2} \xrightarrow{Cl_2+NaOH} CH_3-\underset{\displaystyle | \atop Cl}{\overset{\displaystyle CH_3 \atop |}{C}}-NO_2$$

(f) *Condensation with aldehyde* :

$$CH_3CHO + CH_3NO_2 \rightarrow \underset{\substack{\beta\text{-Hydroxy nitropropane} \\ \text{(nitro alcohol)}}}{CH_3CH(OH)CH_2NO_2}$$

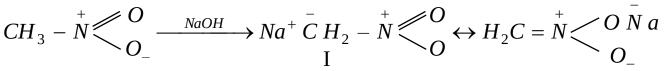
(g) *Reaction with grignard reagent* : The *aci*-form of nitroalkane reacts with Grignard reagent forming alkane.



$$RCH=\overset{+}{N}\begin{smallmatrix}OH\\ \searrow O\end{smallmatrix} + CH_3MgI \rightarrow \underset{\text{Methane}}{CH_4} + RCH=\overset{+}{N}\begin{smallmatrix}OMgI\\ \searrow O\end{smallmatrix}$$

❑ *The nitrogen of –NO₂ carrying a positive charge exerts a powerful – I effect and thus activates the hydrogen atom of the α-carbon. Thus the important reactions of nitroalkanes are those which involve α-hydrogen atom of primary and secondary nitroalkanes* ***(tertiary nitroalkanes have no α-hydrogen atom and hence do not undergo such type of reactions).***

❑ ***Acidic character*** **:***The α-hydrogen atom of primary and secondary nitroalkanes are weakly acidic and thus can be abstracted by strong alkalies like aq. NaOH. Therefore, 1° and 2° nitroalkanes dissolve in aq. NaOH to form salts. For examples.*



$$CH_3-\overset{+}{N}\begin{smallmatrix}\nearrow O\\ \searrow O_-\end{smallmatrix} \xrightarrow{NaOH} Na^+\underset{\text{I}}{\overset{-}{C}}H_2-\overset{+}{N}\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix} \leftrightarrow H_2C=\overset{+}{N}\begin{smallmatrix}O\overset{-}{N}a\\ O_-\end{smallmatrix}$$

Thus 1° and 2° nitroalkanes are acidic mainly due to following two reasons,

(a) Strong electron withdrawing effect of the –NO_2 group.

(b) Resonance stabilisation of the carbanion (I) formed after the removal of proton.

The aci-form of nitroalkanes is relatively more acidic because it produces relatively more conjugate base.

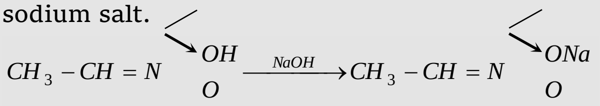
(v) ***Uses*** **:** Nitro alkanes are used,

(a) As solvents for polar substances such as cellulose acetate, synthetic rubber etc.

(b) As an explosive.

(c) For the preparation of amines, hydroxylamines, chloropicrin etc.

Table : 29.1 Distinction between Ethyl nitrite and Nitro ethane

Test	**Ethyl nitrite (C_2H_5ONO)** **(Alkyl nitrite, *RONO*)**	**Nitro ethane ($C_2H_5NO_2$)** **(Nitro alkane, RNO_2)**
Boiling point	Low, 17°*C*	Much higher, 115°*C*
Reduction with metal and acid (*Sn*/*HCl*) or with $LiAlH_4$.	Gives alcohol + hydroxyl amine or NH_3. $C_2H_5ONO + 4H \rightarrow C_2H_5OH + NH_2OH$ $RONO + 6H \rightarrow ROH + NH_3 + H_2O$	Gives corresponding primary amine. $C_2H_5NO_2 + 6H \rightarrow C_2H_5NH_2 + 2H_2O$ $RNO_2 + 6H \rightarrow RNH_2 + 2H_2O$
Action of *NaOH* (alkalies).	Readily hydrolysed to give corresponding alcohol and sodium nitrite (decomposition). $C_2H_5ONO + NaOH \rightarrow C_2H_5OH + NaNO_2$ $RONO + NaOH \rightarrow ROH + NaNO_2$	Not decomposed, *i.e.,* alcohols are not produced. But it may form soluble sodium salt, because in presence of alkali the nitro form changes into aci form, which dissolves in alkalies to form sodium salt.  $CH_3-CH=N\begin{smallmatrix}\nearrow\\ \searrow OH\\ O\end{smallmatrix} \xrightarrow{NaOH} CH_3-CH=N\begin{smallmatrix}\nearrow\\ \searrow ONa\\ O\end{smallmatrix}$
Action of HNO_2 ($NaNO_2$+ *HCl*)	No action with nitrous acid.	Primary nitro alkanes forms nitrolic acid, which dissolve in alkali to give red solution. Secondary nitro alkane yields pseudo-nitrol, which dissolves in alkali to give blue solution. Tertiary nitro alkanes does not react with nitrous acid.

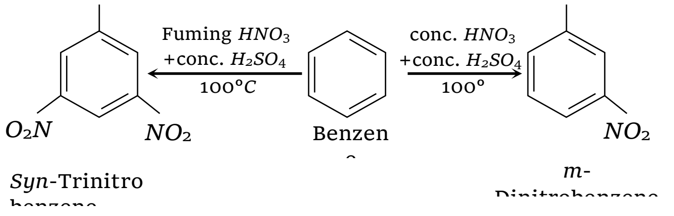
Aromatic Nitro Compounds

Aromatic nitro compounds are the derivatives of aromatic hydrocarbons in which one or more hydrogen atom (s) of the benzene nucleus has been replaced by nitro (– NO_2) group.

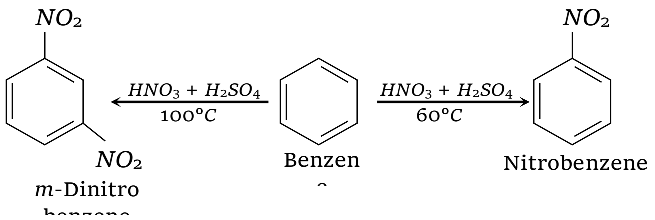
(1) **Preparation**

(i) ***Nitration (Direct method)*** : The number of –NO_2 groups introduced in benzene nucleus depends upon the nature and concentration of the nitrating agent, temperature of nitration and nature of the compound to be nitrated.

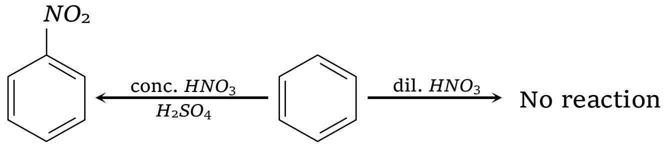
(a) *The nature of the nitrating agent* : For example,

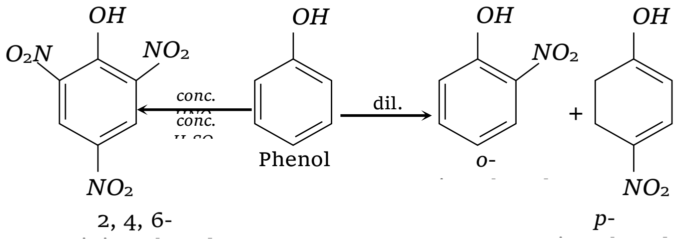


(b) *Temperature of nitration* : For example,



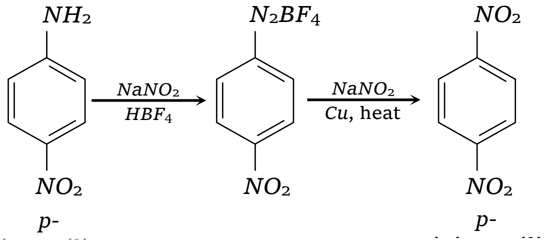
(c) *Nature of the compound to be nitrated : Presence of electron-releasing group like –OH, –NH₂, –CH₃, –OR, etc., in the nucleus facilitates nitration*. Thus aromatic compounds bearing these groups (i.e. phenol, aniline, toluene, etc.) can be nitrated readily as compared to benzene. Thus benzene is not affected by dilute HNO_3 while phenol, aniline and toluene forms the corresponding *ortho*- and para-nitro compounds.





On the other hand, nitration of aromatic compounds having electron withdrawing groups like $-NO_2$, $-SO_3H$ requires powerful nitrating agent (like fuming HNO_3 + conc. H_2SO_4) and a high temperature.

(ii) ***Indirect method*** **:** The aromatic nitro compounds which can not be prepared by direct method may be prepared from the corresponding amino compound.



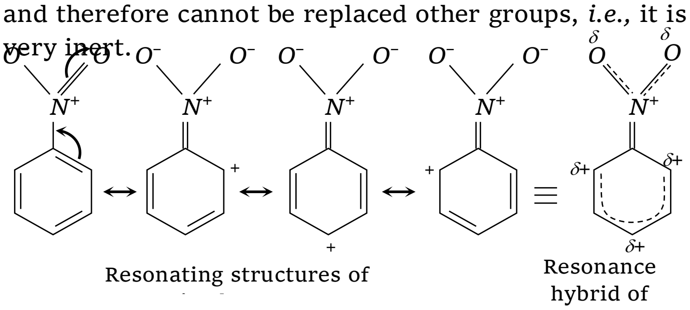
(2) **Physical properties**

(i) Aromatic nitro compounds are insoluble in water but soluble in organic solvents.

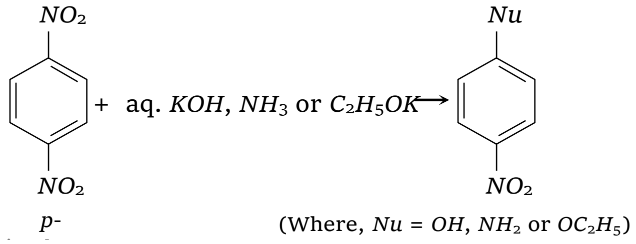
(ii) They are either pale yellow liquids or solids having distinct smells. For example, *nitro benzene* (*oil of Mirabane*) *is a pale yellow liquid having a smell of bitter almonds*.

(3) **Chemical properties**

(i) Resonance in nitrobenzene imparts a partial double bond character to the bond between carbon of benzene nucleus and nitrogen of the – NO_2 group with the result the – NO_2 group is firmly bonded to the ring and therefore cannot be replaced other groups, *i.e.*, it is very inert.



(ii) ***Displacement of the – NO₂ group*** **:** Although – NO_2 group of nitrobenzene cannot be replaced by other groups, but if a second – NO_2 group is present on the benzene ring of nitrobenzene in the *o*- or *p*- position, it can be replaced by a nucleophile. For example,



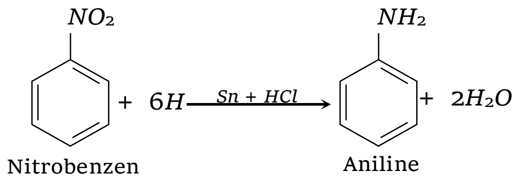
(Where, $Nu = OH$, NH_2 or OC_2H_5)

(iii) ***Reduction*** **:** Aromatic nitro compounds can be reduced to a variety of product as shown below in the case of nitrobenzene.

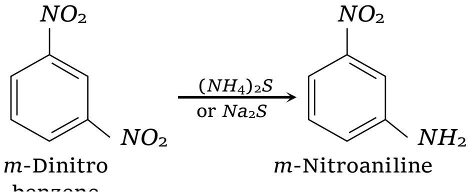
$$\underset{\text{Nitrobenzene}}{C_6H_5NO_2} \rightarrow \underset{\text{Nitrosobenzene}}{C_6H_5NO} \rightarrow \underset{\text{Phenylhydroxylamine}}{C_6H_5NHOH} \rightarrow \underset{\text{Aniline}}{C_6H_5NH_2}$$

The nature of the final product depends mainly on the *nature (acidic, basic or neutral) of the reduction medium and the nature of the reducing agent*.

(a) *Reduction in acidic medium*



Reduction of dinitrobenzene with ammonium sulphide reduces only one – NO_2 group (***selective reduction***)



(b) *Reduction in neutral medium* :

$$\underset{\text{Nitrobenzene}}{C_6H_5NO_2} + 2H \xrightarrow[(-H_2O)]{Zn\ dust + NH_4Cl} \underset{\substack{\text{Nitrosobenzene}\\ \text{(intermediate)}}}{C_6H_5NO} \rightarrow \underset{\text{Phenylhydroxylamine}}{C_6H_5NHOH}$$

(c) *Reduction in alkaline medium* :

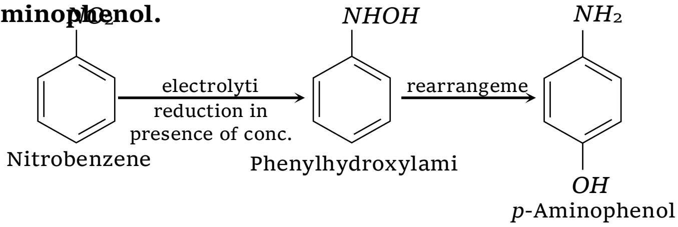
$$\underset{\text{Nitrobenzene}}{C_6H_5NO_2} \xrightarrow{2[H]} \left[\begin{array}{c} C_6H_5NO \\ \text{Nitroso benzene} \\ C_6H_5NHOH \end{array}\right]_{\text{Phenylhydroxylamine}} \xrightarrow{-H_2O} \underset{\text{Azoxy benzene}}{\begin{array}{c} C_6H_5-N\rightarrow O \\ \| \\ C_6H_5-N \end{array}}$$

Azoxybenzene on further reduction yields azobenzene and hydrazobenzene.

$$\underset{\text{Azoxybenzene}}{\begin{array}{c} C_6H_5-N\rightarrow O \\ \| \\ C_6H_5-N \end{array}} \xrightarrow{2[H]} \underset{\text{Azobenzene}}{\begin{array}{c} C_6H_5-N \\ \| \\ C_6H_5-N \end{array}} \xrightarrow{2[H]} \underset{\text{Hydrazobenzene}}{\begin{array}{c} C_6H_5-NH \\ | \\ C_6H_5-NH \end{array}}$$

(d) *Electrolytic reduction* :

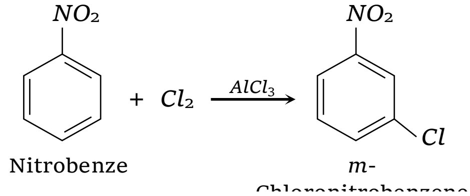
- *Weakly acidic medium* of electrolytic reduction gives **aniline.**
- *Strongly acidic medium* gives phenylhydroxylamine which rearranges to ***p*-aminophenol.**



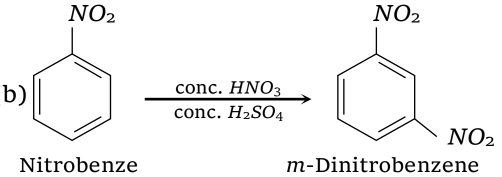
- Alkaline medium of electrolytic reduction gives all the **mono- and di-nuclear reduction products** mentioned above in point (c)**.**

(iv) ***Electrophilic substitution*** **:** Since – NO_2 *group is deactivating and m-directing*, electrophilic substitution (halogenation, nitration and sulphonation) in simple aromatic nitro compounds (*e.g.* nitrobenzene) is very difficult as compared to that in benzene. Hence vigorous reaction conditions are used for such reaction and the new group enters the *m*-position.

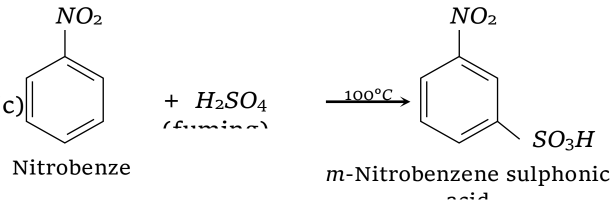
(a)



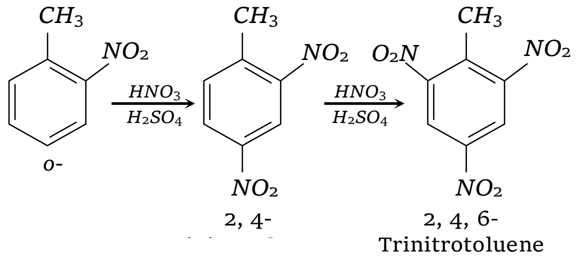
(b)



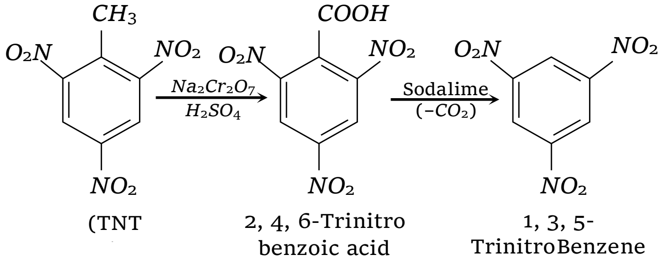
(c)



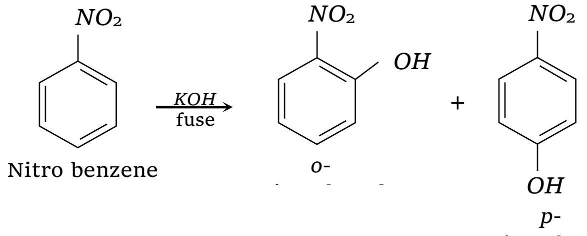
Although nitrobenzene, itself undergoes electrophilic substitution under drastic conditions, nitrobenzene having activating groups like alkyl, – *OR*, – NH_2 etc. undergoes these reactions relatively more readily.



Sym-trinitrobenzene (TNB) is preferentially prepared from easily obtainable TNT rather than the direct nitration of benzene which even under drastic conditions of nitration gives poor yields.

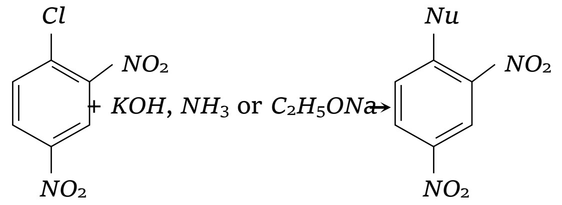


(v) ***Nucleophilic Substitution*** : Benzene is inert to nucleophiles, but the presence of – NO_2 group in the benzene ring activates the latter in *o*- and *p*-positions to nucleophiles.



(vi) ***Effect of the – NO₂ group on other nuclear substituents***

(a) *Effect on nuclear halogen* : The nuclear halogen is ordinarily inert, but if it carries one or more electron-withdrawing groups (like – NO_2) in *o*- or *p*-position, the halogen atom becomes active for nucleophilic substitutions and hence can be easily replaced by nucleophiles $(KOH, NH_3, NaOC_2H_5)$.

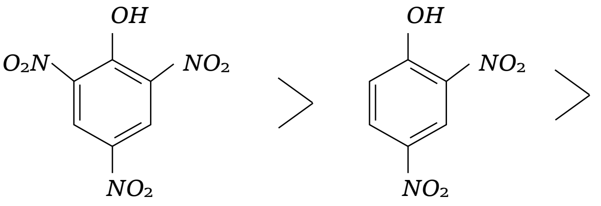


2, 4-

(Where, Nu = OH, NH_2,

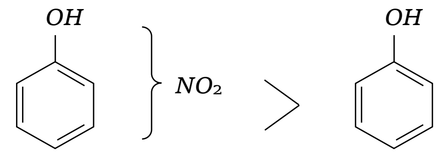
(b) *Effect on phenolic –OH group* : The acidity of the phenolic hydroxyl group is markedly increased by the presence of – NO_2 group in *o*- and *p*-position.

The decreasing order of the acidity of nitrophenols follows following order



2, 4, 6-Trinitro phenal

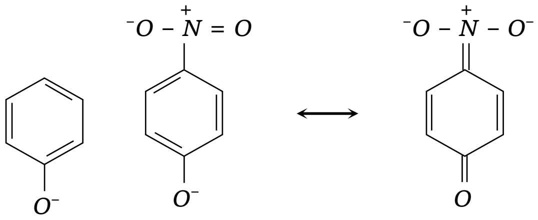
2, 4-Dinitrophenol



o- and *p*-Nitrophenols

Phenol

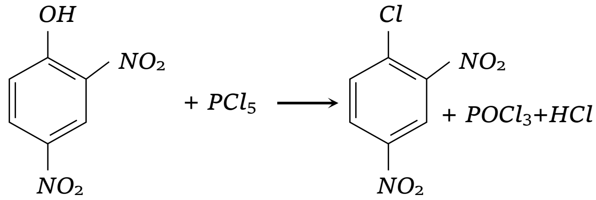
Increased acidity of *o*- **and** *p*-**nitrophenols** *is because of the fact that the presence of electron-withdrawing – NO_2 group in o-and p-position (s) to phenolic –OH group stabilises the phenoxide ions* (recall that acidic nature of phenols is explained by resonance stabilisation of the phenoxide ion) *to a greater extent.*



Phenoxide ion
(no $-NO_2$

Extra stabilisation of *p*-nitrophenate ion

Due to increased acidity of nitrophenols, the latter react with phosphorus pentachloride to give good yields of the corresponding chloro derivative, while phenol itself when treated with PCl_5 gives poor yield of chlorobenzene.



2, 4-Dinitrophenol

2, 4-Dinitrochlorobenzene

(4) **Uses**

(i) On account of their high polarity, aromatic nitro compounds are used as solvents.

(ii) Nitro compounds like TNT, picric acid, TNB etc. are widely used as ***explosives.***

(iii) These are used for the synthesis of aromatic amino compounds.

(iv) Nitro benzene is used *in the preparation of shoe polish and scenting of cheap soaps*.

Cyanides and Isocyanides

Hydrogen cyanide is known to exist as a tautomeric mixture.

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

Hence, it forms two types of alkyl derivatives which are known as alkyl cyanides and alkyl isocyanides.

$$\underset{\text{Alkyl Cyanide}}{R-C\equiv N} \qquad \underset{\text{Alkyl isocyanide}}{R-N \overset{\rightarrow}{=} C}$$

(1) **Alkyl Cyanides**

(i) ***Methods of preparation***

(a) *From alkyl halides* : The disadvantage of this method is that a mixture of nitrile and isonitrile is formed.

$$\underset{\substack{\text{Alkyl}\\\text{halide}}}{RX} + KCN(or NaCN) \rightarrow \underset{\substack{\text{Nitrile}\\\text{(Major product)}}}{RCN} + \underset{\substack{\text{Isonitrile}\\\text{(Minor product)}}}{RNC}$$

(b) *From acid amides* : $RCONH_2 \xrightarrow[-H_2O]{P_2O_5} RCN$

$$\underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow{P_2O_5} \underset{\text{Methylcyanide}}{CH_3CN} + H_2O$$

Industrially, alkyl cyanides are prepared by passing a mixture of carboxylic acid and ammonia over alumina at 500°*C*.

$$\underset{\text{Acid}}{RCOOH} + NH_3 \rightarrow \underset{\text{Ammonium salt}}{RCOONH_4} \xrightarrow[-H_2O]{Al_2O_3}$$

$$\underset{\text{Amide}}{RCONH_2} \xrightarrow[-H_2O]{Al_2O_3} \underset{\text{Alkylcyanide}}{RCN}$$

(c) *From Grignard reagent*

$$\underset{\substack{\text{Grignard}\\\text{reagent}}}{RMgX} + ClCN \rightarrow \underset{\substack{\text{Alkyl}\\\text{cyanide}}}{RCN} + Mg\left\langle\begin{matrix}X\\Cl\end{matrix}\right.$$

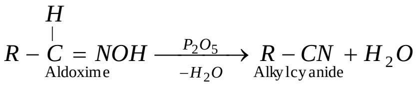
$$\underset{\substack{\text{Methylmagnesium}\\\text{bromide}}}{CH_3MgBr} + \underset{\substack{\text{Cyanogen}\\\text{chloride}}}{ClCN} \rightarrow \underset{\text{Methylcyanide}}{CH_3CN} + Mg\left\langle\begin{matrix}Br\\Cl\end{matrix}\right.$$

(d) *From primary amines* : Primary amines are dehydrogenated at high temperature to form alkyl cyanides. This is also a ***commercial method.***

$$\underset{\text{Primary amine}}{RCH_2NH_2} \xrightarrow[500°C]{Cu \text{ or } Ni} RCN + 2H_2$$

$$\underset{\text{Ethylamine}}{CH_3CH_2NH_2} \xrightarrow[500°C]{Cu \text{ or } Ni} \underset{\text{Methyl cyanide}}{CH_3CN} + 2H_2$$

(e) *From oximes* :



$$\underset{\text{Aldoxime}}{R - \overset{\overset{\displaystyle H}{|}}{C} = NOH} \xrightarrow[-H_2O]{P_2O_5} \underset{\text{Alkyl cyanide}}{R - CN} + H_2O$$

(ii) ***Physical properties***

(a) Alkyl cyanides are neutral substance with pleasant odour, similar to bitter almonds.

(b) Lower members containing upto 15 carbon atoms are liquids, while higher members are solids.

(c) They are soluble in water. The solubility decreases with the increase in number of carbon atoms in the molecule.

(d) They are soluble in organic solvents.

(e) They are poisonous but *less poisonous than HCN*

(iii) ***Chemical properties***

(a) *Hydrolysis*

$$\underset{\substack{\text{Alkyl}\\\text{cyanide}}}{RCN} \xrightarrow[H^+]{H_2O} \underset{\text{Amide}}{RCONH_2} \xrightarrow[H^+]{H_2O} \underset{\text{Acid}}{RCOOH} + NH_3$$

$$\underset{\substack{\text{Methyl}\\\text{cyanide}}}{CH_3CN} \xrightarrow[H^+]{H_2O} \underset{\text{Acetamide}}{CH_3CONH_2}$$

$$\xrightarrow[H^+]{H_2O} \underset{\text{Acetic acid}}{CH_3COOH} + NH_3$$

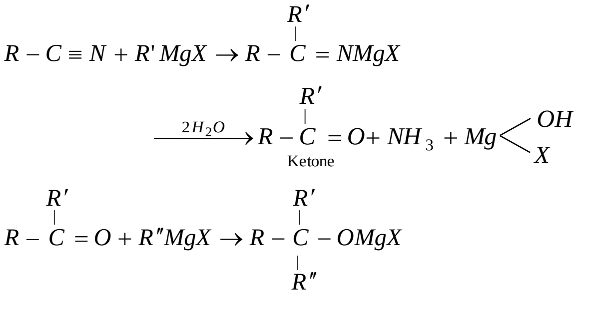
(b) *Reduction* : When reduced with hydrogen in presence of *Pt* or *Ni*, or $LiAlH_4$ (Lithium aluminium hydride) or sodium and alcohol, alkyl cyanides yield primary amines.

$$\underset{\text{Alkyl cyanide}}{RCN} \xrightarrow{4H} \underset{\text{Primary amine}}{RCH_2NH_2}$$

However, when a solution of alkyl cyanides in ether is reduced with stannous chloride and hydrochloric acid and then steam distilled, an aldehyde is formed (***Stephen's reaction***).

$$R - C \equiv N \xrightarrow[[2H]]{SnCl_2/HCl} \underset{\text{Imine hydrochloride}}{RCH = NH.HCl} \xrightarrow{H_2O} \underset{\text{Aldehyde}}{RCHO} + NH_4Cl$$

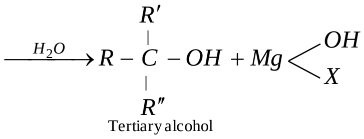
(c) *Reaction with Grignard reagent* : With grignard's reagent, an alkyl cyanide forms a ketone which further reacts to form a tertiary alcohol.



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

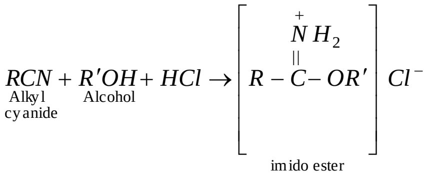
$$\xrightarrow{2H_2O} \underset{\text{Ketone}}{R - \overset{\overset{\displaystyle R'}{|}}{C} = O} + NH_3 + Mg\begin{cases} OH \\ X \end{cases}$$

$$R - \overset{\overset{\displaystyle R'}{|}}{C} = O + R''MgX \rightarrow R - \underset{\underset{\displaystyle R''}{|}}{\overset{\overset{\displaystyle R'}{|}}{C}} - OMgX$$



$$\xrightarrow{H_2O} \underset{\text{Tertiary alcohol}}{R - \underset{\underset{\displaystyle R''}{|}}{\overset{\overset{\displaystyle R'}{|}}{C}} - OH} + Mg\begin{cases} OH \\ X \end{cases}$$

(d) *Alcohololysis* :



$$\underset{\substack{\text{Alkyl}\\\text{cyanide}}}{RCN} + \underset{\text{Alcohol}}{R'OH} + HCl \rightarrow \underset{\text{imido ester}}{\left[R - \overset{\overset{\overset{+}{N}H_2}{||}}{C} - OR' \right]} Cl^-$$

$$\xrightarrow{H_2O} \underset{\text{Ester}}{RCOOR'} + NH_4Cl$$

(iv) ***Uses*** : Alkyl cyanides are important intermediates in the organic synthesis of a large number of compounds like acids, amides, esters, amines etc.

(2) **Alkyl Isocyanides**

(i) ***Methods of preparation***

(a) *From alkyl halides* :

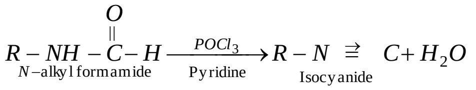
$$\underset{\text{Alkyl halide}}{R - X} + AgCN \rightarrow \underset{\substack{\text{Isocyanide}\\\text{(Isonitrile)}\\\text{Main product}}}{RNC} + \underset{\substack{\text{Cyanide}\\\text{(Nitrile)}\\\text{Minor product}}}{RCN}$$

$$\underset{\text{Methyl chloride}}{CH_3Cl} + AgCN \rightarrow \underset{\substack{\text{Methyl isocyanide}\\\text{(Main product)}}}{CH_3NC} + CH_3CN$$

(b) *From primary amines* (*Carbylamine reaction*) :

$$\underset{\text{Primary amine}}{RNH_2} + \underset{\text{Chloroform}}{CHCl_3} + 3KOH \rightarrow \underset{\text{Isocyanide}}{RNC} + 3KCl + 3H_2O$$

(c) *From N-alkyl formamides* :



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

(ii) ***Physical properties***

(a) Alkyl isocyanides are colourless, unpleasant smelling liquids.

(b) They are insoluble in water but freely soluble in organic solvents.

(c) Isonitriles are much more poisonous than isomeric cyanides.

(iii) ***Chemical properties***

(a) *Hydrolysis* :

$$\underset{\text{Alkyl isocyanide}}{RN \overset{\rightarrow}{\equiv} C} + 2H_2O \xrightarrow{H^+} \underset{\text{Primary amine}}{RNH_2} + \underset{\text{Formic acid}}{HCOOH}$$

(b) *Reduction* : $\underset{\text{Alkyl isocyanide}}{R - N \overset{\rightarrow}{\equiv} C} + 4H \xrightarrow[300^oC]{Ni} \underset{\text{secondary amine}}{RNHCH_3}$

(c) *Action of heat* : When heated for sometime at 250°*C*, a small amount of isonitrile changes into isomeric nitrile.

$$RNC \xrightarrow{\text{heat}} RCN$$

(d) *Addition reaction* : Alkyl isocyanide give addition reactions due to presence of unshared electron pair on carbon atom.

$$R:N:::C: \text{ or } R-\overset{+}{N}\equiv\overset{-}{C}$$

The following are some of the addition reactions shown by alkyl isocyanides.

$$RNC + \underset{\text{(Halogen)}}{X_2} \rightarrow \underset{\text{Alkyliminocarbonyl halide}}{RNCX_2}$$

$$RNC + S \rightarrow \underset{\text{Alkyl isothiocyanate}}{RNCS}\ ;\ RNC + HgO \rightarrow \underset{\text{Alkyl isocyanate}}{RNCO} + Hg$$

(iv) ***Uses*** **:** Due to their unpleasant smell, alkyl isocyanides are used in detection of very minute leakage. Carbylamine reaction is used as a test for the detection of primary amino group.

❑ ***Methyl isocyanate (MIC)gas*** *was responsible for Bhopal gas tragedy in Dec. 1984.*

❑ *Cyanides have more polar character than isocyanides. Hence cyanides have high boiling points and are more soluble in water. However, both isomers are more polar than alkylhalides, hence their boiling points are higher than the* ***corresponding alkyl halides.***

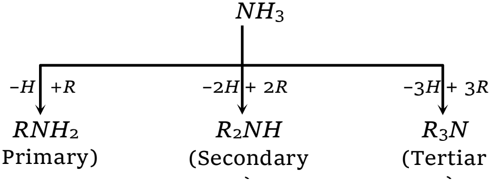
❑ *Being less polar, isocyanides are not attacked by OH^- ions.*

Table : 29.2 *Comparison of Alkyl Cyanides and Alkyl Isocyanides*

Test	Ethyl cyanide	Ethyl isocyanide
Smell	Strong but pleasant	Extremely unpleasant
Dipole moment	More (≈ 4D)	Less (≈ 3D)
B.P.	98°C(i.e. High)	78°C (i.e. low)
Solubility in water.	Soluble	Insoluble
Hydrolysis with acids	Gives propionic acid (Acid, in general)	Give ethyl amine (1° amine, in general)
Hydrolysis with alkalies	Same as above	No action
Reduction	Gives propylamine (1° amine, in general)	Gives ethylmethyl amine (2° amine, in general)
Stephen's reaction	Gives propionaldehyde (Aldehyde, in general)	Does not occur
Heating (250°C)	No effect	Ethyl cyanide is formed

Amines

Amines are regarded as ***derivatives of ammonia*** in which one, two or all three hydrogen atoms are replaced by alkyl or aryl group.

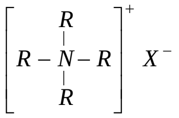


Amines are classified as primary, secondary or tertiary depending on the *number of alkyl groups attached to nitrogen atom.*

The characteristic groups in primary, secondary and tertiary amines are: $\underset{\text{(amino)}}{-NH_2}$; $\underset{\text{(imino)}}{-\overset{|}{N}H}$; $\underset{(tert\text{–nitrogen})}{-\overset{|}{\underset{|}{N}}}$

In addition to above amines, tetra-alkyl derivatives similar to ammonium salts also exist which are called ***quaternary ammonium compounds.***

NH_4I ; $\underset{\text{Quaternary ammonium iodide}}{R_4NI}$; $\underset{\text{Tetramethyl ammonium iodide}}{(CH_3)_4NI}$ or

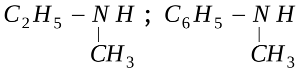


$$\left[R-\overset{\overset{R}{|}}{\underset{\underset{R}{|}}{N}}-R\right]^+ X^-$$

Tetra-alkyl ammonium salt

(1) **Simple and mixed amines :** Secondary and tertiary amines may be classified as ***simple*** or ***mixed*** amines according as all the alkyl or aryl groups attached to the nitrogen atom are same or different. For example,

Simple amines : $\underset{\text{Dimethylamine}}{(CH_3)_2NH}$; $\underset{\text{Triethylamine}}{(CH_3CH_2)_3N}$



Mixed amines : $\underset{\text{Ethylmethylamine}}{C_2H_5-\underset{\underset{CH_3}{|}}{N}H}$; $\underset{\text{Methylaniline}}{C_6H_5-\underset{\underset{CH_3}{|}}{N}H}$

The aliphatic amines have *pyramidal shape* with one electron pair. In amines, *N undergoes* ***sp^3 hybridisation***.

(2) **General methods of preparation**

(i) ***Methods yielding mixture of amines (Primary, secondary and tertiary)***

(a) *Hofmann's method* :The mixture of amines (1°, 2° and 3°) is formed by the ***alkylation of ammonia with alkyl halides.***

$$\underset{\text{Methyliodide}}{CH_3I} + NH_3 \rightarrow \underset{\substack{\text{Methylamine}\\(1°)}}{CH_3NH_2} \xrightarrow{CH_3I} \underset{\substack{\text{Dimethylamine}\\(2°)}}{(CH_3)_2NH}$$

$$\xrightarrow{CH_3I} \underset{\substack{\text{Trimethylamine}\\(3°)}}{(CH_3)_3N} \xrightarrow{CH_3I} \underset{\substack{\text{Tetramethyl}\\\text{ammonium iodide}}}{(CH_3)_4NI}$$

The primary amine may be obtained in a good yield by using a large excess of ammonia. The process is also termed as ***ammonolysis of alkyl halides.*** It is a nucleophilic substitution reaction.

(b) *Ammonolysis of alcohols* :

$$CH_3OH + NH_3 \xrightarrow[350°C]{Al_2O_3} CH_3NH_2$$

$$\xrightarrow{CH_3OH} (CH_3)_2NH \xrightarrow{CH_3OH} (CH_3)_3N$$

Primary amine may be obtained in a good yield by using a excess of ammonia.

(ii) ***Methods yielding primary amines***

(a) *Reduction of nitro compounds*

$$R - NO_2 + 6[H] \xrightarrow[Zn/HCl \text{ or } Ni \text{ or } LiAlH_4]{Sn/HCl \text{ or}} RNH_2 + 2H_2O$$

$$C_2H_5 - NO_2 + 6[H] \rightarrow C_2H_5NH_2 + 2H_2O$$

(b) *Reduction of nitriles (Mendius reaction)*

$$R - C \equiv N + 4[H] \rightarrow R - CH_2NH_2$$

$$\underset{\text{Methylcyanide}}{CH_3C \equiv N} + 4[H] \rightarrow \underset{\text{Ethylamine}}{CH_3 - CH_2NH_2}$$

The start can be made from alcohol or alkyl halide.

$$\underset{\text{Alcohol}}{R - OH} \xrightarrow{SOCl_2} \underset{\text{Alkylchloride}}{R - Cl} \xrightarrow{KCN}$$

$$\underset{\text{Alkylnitrile}}{R - CN} \xrightarrow[Na + C_2H_5OH]{LiAlH_4 or} \underset{\text{Primaryamine}}{RCH_2NH_2}$$

This sequence gives an amine containing one more carbon atom than alcohol.

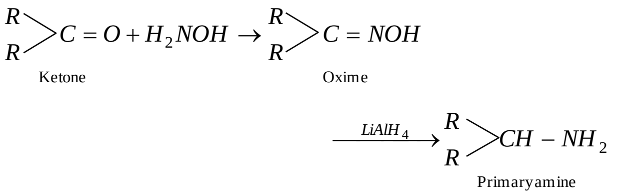
(c) *By reduction of amides with LiAlH₄*

$$RCONH_2 \xrightarrow{LiAlH_4} RCH_2NH_2$$

$$\underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow{LiAlH_4} \underset{\text{Ethylamine}}{CH_3CH_2NH_2}$$

(d) *By reduction of oximes* : The start can be made from an aldehyde or ketone.

$$\underset{\text{Aldehyde}}{RCHO} \xrightarrow{H_2NOH} \underset{\text{Oxime}}{RCH = NOH} \xrightarrow[orH_2/Ni]{LiAlH_4} \underset{\text{Primaryamine}}{RCH_2NH_2}$$



$$\underset{\text{Ketone}}{\begin{matrix}R\\R\end{matrix}\!\!>C = O} + H_2NOH \rightarrow \underset{\text{Oxime}}{\begin{matrix}R\\R\end{matrix}\!\!>C = NOH}$$

$$\xrightarrow{LiAlH_4} \underset{\text{Primaryamine}}{\begin{matrix}R\\R\end{matrix}\!\!>CH - NH_2}$$

(e) *Hofmann's bromamide reaction or degradation (Laboratory method)* : By this method the *amide (–CONH₂) group is converted into primary amino (– NH₂) group.*

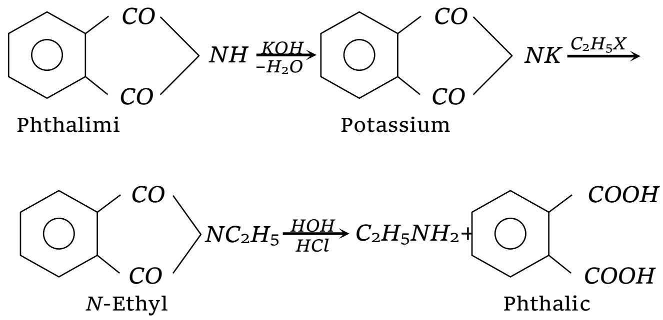
$$\underset{\text{Amide}}{R - CO - NH_2} + Br_2 + 4KOH \rightarrow \underset{\text{Pri-amine}}{R - NH_2} + 2KBr + K_2CO_3 + 2H_2O$$

This is the most convenient method for preparing primary amines.

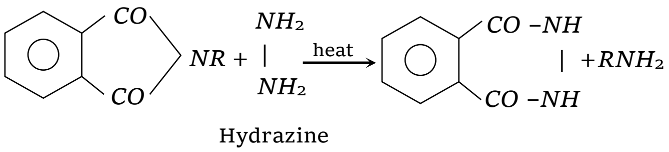
This method gives an ***amine containing one carbon atom less than amide***.

(f) *Gabriel phthalimide synthesis* : This method involves the following three steps.

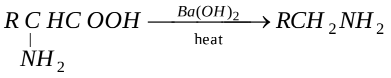
- Phthalimide is reacted with *KOH* to form potassium phthalimide.
- The potassium salt is treated with an alkyl halide.
- The product *N*-alkyl phthalimide is put to hydrolysis with hydrochloric acid when primary amine is formed.



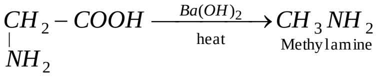
When hydrolysis is difficult, the *N*-alkyl phthalimide can be treated with hydrazine to give the required amine.



(g) *By decarboxylation of α-amino acids*



$$\underset{NH_2}{\underset{|}{RCHCOOH}} \xrightarrow[\text{heat}]{Ba(OH)_2} RCH_2NH_2$$



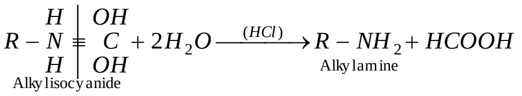
$$\underset{NH_2}{\underset{|}{CH_2-COOH}} \xrightarrow[\text{heat}]{Ba(OH)_2} \underset{\text{Methylamine}}{CH_3NH_2}$$

α-amino acetic acid
(Glycine)

(h) *By means of a Grignard reagent and chloramine* :

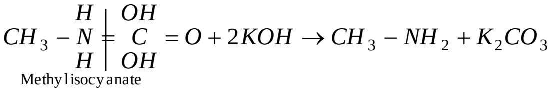
$$RMgX + ClNH_2 \rightarrow RNH_2 + MgXCl$$

(i) *By hydrolysis of Isocyanides or Isocyanates*



$$\underset{\text{Alkylisocyanide}}{R-\overset{H}{\underset{H}{N}} \equiv \overset{OH}{\underset{OH}{C}}} + 2H_2O \xrightarrow{(HCl)} \underset{\text{Alkylamine}}{R-NH_2} + HCOOH$$

$$\underset{\text{methylisonitile}}{CH_3-NC} + 2HOH \xrightarrow{H^+} CH_3-NH_2 + HCOOH$$



$$\underset{\text{Methylisocyanate}}{CH_3-\overset{H}{\underset{H}{N}} = \overset{OH}{\underset{OH}{C}} = O} + 2KOH \rightarrow CH_3-NH_2 + K_2CO_3$$

$$\underset{\text{Alkylisocyanate}}{R-NCO} + 2KOH \rightarrow R-NH_2 + K_2CO_3$$

(j) *By Schmidt reaction* :

$$\underset{\text{Acid}}{R-COOH} + \underset{\substack{\text{Hydrazoic}\\\text{acid}}}{N_3H} \xrightarrow{Conc.H_2SO_4} \underset{\substack{\text{Alkyl}\\\text{amine}}}{R-NH_2} + N_2 + CO_2$$

In this reaction the acyl azide ($R-CON_3$) and alkyl isocyanate ($R-NCO$) are formed as an intermediate.

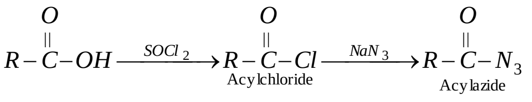
$$R-COOH + N_3H \rightarrow \underset{\text{Acylazide}}{RCON_3} + H_2O$$

$$\underset{\text{Acylazide}}{RCON_3} \rightarrow \underset{\text{Alkylisocyanate}}{R-N=C=O} + N_2$$

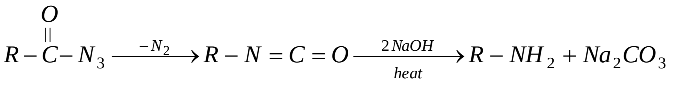
$$R-N=C=O + H_2O \rightarrow \underset{\text{Alkylamine}}{R-NH_2} + CO_2$$

The overall reaction which proceeds by the elimination of nitrogen from acyl azide followed by acidic or alkaline hydrolysis to yield primary amine containing one carbonless, is called ***Curtius Degradation***.

The method uses acid chloride to prepare primary amine through acyl azide.

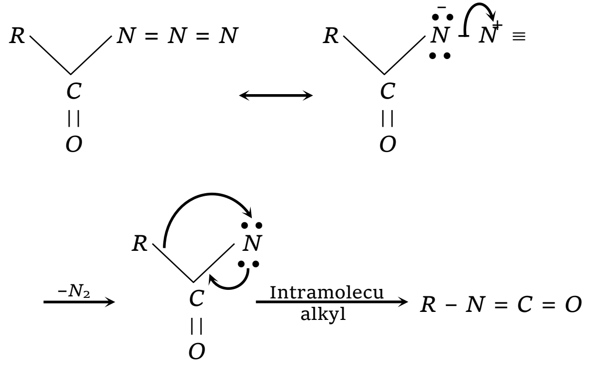


$$R-\overset{\overset{O}{||}}{C}-OH \xrightarrow{SOCl_2} \underset{\text{Acylchloride}}{R-\overset{\overset{O}{||}}{C}-Cl} \xrightarrow{NaN_3} \underset{\text{Acylazide}}{R-\overset{\overset{O}{||}}{C}-N_3}$$

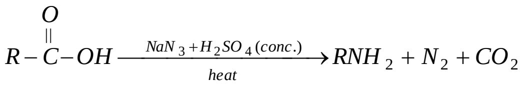


$$R-\overset{\overset{O}{||}}{C}-N_3 \xrightarrow{-N_2} R-N=C=O \xrightarrow[heat]{2NaOH} R-NH_2 + Na_2CO_3$$

The mechanism of **curtius rearrangement** is very similar to Hofmann degradation.



Schmidt reaction converts $R-COOH$ to $R-NH_2$, which is a modification of curtius degradation. In this reaction a carboxylic acid is warmed with sodium azide ($Na^+N_3^-$) and conc. H_2SO_4. The carboxylic acid is directly converted to the primary amine without the necessity of isolating alkyl azide.



$$R-\overset{\overset{O}{||}}{C}-OH \xrightarrow[heat]{NaN_3+H_2SO_4(conc.)} RNH_2 + N_2 + CO_2$$

$$(NaN_3 + H_2SO_4 \rightarrow N_3H + NaHSO_4)$$

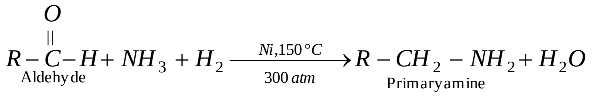
(k) *By Ritter reaction* : It is a good method for preparing primary amines having α-tertiary alkyl group.

$$\underset{\text{Tert-butyl alcohol}}{(CH_3)_3C-OH} + H_2SO_4 + HCN \rightarrow \underset{\substack{\text{Tert–butylamine}\\\text{(1°amine)}}}{(CH_3)_3C-NH_2}$$

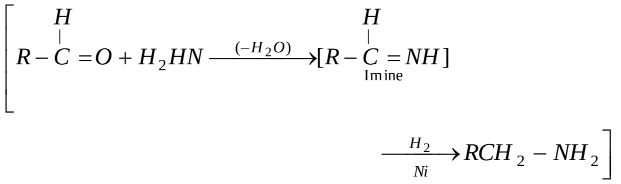
$$\left[R_3C-OH \xrightarrow{H^+} H_2O + \underset{\text{Tert-carboniumion}}{R_3C^+} \xrightarrow{HCN} R_3C\overset{+}{N} \equiv CH\right.$$

$$\left.\xrightarrow{H_2O} CHO-R_3CNH \xrightarrow{OH^-} \underset{\text{Pri-amine}}{R_3C-NH_2} + HCOO^-\right]$$

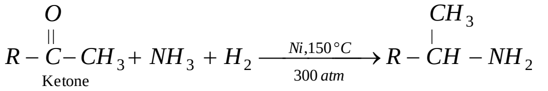
(l) *Reductive amination of aldehydes and ketones* :



$$\underset{\text{Aldehyde}}{R-\overset{\overset{O}{||}}{C}-H} + NH_3 + H_2 \xrightarrow[300\,atm]{Ni,150°C} \underset{\text{Primaryamine}}{R-CH_2-NH_2} + H_2O$$



$$\left[R-\overset{\overset{H}{|}}{C}=O + H_2HN \xrightarrow{(-H_2O)} [\underset{\text{Imine}}{R-\overset{\overset{H}{|}}{C}=NH}] \xrightarrow[Ni]{H_2} RCH_2-NH_2\right]$$



$$\underset{\text{Ketone}}{R-\overset{\overset{O}{||}}{C}-CH_3} + NH_3 + H_2 \xrightarrow[300\,atm]{Ni,150°C} R-\overset{\overset{CH_3}{|}}{CH}-NH_2$$

This reaction probably takes place through the formation of an imine (Schiff's base).

The primary amine can also be converted into sec. or tert. amines by the following steps

$$R-CHO + R'NH_2 \xrightarrow{H_2/Ni} \underset{\text{Sec. amine}}{RCH_2NHR'}$$

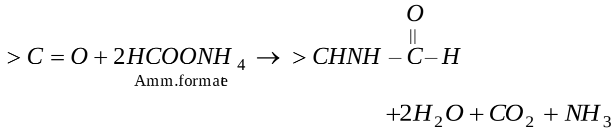
$$RNH_2 + 2H_2C=O + 2HCOOH$$

$$\rightarrow \underset{\text{Tert.-amine}}{RN(CH_3)_2} + 2H_2O + 2CO_2$$

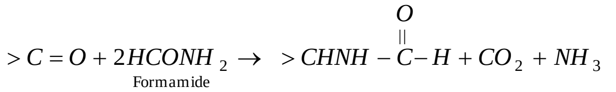
(m) *By reduction of azide with $NaBH_4$*

$$\underset{\substack{\text{Alkylhalide}\\\text{(1°or2°)}}}{R-X} + \underset{\substack{\text{Sodium}\\\text{azide}}}{NaN_3} \rightarrow \underset{\substack{\text{Alkyl}\\\text{azide}}}{RN_3} \xrightarrow[H_2O]{NaBH_4} \underset{\text{1°amine}}{RNH_2}$$

(n) *By Leuckart reaction* : Aldehydes or ketones react with ammonium formate or with formamide to give formyl derivative of primary amine.

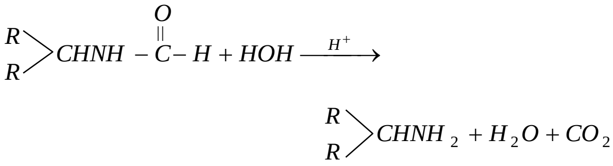


$$>C=O+\underset{\text{Amm.formate}}{2HCOONH_4}\rightarrow\ >CHNH-\overset{O}{\overset{||}{C}}-H$$
$$+2H_2O+CO_2+NH_3$$



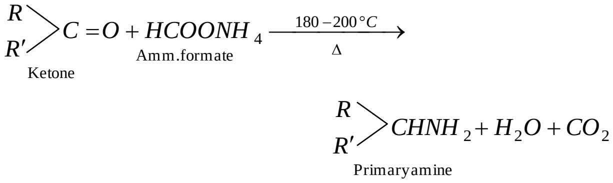
$$>C=O+\underset{\text{Formamide}}{2HCONH_2}\rightarrow\ >CHNH-\overset{O}{\overset{||}{C}}-H+CO_2+NH_3$$

These formyl derivatives are readily hydrolysed by acid to yield primary amine.



$$\begin{matrix}R\\R\end{matrix}\!\!>CHNH-\overset{O}{\overset{||}{C}}-H+HOH\xrightarrow{H^+}$$
$$\begin{matrix}R\\R\end{matrix}\!\!>CHNH_2+H_2O+CO_2$$

This is called Leuckart reaction, *i.e.,*



$$\underset{\text{Ketone}}{\begin{matrix}R\\R'\end{matrix}\!\!>C=O}+\underset{\text{Amm.formate}}{HCOONH_4}\xrightarrow[\Delta]{180-200^\circ C}$$
$$\underset{\text{Primaryamine}}{\begin{matrix}R\\R'\end{matrix}\!\!>CHNH_2}+H_2O+CO_2$$

❑ *On commercial scale, ethylamine is obtained by heating a mixture of ethylene and ammonia at 450°C under 20 atmospheric pressure in presence of cobalt catalyst.*

$$\underset{\text{Ethylene}}{CH_2=CH_2}+NH_3\xrightarrow[450^\circ C,20\,atm]{\text{Cobalt catalyst}}CH_3CH_2NH_2$$

(iii) ***Methods yielding secondary amines***

(a) *Reaction of primary amines with alkyl halides*

$$R-NH_2+R-X\xrightarrow{\Delta}R_2NH+HX\rightarrow\underset{\text{dialkyl ammonium salt}}{R_2\overset{+}{N}H_2\overset{-}{X}}$$

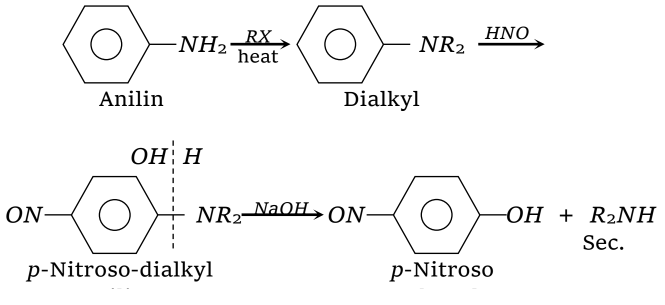
$$R_2\overset{+}{N}H_2\overset{-}{X}+NaOH\rightarrow\underset{\text{Secondary amine}}{R_2NH}+H_2O+NaX$$

(b) *Reduction of isonitriles* :

$$\underset{\text{Alkylisonitrile}}{R-NC}+4[H]\xrightarrow{Pt}\underset{\text{Sec. amine}}{RNHCH_3}$$

Secondary amine formed by this method always possesses one $-CH_3$ group linked directly to nitrogen.

(c) *Reaction of p-nitroso-dialkyl aniline with strong alkali solution* :



This is one of the best method for preparing pure secondary amines.

(d) *Hydrolysis of dialkyl cyanamide*

$$\left[\underset{\text{Calcium cyanamide}}{CaN-CN}\xrightarrow{2NaOH}\underset{\text{Sodium cyanamide}}{Na_2N-CN}\xrightarrow{2RX}\underset{\text{Dialkyl cyanamide}}{R_2N-CN}\right]$$

$$R_2N-CN+2HOH\xrightarrow[OH^-]{H^+ or}\underset{\text{Dialkylamine}}{R_2NH}+CO_2+NH_3$$

(e) *Reduction of N-substituted amides* : Reduction of *N*-substituted amides with $LiAlH_4$ yields secondary amines.

Alkyl *β*-amino ketones are formed by the action of ketone with formaldehyde and NH_3 (or primary or secondary amines).

The product is referred to as Mannich base and the reaction is called **Mannich Reaction.**

$$CH_3COCH_3+HCHO+RNH_2\xrightarrow{heat}CH_3COCH_2CH_2NHR$$

Which can be reduced to alkyl amines.

$$\underset{N\text{-Alkylacid amide}}{R-CONHR'}+4[H]\xrightarrow{LiAlH_4}\underset{\text{Sec.amine}}{RCH_2NHR'}+H_2O$$

(iv) ***Methods yielding tertiary amines***

(a) *Reaction of alkylhalides with ammonia*

$$3RX+NH_3\rightarrow R_3N+3HX\rightarrow\underset{\text{Trialkylammonium salt}}{R_3\overset{+}{N}H\overset{-}{X}}$$

$$R_3\overset{+}{N}H\overset{-}{X}+NaOH\rightarrow R_3N+NaX+H_2O$$

(b) *Reduction of N, N-disubstituted amides* : The carbonyl group is converted into – CH_2 group.

$$\underset{N,N\text{-disubstituted amide}}{RCONR'_2}\xrightarrow[4[H]]{LiAlH_4}\underset{\text{ter. amine}}{RCH_2NR'_2}+H_2O$$

(c) *Decomposition of tetra-ammonium hydroxides* : The tetra-alkyl ammonium hydroxides are formed when corresponding halides are treated with moist silver oxide.

$$R_4\overset{+}{N}\overset{-}{I}+AgOH\rightarrow R_4\overset{+}{N}O\overset{-}{H}+AgI$$

The hydroxides thus formed on heating decompose into tertiary amines. Tetramethyl ammonium hydroxide gives methyl alcohol as one of the products while all other tetra-alkyl ammonium hydroxides give an olefin and water besides tertiary amines.

$$(CH_3)_4NOH\rightarrow(CH_3)_3N+CH_3OH$$

$$(R)_4NOH\rightarrow(R)_3N+\text{olefin}+H_2O$$

(3) **Separation of mixture of amines :** When the mixture consists of salts of primary, secondary and tertiary amines along with quaternary salt, ***it is first distilled with KOH solution***. The mixture of three amines distils over leaving behind non-volatile quaternary salt.

$$RNH_2.HI \text{ or } RN\overset{+}{H}_3 - \overset{-}{I} + \overset{+}{K}O\overset{-}{H} \rightarrow \underset{\substack{\text{Primary amine}\\ \text{(Volatile), Distillate}}}{RNH_2} + KI + H_2O$$

$$R_2NH.HI \text{ or } R_2N\overset{+}{H}_2 - \overset{-}{I} + \overset{+}{K}O\overset{-}{H} \rightarrow R_2NH + KI + H_2O$$

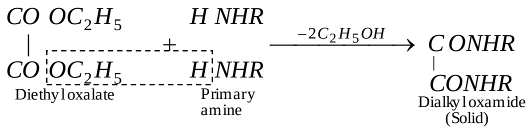
$$R_3N.HI \text{ or } R_3N\overset{+}{H} - \overset{-}{I} + \overset{+}{K}O\overset{-}{H} \rightarrow R_3N + KI + H_2O$$

$R_4\overset{+}{N}\overset{-}{I}$ (non-volatile tetra-alkyl ammonium salt) has no reaction with *KOH*, however remains as residue.

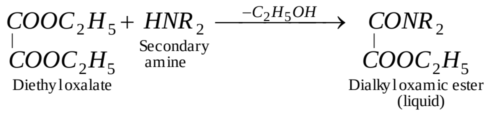
This mixture is separated into primary, secondary and tertiary amines by the application of following methods.

(i) ***Fractional distillation*** **:** The boiling points of primary, secondary and tertiary amines are quite different, *i.e., the boiling point of $C_2H_5NH_2$ is 17°C, $(C_2H_5)_2NH$ is* 56°*C* and $(C_2H_5)_3N$ is 95°*C* and thus, these can be separated by fractional distillation. This method is used satisfactorily in industry.

(ii) ***Hofmann's method*** **:** The mixture of three amines is treated with diethyl oxalate. The primary amine forms a solid oxamide, a secondary amine gives a liquid oxamic ester while tertiary amine does not react.

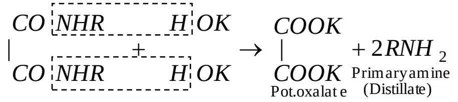


$$\underset{\text{Diethyl oxalate}}{\begin{array}{l} CO\,OC_2H_5 \\ | \\ CO\,\boxed{OC_2H_5} \end{array}} + \underset{\text{Primary amine}}{\begin{array}{l} H\,NHR \\ \\ \boxed{H}\,NHR \end{array}} \xrightarrow{-2C_2H_5OH} \underset{\substack{\text{Dialkyl oxamide}\\ \text{(Solid)}}}{\begin{array}{l} CONHR \\ | \\ CONHR \end{array}}$$



$$\underset{\text{Diethyl oxalate}}{\begin{array}{l} COOC_2H_5 \\ | \\ COOC_2H_5 \end{array}} + \underset{\text{Secondary amine}}{HNR_2} \xrightarrow{-C_2H_5OH} \underset{\substack{\text{Dialkyl oxamic ester}\\ \text{(liquid)}}}{\begin{array}{l} CONR_2 \\ | \\ COOC_2H_5 \end{array}}$$

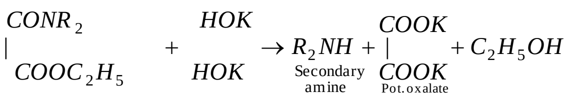
Primary amine is recovered when solid oxamide is heated with caustic potash solution and collected as distillate on distilling the reaction mixture.



$$\begin{array}{l} CO\,\boxed{NHR \quad H}\,OK \\ | \qquad + \\ CO\,\boxed{NHR \quad H}\,OK \end{array} \rightarrow \underset{\text{Pot. oxalate}}{\begin{array}{l} COOK \\ | \\ COOK \end{array}} + \underset{\substack{\text{Primary amine}\\ \text{(Distillate)}}}{2RNH_2}$$

The liquid (mixture of oxamic ester+ tertiary amine) is subjected to fractional distillation when tertiary amine distils over.

The remaining liquid is distilled with *KOH* to recover secondary amine.



$$\begin{array}{l} CONR_2 \\ | \\ COOC_2H_5 \end{array} + \begin{array}{l} HOK \\ \\ HOK \end{array} \rightarrow \underset{\text{Secondary amine}}{R_2NH} + \underset{\text{Pot. oxalate}}{\begin{array}{l} COOK \\ | \\ COOK \end{array}} + C_2H_5OH$$

(iii) ***Hinsberg's method*** **:** It involves the treatment of the mixture with benzene sulphonyl chloride, *i.e.,* ***Hinsberg's reagent*** ($C_6H_5SO_2Cl$). The solution is then made alkaline with aqueous alkali to form *sodium or potassium salt of monoalkyl benzene sulphonamide* (soluble in water).

$$C_6H_5SO_2Cl + \underset{\text{Primary amine}}{HNHR} \rightarrow \underset{\substack{N\text{-Alkyl benzene}\\ \text{sulphonamide}}}{C_6H_5SO_2NHR}$$

$$\xrightarrow{NaOH} \underset{\text{Soluble salt}}{C_6H_5SO_2N(Na)R}$$

The secondary amine forms *N,N*-dialkyl benzene sulphonamide which does not form any salt with *NaOH* and remains as insoluble in alkali solution.

$$C_6H_5SO_2Cl + \underset{\text{Sec. amine}}{HNR_2} \rightarrow C_6H_5SO_2NR_2$$

$$\xrightarrow{NaOH} \underset{\substack{\text{(Insoluble in water,}\\ \text{soluble in ether)}}}{\text{No reaction}}$$

Tertiary amine does not react.

The above alkaline mixture of the amines is extracted with ether.

Two distinct layers are formed. Lower layer, the aqueous layer consists of sodium salt of *N*-alkyl benzene sulphonamide (primary amine) and upper layer, the ether layer consists of *N,N*-dialkyl benzene sulphonamide (secondary amine) and tertiary amine.

Two layers are separated. The upper layer is fractionally distilled. One fraction obtained is tertiary amine and the other fraction is treated with concentrated *HCl* to recover secondary amine hydrochloride which gives free secondary amine on distillation with *NaOH*.

$$C_6H_5SO_2NR_2 + HCl + H_2O \rightarrow C_6H_5SO_2.OH + R_2NH.HCl$$

$$R_2NH.HCl + NaOH \rightarrow \underset{\text{Sec. amine}}{R_2NH} + NaCl + H_2O$$

The aqueous layer is acidified and hydrolysed with dilute *HCl*. The hydrochloride formed is then distilled with *NaOH* when primary amine distils over.

$$C_6H_5SO_2N(Na)R + HCl \rightarrow \underset{\substack{\text{Sulphonamide of}\\ \text{primary amine}}}{C_6H_5SO_2NHR} + NaCl$$

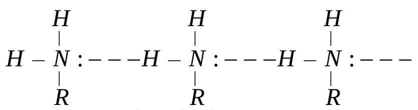
$$C_6H_5SO_2NHR + HCl + H_2O \rightarrow C_6H_5SO_2.OH + \underset{\substack{\text{Primary amine}\\ \text{hydrochloride}}}{RNH_2.HCl}$$

$$RNH_2.HCl + NaOH \rightarrow RNH_2 + NaCl + H_2O$$

(4) **Physical properties**

(i) Lower amines are gases or low boiling point liquids and possess a ***characteristic ammonia like smell (fishy odour).*** Higher members are solids.

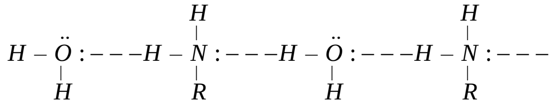
(ii) *The boiling points rise gradually with increase of molecular mass.* Amines are polar compounds like NH_3 and have comparatively higher boiling points than non-polar compounds of similar molecular masses. This is due to the presence of ***intermolecular hydrogen bonding.***



$$\begin{array}{c} H \\ | \\ H-N:--- \\ | \\ R \end{array} \begin{array}{c} H \\ | \\ H-N:--- \\ | \\ R \end{array} \begin{array}{c} H \\ | \\ H-N:--- \\ | \\ R \end{array}$$

Hydrogen bonding in amines

(iii) Amines are soluble in water. This is due to hydrogen bonding between amine and water molecules. Amines are also soluble in benzene and ether.



$$H-\ddot{O}:---H-\underset{R}{\overset{H}{N}}:---H-\ddot{O}:---H-\underset{R}{\overset{H}{N}}:---$$

Hydrogen bonding between amine and water molecules

Solubility decreases with increase of molecular mass.

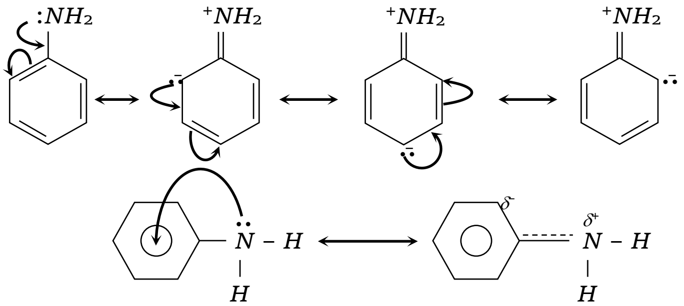
(5) **Chemical properties :** The main reactions of amines are due to the presence of a lone pair of electrons on nitrogen atom. Amines are **electrophilic reagents** as the lone pair of electrons can be donated to electron seeking reagents, (*i.e.*, electrophiles).

Except the amines containing tertiary butyl group, all *lower aliphatic amines are stronger bases than ammonia because of + I (inductive) effect*. The alkyl groups, which are electron releasing groups, increase the electron density around the nitrogen thereby increasing the availability of the lone pair of electrons to proton or Lewis acids and making the amine more basic (larger K_b). Thus, it is expected that the basic nature of amines should be in the order tertiary > secondary > primary, but the *observed order in the case of lower members is found to be as* ***secondary > primary > tertiary***. This anomalous behaviour of tertiary amines is ***due to steric factors***, *i.e.*, crowding of alkyl groups cover nitrogen atom from all sides and thus makes the approach and bonding by a proton relatively difficult which results the maximum steric strain in tertiary amines. The electrons are there but the path is blocked, resulting the reduced in its basicity.

(i) The order of basic nature of various amines has been found ***to vary with nature of alkyl groups***.

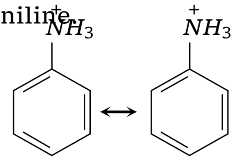
Alkyl group	**Relative strength**
CH_3-	$R_2NH > RNH_2 > R_3N > NH_3$
C_2H_5-	$R_2NH > RNH_2 > NH_3 > R_3N$
$(CH_3)_2CH-$	$RNH_2 > NH_3 > R_2NH > R_3N$
$(CH_3)_3C-$	$NH_3 > RNH_2 > R_2NH > R_3N$

(ii) ***Basic nature of aromatic amines*** **:** In aniline or other aromatic amines, the lone pair present on nitrogen atom *is delocalized with benzene ring by resonance*.



Resonance

But anilinium ion is less resonance stabilized than aniline.



No other resonating structure possible

Thus, electron density is less on N atom due to which *aniline or other aromatic amines are less basic than aliphatic amines*.

However, any group which when present on benzene ring has electron withdrawing effect (– NO_2, – CN, – SO_3H, – COOH – Cl, C_6H_5, etc.) decreases basicity of aniline (Nitroaniline is less basic than aniline as nitro group is electron withdrawing group (– I group) and aniline is more basic than diphenyl amine), *while a group which has electron repelling effect (– NH_2, – OR, R –, etc.) increases basicity of aniline*. Toluidine is more basic than aniline as – CH_3 group is electron repelling group (+ I group).

Further *greater the value of K_b or lower the value of pK_b, stronger will be the base*. The basic character of some amines have the following order,

$$R_2NH > RNH_2 > C_6H_5CH_2NH_2 > NH_3 > C_6H_5NH_2$$

N-alkylated anilines are stronger bases than aniline because of steric effect. Ethyl group being bigger than methyl has more steric effect, so N-ethyl aniline is stronger base than N-methyl aniline. Thus, basic character is,

$$C_6H_5N(C_2H_5)_2 > C_6H_5NHC_2H_5 > C_6H_5N(CH_3)_2$$
$$> C_6H_5NHCH_3 > C_6H_5NH_2NH_3 > C_6H_5NHC_2H_5$$
$$> C_6H_5NHCH_3 > C_6H_5NH_2 > C_6H_5NHC_6H_5$$

In Toluidines –*p*-isomer > *m*- > *o*-

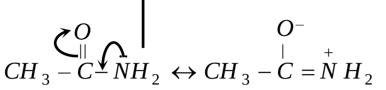
Chloroanilines–*p*-isomer>*m*-> *o*-

Phenylene diamines –*p*-isomer > *m*- > *o*-

Nitroanilines–*m*-isomer > *p*- > *o*-

❑ *Aniline is less basic than ammonia. The phenyl group exerts –I (inductive) effect, i.e., it withdraws electrons. This results to the lower availability of electrons on nitrogen for protonation.*

❑ *Ethylamine and acetamide both contain an amino group but acetamide does not show basic nature. This is because lone pair of electrons on nitrogen is delocalised by resonance with the carbonyl group which makes it less available for protonation.*



Not available due to

$$CH_3-\overset{O}{\overset{\|}{C}}-\ddot{N}H_2 \leftrightarrow CH_3-\overset{O^-}{\overset{|}{C}}=\overset{+}{N}H_2$$

❑ *The compounds with least 's' character (sp^3-hybridized) is most basic and with more 's' character (sp-hybridized) is least basic. Examples in decreasing order of basicity are,*

$$\underset{(sp^3)}{CH_3\ddot{N}H_2} > \underset{(sp^2)}{CH_3-\ddot{N}=CHCH_3} > \underset{(sp)}{CH_3-C\equiv\ddot{N}}$$

$$CH_3CH_2CH_2NH_2 > H_2C=CHCH_2NH_2 > HC\equiv CCH_2NH_2$$

$$(CH_3)_2NH > CH_3NH_2 > NH_3 > C_6H_5NH_2$$

❑ *Electron withdrawing (C_6H_5-) groups decrease electron density on nitrogen atom and thereby decreasing basicity.*

$$(CH_3)_2NH > CH_3NH_2 > C_6H_5NHCH_3 > C_6H_5NH_2$$

$$CH_3CH_2NH_2 > HO(CH_2)_3NH_2 > HO(CH_2)_2NH_2$$

❑ *Electron withdrawing inductive effect of the –OH group decreases the electron density on nitrogen. This effect diminishes with distance from the amino group.*

$$CH_3CH_2NH_2 > C_6H_5CONH_2 > CH_3CONH_2$$

(iii) ***Salt formation*** **:** Amines being basic in nature, combine with mineral acids to form salts.

$$R-NH_2+HCl\rightarrow \underset{\substack{\text{Alkylammonium}\\\text{chloride}}}{R\overset{+}{N}H_3\overset{-}{Cl}}$$

$$2R-NH_2+H_2SO_4\rightarrow \underset{\text{Alkylammonium sulphate}}{(R\overset{+}{N}H_3)_2SO_4^-}$$

(iv) ***Nature of aqueous solution*** **:** Solutions of amines are alkaline in nature.

$$RNH_2+HOH\rightleftharpoons R\overset{+}{N}H_3OH^-\rightleftharpoons[RNH_3]^++OH^-$$

$$R_2NH+HOH\rightleftharpoons R_2\overset{+}{N}H_2OH^-\rightleftharpoons[R_2NH_2]^++OH^-$$

$$R_3N+HOH\rightleftharpoons R_3\overset{+}{N}HOH^-\rightleftharpoons[R_3NH]^++OH^-$$

The aqueous solutions of amines behaves like NH_4OH and give ferric hydroxide precipitate with ferric chloride and blue solution with copper sulphate.

$$3RNH_3OH+FeCl_3\rightarrow Fe(OH)_3+3RNH_3Cl$$

(v) ***Reaction with alkyl halides (Alkylation)***

$$\underset{\text{Pri.amine}}{RNH_2}\xrightarrow[-HX]{R'X}\underset{\text{Sec.amine}}{RNHR'}\xrightarrow[-HX]{R'X}\underset{\text{Tert. amine}}{R-NR'_2}\xrightarrow{R'X}\underset{\text{Quaternary salt}}{(R-\overset{+}{N}R'_3)X^-}$$

(vi) ***Reaction with acetyl chloride (Acylation)***

$$\underset{\text{Pri. amine}}{RNH_2}+ClOCCH_3\xrightarrow{-HCl}\underset{N\text{-Alkylacetamide}}{RNHOCCH_3}$$

$$\underset{\text{Sec. amine}}{R_2NH}+ClOCCH_3\xrightarrow{-HCl}\underset{N,N\text{-Dialkylacetamide}}{R_2NOCCH_3}$$

Tertiary amines do not react since they do not have replaceable hydrogen on nitrogen.

Therefore, all these above reactions are used to distinguish between $1^o, 2^o$ and 3^o -amines.

(vii) ***Action of sodium***

$$\underset{1^o\text{ amine}}{2RNH_2}+2Na\xrightarrow{\Delta}\underset{\text{Sod. salt}}{2[RNH]^-Na^+}+H_2\uparrow$$

$$\underset{2^o\text{ amine}}{2R_2NH}+2Na\xrightarrow{\Delta}\underset{\text{Sod.salt}}{2[R_2N]^-Na^+}+H_2\uparrow$$

(viii) ***Action of halogens***

$$\underset{\text{Alkylamine}}{RNH_2}\xrightarrow[NaOH]{X_2}RNHX\xrightarrow[NaOH]{X_2}\underset{\substack{\text{Dihalo-alkyl}\\\text{amine}}}{RNX_2}$$

$$\underset{\text{Dialkylamine}}{R_2NH}\xrightarrow[NaOH]{X_2}\underset{\substack{\text{Halo-dialkyl}\\\text{amine}}}{R_2NX}$$

(ix) ***Reaction with Grignard reagent***

$$RNH_2+Mg\left\langle\begin{matrix}CH_3\\I\end{matrix}\right.\rightarrow CH_4+RNH-Mg-I$$

$$R_2NH+CH_3-Mg-I\rightarrow CH_4+R_2N-Mg-I$$

(x) ***Carbylamine reaction*** **:** This reaction is shown by only ***primary amines*****.** This is a test of primary amines and is used to distinguish primary amines from secondary and tertiary amines.

$$RNH_2+CHCl_3+\underset{\text{(Alc.)}}{3KOH}\rightarrow\underset{\substack{\text{Alkylisocyanide}\\\text{(carbylamine)}}}{RNC}+3KCl+3H_2O$$

Isocyanides are bad smelling compounds and can be easily detected.

(xi) ***Reaction with nitrous acid***

(a) Primary amines form alcohols with nitrous acid ($NaNO_2$+ HCl). Nitrogen is eliminated.

$$\underset{\text{Pri. amine}}{RNH_2}+HONO\rightarrow\underset{\text{Alcohol}}{ROH}+N_2+H_2O$$

Methyl amine is an exception to this reaction, *i.e.,*

$$CH_3NH_2+2HONO\rightarrow\underset{\text{Methylnitrite}}{CH_3-O-N=O}+N_2+2H_2O$$

$$2CH_3NH_2+2HONO\rightarrow\underset{\text{Dimethylether}}{CH_3-O-CH_3}+2N_2+3H_2O$$

(b) Secondary amines form nitrosoamines which are water insoluble yellow oily liquids.

$$\underset{\text{Sec. amine}}{R_2NH}+HONO\rightarrow\underset{\substack{\text{Dialkyl}\\\text{nitrosoamine}}}{R_2NNO}+H_2O$$

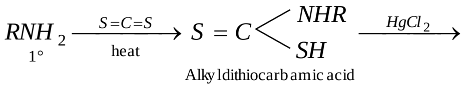
Nitrosoamine on warming with phenol and conc. H_2SO_4 give a brown or red colour which soon changes to blue green. The colour changes to red on dilution and further changes to blue or violet with alkali. This colour change is referred to **Liebermann's nitroso reaction** and is used for the test of secondary amines.

(c) Tertiary amines react nitrous acid to form nitrite salts which are soluble in water. These salts on heating give alcohols and nitrosoamines.

$$\underset{\text{Tert.amine}}{R_3N} + HONO \rightarrow \underset{\text{Trialkylammoniumnitrite}}{[R_3NH]^+ NO_2^-} \xrightarrow{heat} \underset{\text{Alcohol}}{R-OH} + \underset{\text{Nitrosoamine}}{R_2N–N=O}$$

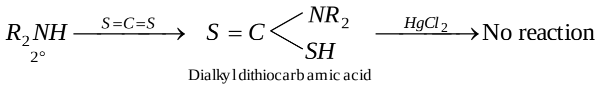
This reaction (nitrous acid test) is used to make distinction between primary, secondary and tertiary amines.

(xii) ***Reaction with carbon di sulphide*** **:** This **Hofmann’s mustard oil reaction** is used as a **test for primary amines**.



$$\underset{1^\circ}{RNH_2} \xrightarrow[\text{heat}]{S=C=S} \underset{\text{Alkyldithiocarbamic acid}}{S=C\begin{matrix}NHR\\ SH\end{matrix}} \xrightarrow{HgCl_2}$$

$$\underset{\substack{\text{Alkylisothiocyanate}\\ \text{(Mustard oil smell)}}}{RNC=S} + \underset{\text{Black ppt.}}{HgS} + 2HCl$$



$$\underset{2^\circ}{R_2NH} \xrightarrow{S=C=S} \underset{\text{Dialkyldithiocarbamic acid}}{S=C\begin{matrix}NR_2\\ SH\end{matrix}} \xrightarrow{HgCl_2} \text{No reaction}$$

(xiii) ***Oxidation*** **:** All the three types of amines undergo oxidation. The product depends upon the nature of oxidising agent, class of amine and the nature of the alkyl group.

(a) *Oxidation of primary amines*

$$\underset{\text{Pri.amine}}{RCH_2NH_2} \xrightarrow[KMnO_4]{[O]} \underset{\text{Aldimine}}{RCH=NH} \xrightarrow{H_2O} \underset{\text{Aldehyde}}{RCHO} + NH_3$$

$$R_2CHNH_2 \xrightarrow[KMnO_4]{[O]} \underset{\text{Ketimine}}{R_2C=NH} \xrightarrow{H_2O} \underset{\text{Ketone}}{R_2CO} + NH_3$$

(b) *Oxidation of secondary amines*

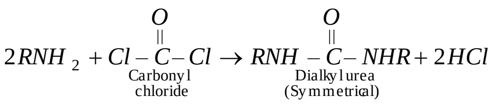
$$\underset{\text{Sec. amine}}{R_2NH} \xrightarrow[KMnO_4]{[O]} \underset{\text{Tetra-alkylhydrazine}}{R_2N-NR_2} \;;\; R_2NH \xrightarrow[H_2SO_5]{[O]} \underset{\text{Dialkylhydroxylamine}}{R_2NOH}$$

(c) *Oxidation of tertiary amines* : Tertiary amines are not oxidised by potassium permanganate but are oxidised by Caro's acid or Fenton's reagent to amine oxides.

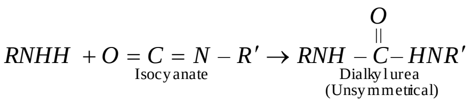
$$\underset{\text{Tert. amine}}{R_3N} + [O] \rightarrow \underset{\text{Amine oxide}}{[R_3N \rightarrow O]}$$

(xiv) ***Reaction with other electrophilic reagents***

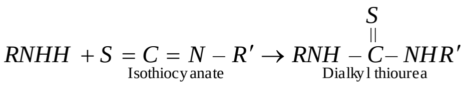
$$\underset{\text{Pri.amine}}{RNH_2} + \underset{\text{Aldehyde}}{O=CHR'} \rightarrow \underset{\text{Schiff's base}}{RN=CH\,R'}$$



$$2RNH_2 + \underset{\substack{\text{Carbonyl}\\ \text{chloride}}}{Cl-\overset{\overset{\displaystyle O}{||}}{C}-Cl} \rightarrow \underset{\substack{\text{Dialkylurea}\\ \text{(Symmetrical)}}}{RNH-\overset{\overset{\displaystyle O}{||}}{C}-NHR} + 2HCl$$



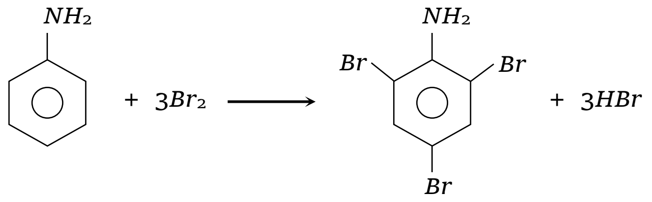
$$RNHH + \underset{\text{Isocyanate}}{O=C=N-R'} \rightarrow \underset{\substack{\text{Dialkylurea}\\ \text{(Unsymmetrical)}}}{RNH-\overset{\overset{\displaystyle O}{||}}{C}-HNR'}$$



$$RNHH + \underset{\text{Isothiocyanate}}{S=C=N-R'} \rightarrow \underset{\text{Dialkyl thiourea}}{RNH-\overset{\overset{\displaystyle S}{||}}{C}-NHR'}$$

(xv) ***Ring substitution in aromatic amines*** **:** Aniline is more reactive than benzene. The *presence of amino group activates the aromatic ring and directs the incoming group preferably to ortho and para positions.*

(a) *Halogenation*

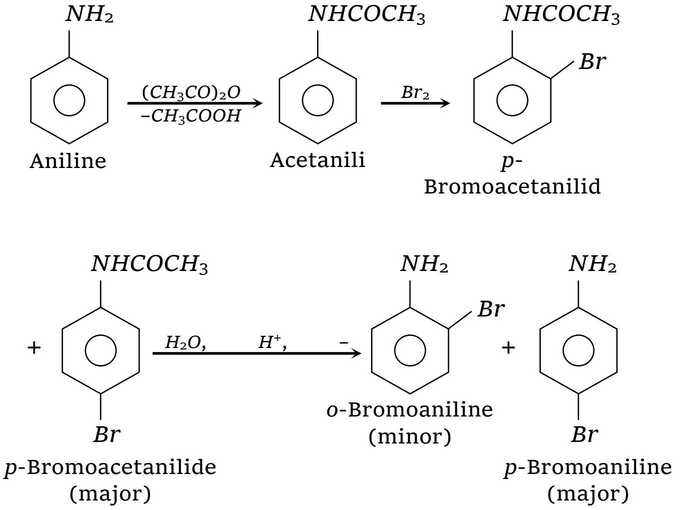


2, 4, 6-Tri
Bromoaniline (white

This reaction is used as a test for aniline.

However, if monosubstituted derivative is desired, aniline is first acetylated with acetic anhydride and then halogenation is carried out. After halogenation, the acetyl group is removed by hydrolysis and only monosubstituted halogen derivative is obtained.

It may be noted that – NH_2 group directs the attacking group at *o*- and *p*-positions and therefore, both *o*- and *p*-derivatives are obtained.

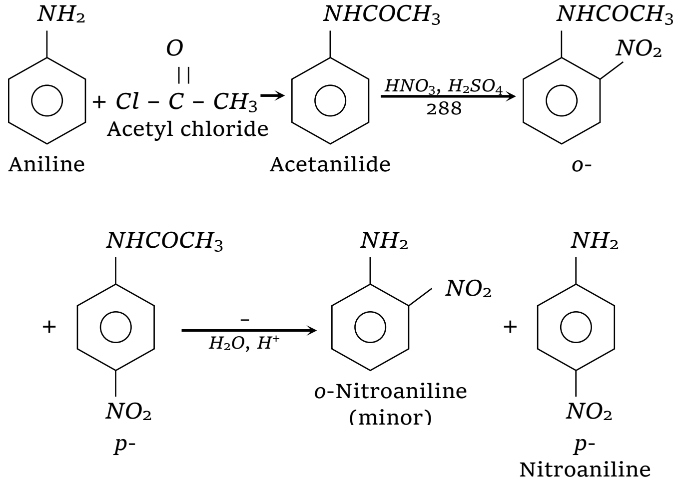


Acetylation deactivates the ring and controls the reaction to monosubstitution stage only because *acetyl group is electron withdrawing group and therefore, the electron pair of N-atom is withdrawn towards the carbonyl group.*

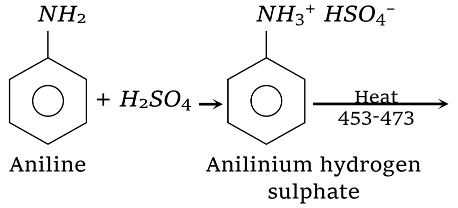
(b) *Nitration* : Aromatic amines cannot be nitrated directly because they are readily oxidized. This is because, HNO_3 is a strong *oxidising agent and results in partial oxidation of the ring to form a black mass.*

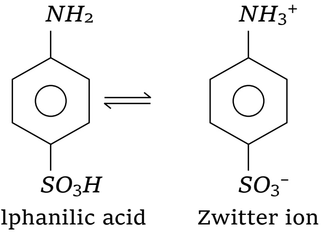
Therefore, to solve this problem, nitration is carried out by *protecting the* $-NH_2$ *group by acetylation. The acetylation deactivates the ring and therefore, controls the reaction.*

The hydrolysis of nitroacetanilides removes the protecting acyl group and gives back amines.



(c) *Sulphonation*





The sulphanilic acid exists as a dipolar ion (structure II) which has acidic and basic groups in the same molecule. Such ions are called ***Zwitter ions or inner salts.***

(6) **Uses**

(i) Ethylamine is used in solvent extraction processes in ***petroleum refining*** and as a **stabiliser** for ***rubber latex.***

(ii) The quaternary ammonium salts derived from long chain aliphatic tertiary amines are widely used as detergents.

(iii) Aliphatic amines of low molecular mass are used as solvents.

Table : 29.3 Distinction between primary, secondary and tertiary amines

Test	Primary amine	Secondary amine	Tertiary amine
Action of $CHCl_3$ and alcoholic KOH. (Carbylamine test)	Bad smelling carbylamine (Isocyanide) is formed.	No action.	No action.
Action of CS_2 and $HgCl_2$. (Mustard oil test)	Alkyl isothiocyanate is formed which has pungent smell like mustard oil.	No action.	No action
Action of nitrous acid.	Alcohol is formed with evolution of nitrogen.	Forms nitrosoamine which gives green colour with phenol and conc. H_2SO_4 (Liebermann's test).	Forms nitrite in cold which on heating gives nitrosoa- mine which responds to Liebermann's test.
Action of acetyl chloride.	Acetyl derivative is formed.	Acetyl derivative is formed.	No action.
Action of Hinsberg's reagent.	Monoalkyl sulphonamide is formed which is soluble in KOH.	Dialkyl sulphonamide is formed which is insoluble in KOH.	No action.
Action of methyl iodide.	3 molecules (moles) of CH_3I to form quaternary salt with one mole of primary amine.	2 moles of CH_3I to form quaternary salt with one mole of secondary amine.	One mole of CH_3I to form quaternary salt with one mole of tertiary amine.

❑ *Aniline does not form alcohol with nitrous acid but it forms benzene diazonium chloride which* ***shows dye test.***

Aniline

Aniline was first prepared by ***Unverdorben (1826) by dry distillation of indigo.*** In the laboratory, it can be prepared by the reduction of nitrobenzene with tin and hydrochloric acid.

$$\underset{\text{Nitrobenzene}}{C_6H_5NO_2} + 6H \xrightarrow{Sn,HCl} \underset{\text{Aniline}}{C_6H_5NH_2} + 2H_2O$$

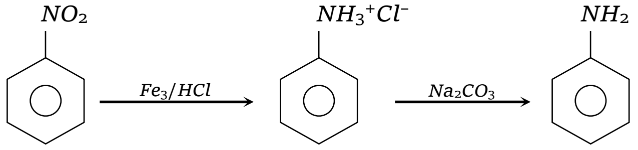
Aniline produced combines with $H_2SnCl_6(SnCl_4 + 2HCl)$ to form a double salt.

$$2C_6H_5NH_2 + SnCl_4 + 2HCl \to \underset{\text{Double salt}}{(C_6H_5NH_3)_2\,SnCl_6}$$

From double salt, aniline is obtained by treating with conc. caustic soda solution.

$$(C_6H_5NH_3)_2SnCl_6 + 8NaOH \to 2C_6H_5NH_2$$
$$+6NaCl + Na_2SnO_3 + 5H_2O$$

On a commercial scale, aniline is obtained by reducing nitrobenzene with iron filings and hydrochloric acid.



Aniline is also obtained on a large scale by the action of amine on chlorobenzene at 200°C under 300-400 *atm* pressure in presence of cuprous catalyst.

$$2C_6H_5Cl + 2NH_3 + Cu_2O \xrightarrow[300-400\ atm]{200°C} 2C_6H_5NH_2 + Cu_2Cl_2 + H_2O$$

Properties Aniline when freshly prepared is a ***colourless oily liquid (b.p. 184°C).*** It has a characteristic unpleasant odour and is not poisonous in nature. It is heavier than water and is only slightly soluble. It is soluble in alcohol, ether and benzene. Its colour changes to dark brown on standing.

It shows all the characteristic reactions discussed earlier.

Uses : (1) It is used in the preparation of diazonium compounds which are used in dye industry.

(2) Anils (Schiff's bases from aniline) are used as antioxidants in rubber industry.

(3) It is used for the manufacture of its some derivatives such as acetamide, sulphanilic acid and sulpha drugs, etc.

(4) It is used as an accelerator in vulcanizing rubber.

Some important conversions

(1) **Conversion of methylamine to ethylamine (Ascent)**

$$\underset{\text{Methylamine}}{CH_3NH_2} \xrightarrow{HNO_2} \underset{\text{Methylalcohol}}{CH_3OH} \xrightarrow{PI_3} \underset{\text{Methyliodide}}{CH_3I}$$
$$\xrightarrow{NaCN} \underset{\text{Methylcyanide}}{CH_3CN} \xrightarrow{LiAlH_4} \underset{\text{Ethylamine}}{CH_3CH_2NH_2}$$

(2) **Conversion of ethylamine to methylamine (Descent)**

$$\underset{\text{Ethylamine}}{CH_3CH_2NH_2} \xrightarrow{HNO_2} \underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[K_2Cr_2O_7/H_2SO_4]{[O]} \underset{\text{Acetaldehyde}}{CH_3CHO}$$
$$\xrightarrow{[O]} \underset{\text{Aceticacid}}{CH_3COOH} \xrightarrow{SOCl_2} \underset{\text{Acetylchloride}}{CH_3COCl}$$
$$\xrightarrow{NH_3} \underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow[KOH]{Br_2} \underset{\text{Methylamine}}{CH_3NH_2}$$

(3) **Conversion of ethylamine to acetone**

$$\underset{\text{Ethylamine}}{C_2H_5NH_2} \xrightarrow{HNO_2} \underset{\text{Ethylalcohol}}{C_2H_5OH} \xrightarrow[H_2SO_4]{K_2Cr_2O_7}$$
$$\underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{\text{Aceticacid}}{CH_3COOH} \xrightarrow{Ca(OH)_2} \underset{\text{Calcium acetate}}{(CH_3COO)_2Ca}$$
$$\xrightarrow{heat} \underset{\text{Acetone}}{CH_3COCH_3}$$

(4) **Conversion of propionic acid to**

(i) Ethylamine, (ii) *n*-Butylamine.

(i) $\underset{\text{Propionic aicd}}{CH_3CH_2COOH} \xrightarrow{SOCl_2} \underset{\text{Propionyl chloride}}{CH_3CH_2COCl} \xrightarrow{NH_3}$

$$\underset{\text{Propionamide}}{CH_3CH_2CONH_2} \xrightarrow[KOH]{Br_2} \underset{\text{Ethylamine}}{CH_3CH_2NH_2}$$

or $C_2H_5COOH \xrightarrow[H_2SO_4(conc.)]{N_3H} C_2H_5NH_2$

(ii) $\underset{\text{Propionic acid}}{CH_3CH_2COOH} \xrightarrow[Ether]{LiAlH_4} \underset{n\text{-Propylalcohol}}{CH_3CH_2CH_2OH} \xrightarrow{PBr_5}$

$$\underset{\text{Propyl bromide}}{CH_3CH_2CH_2Br} \xrightarrow{KCN} \underset{\text{Propylcyanide}}{CH_3CH_2CH_2CN}$$
$$\xrightarrow[\text{or } LiAlH_4]{Na+C_2H_5OH} \underset{n\text{-Butylamine}}{CH_3CH_2CH_2CH_2NH_2}$$

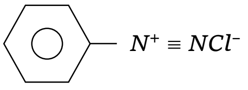
(5) **Conversion of ethylene to 1,4-diaminobutane**

$$\underset{\text{Ethylene}}{CH_2=CH_2} \xrightarrow[CCl_4]{Br_2} \underset{\text{Ethylene bromide}}{CH_2Br.CH_2Br} \xrightarrow{NaCN}$$
$$\underset{\text{Ethylene cyanide}}{NCCH_2CH_2CN} \xrightarrow{LiAlH_4} \underset{\text{1,4-Diaminobutane}}{NH_2CH_2CH_2CH_2CH_2NH_2}$$

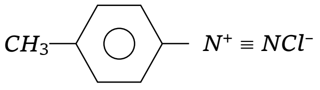
Diazonium salts

The diazonium salts have the general formula $ArN_2^+X^-$, where X^- may be an anion like Cl^-, Br^- etc. and the group $N_2^+(-N\equiv N^+)$ is called diazonium ion group.

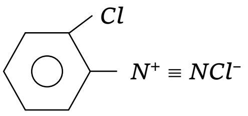
(1) **Nomenclature :** The diazonium salts are named by adding the word diazonium to the name of the parent aromatic compound to which they are related followed by the name of the anion. For example,



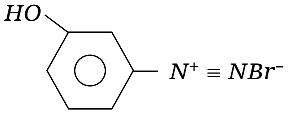
Benzenediazonium



p-Toluenediazonium

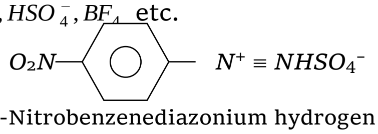


o-chlorobenzenediazonium



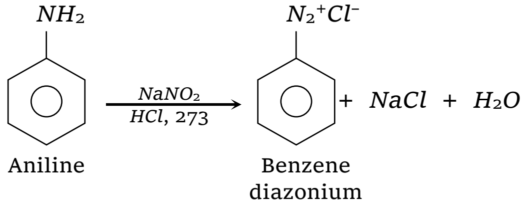
m-Hydroxybenzenediazonium

The diazonium salt may contain other anions also such as NO_3^-, HSO_4^-, BF_4^- etc.



(2) **Preparation of diazonium salts :**

$$NaNO_2 + HCl \rightarrow NaCl + HONO$$



The reaction of converting aromatic primary amine to diazonium salt is called **diazotisation.**

(3) **Physical properties of diazonium salts**

(i) Diazonium salts are generally colourless, crystalline solids.

(ii) These are readily soluble in water but less soluble in alcohol.

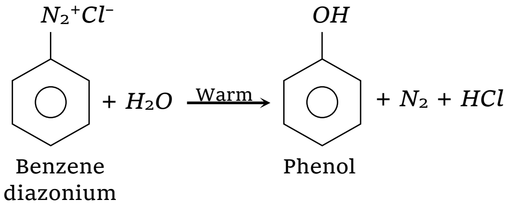
(iii) They are unstable and explode in dry state. Therefore, they are generally used in solution state.

(iv) Their aqueous solutions are neutral to litmus and conduct electricity due to the presence of ions.

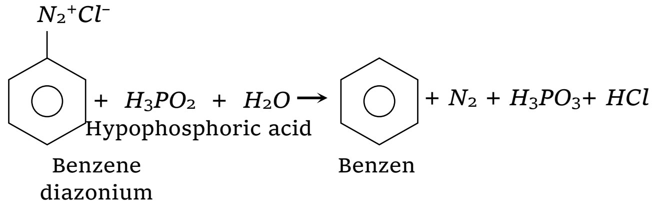
(4) **Chemical properties of diazonium salts**

(i) ***Substitution reaction*** **:** In substitution or replacement reactions, nitrogen of diazonium salts is lost as N_2 and different groups are introduced in its place.

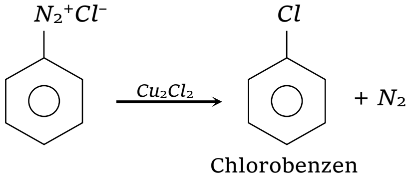
(a) *Replacement by –OH group*



(b) *Replacement by hydrogen*

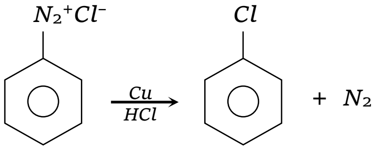


(c) *Replacement by–Cl group*

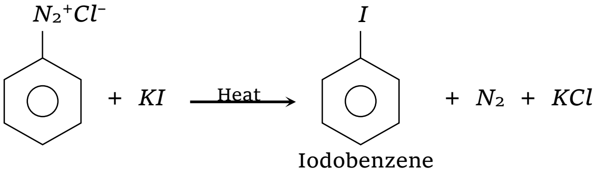


This reaction is called ***Sandmeyer reaction.***

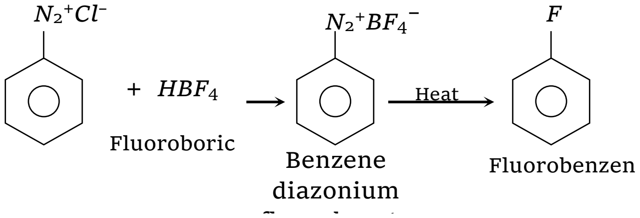
When the diazonium salt solution is warmed with copper powder and the corresponding halogen acid, the respective halogen is introduced. The reaction is a modified form of Sandmeyer reaction and is known as ***Gattermann reaction.***



(d) *Replacement by iodo (–I) group*

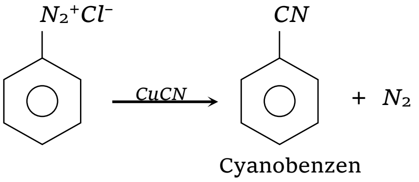


(e) *Replacement by – F group*

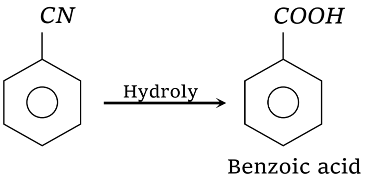


This reaction is called **Balz Schiemann reaction.**

(f) *Replacement by Cyano (– CN) group*

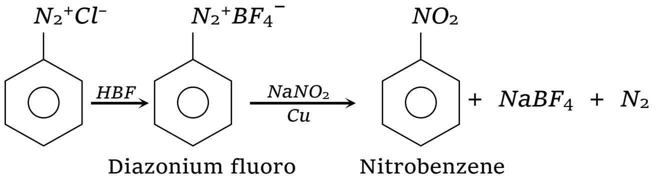


The nitriles can be hydrolysed to acids.

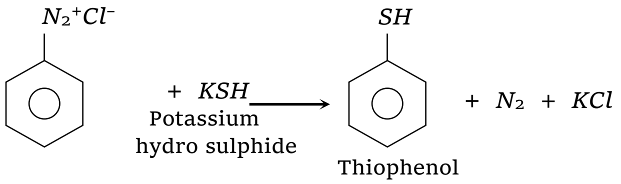


This method of preparing carboxylic acids is more useful than carbonation of Grignard reagents.

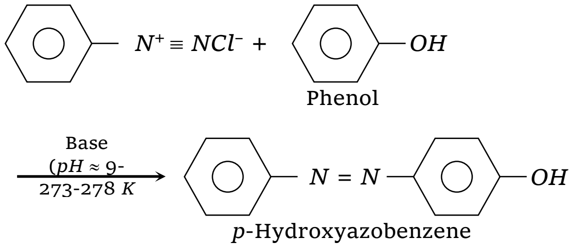
(g) *Replacement by – NO_2 group*

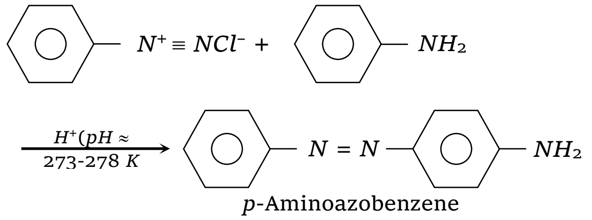


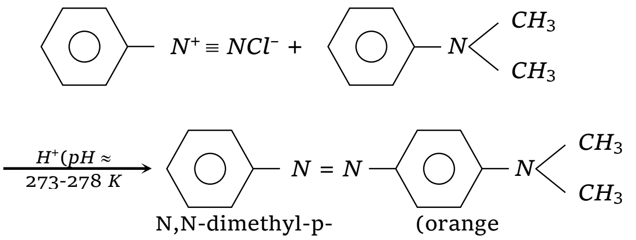
(h) *Replacement by thio (–SH) group*



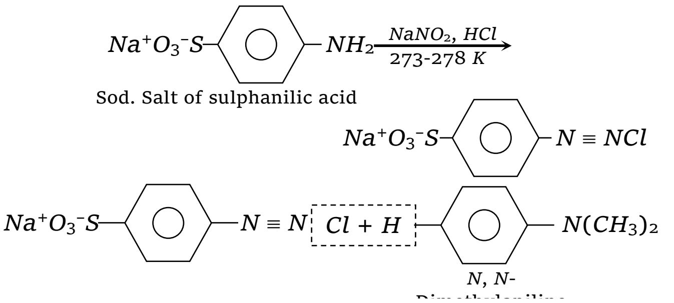
(ii) ***Coupling reactions*** **:** The diazonium ion acts as an electrophile because there is positive charge on terminal nitrogen. It can react with nucleophilic aromatic compounds ($Ar–H$) activated by electron donating groups (– OH and – NH_2), which as strong nucleophiles react with aromatic diazonium salts. Therefore, benzene diazonium chloride couples with electron rich aromatic compounds like phenols and anilines to give azo compounds. The azo compounds contain $–N = N–$ bond and the reaction is called **coupling reaction.**

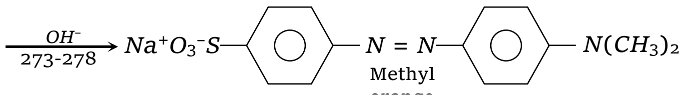




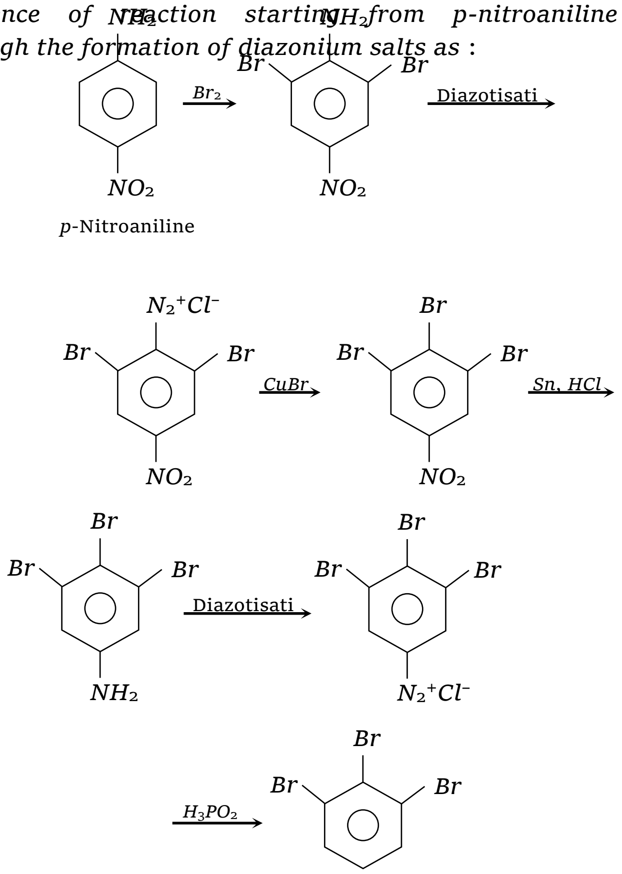


Coupling occurs para to hydroxy or amino group. *All azo compounds are strongly coloured and are used as dyes*. Methyl orange is an important dye obtained by coupling the diazonium salt of sulphanilic acid with *N*, *N*-dimethylaniline.





❑ *Diazonium salts are highly* ***useful intermediates*** *in the synthesis of large variety of aromatic compounds. These can be used to prepare many classes of organic compounds especially aryl halides in pure state. For example,. 1, 2, 3-tribromo benzene is not formed in the pure state by direct bromination of benzene. However, it can be prepared by the following sequence of reaction starting from p-nitroaniline through the formation of diazonium salts as :*



1, 2, 3-Tribromo benzene

(5) **Uses of diazonium salts**

(i) For the manufacture of azo dyes.

(ii) For the industrial preparation of important organic compounds like *m*-bromotoluene, *m*-bromophenol, etc.

(iii) For the preparation of a variety of useful halogen substituted arenes.

Tips & Tricks

- Alkyl nitrites are the esters of nitrous acid.
- Nitroparaffins are used as solvents for oils, fats, resins, esters, rubbers and cellulose etc. nitromethane is used as high power fuel in racing automobiles.
- Nitrobenzene is good solvent in friedel crafts reaction because it dissolves $AlCl_3$
- All amines have basic properties. The basic property, that is, the tendency of primary, secondary and tertiary amines to bind a proton, is due to the unshared pair of electrons on the nitrogen. When a proton is bound, positive ion is formed and originally electrically neutral amine takes on the charge of the proton. When ions are formed in this way, they are called onium ions. The ion formed in case of amines are substituted ammonium ions. The hydronium ion, H_3O^+ is also the onium ion, which belongs to the class of oxonium ions.
- Some derivatives of ammonia arranged in order of deecreasing basicity are $(CH_3)_4N^+OH^-$, $(CH_3)_2NH$, CH_3NH_2, $(CH_3)_3N$, NH_3, $C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5NH_2$, $(C_6H_5)_2NH$, CH_3CONH_2.
- In water the basicity follows the order : Primary < Tertiary < Secondary amine, with reference to hydronium ion, H_3O^+. In this case solvation factor and steric effect alter, to some extent, the order of basicity because of inductive effect alone.
- In a non-polar solvent such as benzene, using trichloroacetic acid as the reference acid, the basicity follows the order Tertiary < Secondary < Primary amines. The solvation factor is absent but steric effect upsets the inductive effect of alkyl groups.
- Carylamine test is specific for primary amines.

Ordinary Thinking

Objective Questions

Introduction of Nitrogen Containing Compounds

1. Cyanide ion is

(a) Nucleophilic (b) Electrophilic

(c) Strongly acidic (d) Non-reactive and neutral

2. Compounds containing both amino and COOH groups are known as

(a) Diamines (b) Unknown

(c) Amino acids (d) Enzymes

3. Which of the following is 1^o amine

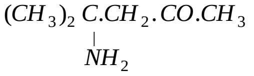
(a) Ethylene diamine (b) Dimethyl amine

(c) Trimethyl amine (d) N-methyl aniline

4. C_3H_9N represents **[AMU 1988]**

(a) Primary amine (b) Secondary amine

(c) Tertiary amine (d) All of these

5. 
$(CH_3)_2\underset{|\atop NH_2}{C}.CH_2.CO.CH_3$ is **[MP PET/PMT 1988]**

(a) Diacetone (b) Acetoneamine

(c) Diacetoneamine (d) Aminoacetone

6. A secondary amine is **[KCET 1992]**

(a) An organic compound with two $-NH_2$ groups

(b) A compound with two carbon atoms and an $-NH_2$ group

(c) A compound with an $-NH_2$ group on the carbon atom in number 2 position

(d) A compound in which two of the hydrogens of NH_3 have been replaced by organic groups

7. The structural formula of methyl aminomethane is **[MP PMT 1991]**

(a) $(CH_3)_2CHNH_2$ (b) $(CH_3)_3N$

(c) $(CH_3)_2NH$ (d) CH_3NH_2

8. Allyl isocyanide has **[IIT 1995]**

(a) 9 sigma bonds and 4 pi bonds

(b) 8 sigma bonds and 5 pi bonds

(c) 8 sigma bonds, 3 pi bonds and 4 non-bonding electrons

(d) 9 sigma bonds, 3 pi bonds and 2 non-bonding electrons

9. Triaminobenzene is a **[BHU 1996]**

(a) 2^o amine (b) 3^o amine

(c) 1^o amine (d) Quarternary salt

10. $CH_2=CH-CH_2-NH-CH_3$ is a **[RPET 2000]**

(a) Secondary amine (b) Primary amine

(c) Tertiary amine (d) None of these

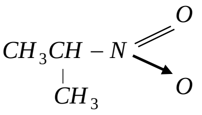
11. Leakage of which gas was responsible for the Bhopal tragedy in 1984 **[MP PET 2001]**

(a) $CH_3-N=C=O$ (b) $CH_3-C-N=S$

(c) $CHCl_3$ (d) C_6H_5COCl

12. Which of the following is not a nitro-derivative **[DCE 2004]**

(a) $C_6H_5NO_2$ **(b)** CH_3CH_2ONO

(c) 

$CH_3\underset{|\atop CH_3}{CH}-N$ (d) $C_6H_4(OH)NO_2$

13. Acetonitrile is: **[MP PMT 2004]**

(a) C_2H_5CN (b) CH_3CN

(c) CH_3COCN (d) $C_6H_5CH_2CN$

14. In alkyl cyanide alkyl group attached with **[BCECE 2005]**

(a) C of CN group

(b) N of CN group

(c) Either C or N of CN group

(d) Both C and N of CN group

15. Number of isomeric primary amines obtained from $C_4H_{11}N$ are

(a) 3 (b) 4

(c) 5 (d) 6

Preparation of Nitrogen Containing Compounds

1. Amides may be converted into amines by reaction named after **[CPMT 1974; MP PET 1992; CBSE PMT 1999]**

(a) Perkin (b) Claisen

(c) Hoffmann (d) Kolbe

2. Reaction $CH_3CONH_2 \xrightarrow{NaOBr}$ gives

[CPMT 1983, 93, 97]

(a) CH_3Br (b) CH_4

(c) CH_3COBr (d) CH_3NH_2

3. Acetamide is treated separately with the following reagents. Which would give methyl amine

[IIT 1983; CPMT 1988, 94; MP PET 1993; MP PMT 1996; AIIMS 1998]

(a) PCl_5 (b) $NaOH + Br_2$

(c) Sodalime (d) Hot conc. H_2SO_4

4. The amine formed from an amide by means of bromine and alkali has

(a) Same number of C atoms as that of amide

(b) One less C atom than that of amide

(c) One more C atom than that of amide

(d) Two more C atoms than that of amide

5. $CH_3CN \xrightarrow{Na + C_2H_5OH} X$

The compound X is **[MP PMT 1983; BHU 1984]**

(a) CH_3CONH_2 (b) $CH_3CH_2NH_2$

(c) C_2H_6 (d) CH_3NHCH_3

6. Ethylamine can be prepared by the action of bromine and caustic potash on **[CPMT 1994]**

(a) Acetamide (b) Propionamide

(c) Formamide (d) Methyl cyanide

7. Ethylamine can be obtained by the **[CPMT 1985]**

(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

8. Aniline is usually purified by

[CPMT 1983, 93; JIPMER 1997]

(a) Steam distillation (b) Simple distillation

(c) Vacuum distillation (d) Extraction with a solvent

9. Reduction of nitroalkanes yields

(a) Acid (b) Alcohol

(c) Amine (d) Diazo compounds

10. Acetamide changes into methylamine by

(a) Hofmann bromamide reaction

(b) Hofmann reaction

(c) Friedel-Craft's reaction

(d) Hinsberg reaction **[DPMT 2005]**

11. 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

12. Acetanilide can be prepared from aniline and which of the following

(a) Ethanol (b) Acetaldehyde

(c) Acetone (d) Acetic anhydride

13. Reduction of nitroalkanes in neutral medium (e.g. $Zn\ /\ NH_4Cl$) forms mainly

(a) $R-NH_2$ (b) $R-NHOH$

(c) $R-N=N-Cl$ (d) All of these

14. Nitrosobenzene can be prepared by oxidizing aniline from

(a) H_2SO_4 (b) H_2SO_5

(c) H_2SO_3 (d) $K_2Cr_2O_7$

15. The Hinsberg's method is used for

(a) Preparation of primary amines

(b) Preparation of secondary amines

(c) Preparation of tertiary amines

(d) Separation of amine mixtures

16. Which one of the following compound gives a secondary amine on reduction

(a) Nitromethane (b) Nitrobenzene

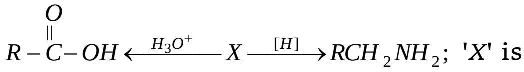
(c) Methyl isocyanide (d) Methyl cyanide

17. Chloropicrin is manufactured by the reaction between Cl_2, $NaOH$ and

(a) Nitromethane (b) Nitroethane

(c) Nitrophenol (d) Nitrostyrene

18. In the reaction



$$R-\overset{\overset{O}{||}}{C}-OH \xleftarrow{H_3O^+} X \xrightarrow{[H]} RCH_2NH_2;$$ 'X' is

[MP PMT 1990]

(a) Isonitrile (b) Nitrile

(c) Nitrite (d) Oxime

19. When ethanol is mixed with ammonia and passed over alumina the compound formed is **[CBSE PMT 1990]**

(a) $C_2H_5NH_2$ (b) C_2H_4

(c) $C_2H_5OC_2H_5$ (d) CH_3OCH_3

20. Which of the following reactions does not yield an amine

[CPMT 1989, 93]

(a) $RX + NH_3 \longrightarrow$

(b) $RCH = NOH + [H] \xrightarrow[C_2H_5OH]{Na}$

(c) $RCN + H_2O \xrightarrow{H^+}$

(d) $RCONH_2 + 4H \xrightarrow{LiAlH_4}$

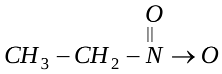
21. Identify 'B' in the reaction

Acetamide $\xrightarrow[\Delta]{P_2O_5} A \xrightarrow{4H} B$ **[MP PET 1995]**

(a) CH_3NH_2 (b) $CH_3CH_2NH_2$

(c) CH_3CN (d) CH_3COONH_4

22. Which of the following gives primary amine on reduction **[MP PMT 1995]**

(a) 
$CH_3 - CH_2 - \overset{\overset{\displaystyle O}{||}}{N} \rightarrow O$

(b) $CH_3 - CH_2 - O - N = O$

(c) $CH_3CH_2NO_3$

(d) None of these

23. Which of the following is converted into an alcohol on treatment with HNO_2 **[MP PET 1996; MP PMT 1999]**

(a) Methyl amine (b) Aniline

(c) Dimethyl amine (d) Triethyl amine

24. Which of the following gives RNC, when reacted with $CHCl_3$ and KOH **[MP PET 1996]**

(a) RNH_2 (b) R_2NH

(c) R_3N (d) $R_4N^+Cl^-$

25. When aniline reacts with $NaNO_2$ and dil. HCl at $0^o - 5^oC$, the product formed is **[MP PMT 1996; AIIMS 1994]**

(a) Nitroaniline

(b) Benzene diazonium chloride

(c) Benzene

(d) Trinitroaniline

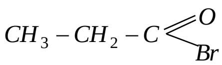
26. Starting from propanoic acid, the following reactions were carried out

Propanoic acid $\xrightarrow{SOCl_2} X \xrightarrow{NH_3} Y \xrightarrow{Br_2 + KOH} Z$

What is the compound Z

(a) $CH_3 - CH_2 - Br$

(b) $CH_3 - CH_2 - NH_2$

(c) 
$CH_3 - CH_2 - C \begin{smallmatrix} \nearrow O \\ \searrow Br \end{smallmatrix}$

(d) $CH_3 - CH_2 - CH_2 - NH_2$

27. 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

28. In the following reaction, X is

$X \xrightarrow{\text{Bromination}} Y \xrightarrow{NaNO_2 + HCl} Z \xrightarrow[C_2H_5OH]{\text{Boiling}}$ Tribromobenzene

[CPMT 1999]

(a) Benzoic acid (b) Salicylic acid

(c) Phenol (d) Aniline

29. Which of the following reactions will not give primary amine **[CPMT 1999]**

(a) $CH_3CONH_2 \xrightarrow{KOH.Br_2}$

(b) $CH_3CN \xrightarrow{LiAlH_4}$

(c) $CH_3NC \xrightarrow{LiAlH_4}$

(d) $CH_3CONH_2 \xrightarrow{LiAlH_4}$

30. Carbylamine reaction is given by **[BHU 1996; EAMCET 1990]**

(a) 1^o amine (b) 3^o amine

(c) 2^o amine (d) Quarternary salts

31. The reaction

$C_6H_5NH_2 + CHCl_3 + 3KOH \rightarrow C_6H_5NC + 3KCl + 2H_2O$

is known as **[BHU 1996]**

(a) Carbylamine reaction

(b) Reimer-Tiemann reaction

(c) Kolbe reaction

(d) Hofmann's degradation

32. $CH_3CONH_2 \xrightarrow{Na + ROH} Z + H_2O$.

What is Z ? **[CPMT 1996]**

(a) $CH_3CH_2NH_2$ (b) CH_3CH_2NC

(c) $CH_3CH_2CH_3$ (d) NH_2CONH_2

33. Which of the following reacts with chloroform and a base to form phenyl isocyanide **[AFMC 1997]**

(a) Aniline (b) Phenol

(c) Benzene (d) Nitrobenzene

34. Aromatic primary amine when treated with cold HNO_2 gives **[Pb. CET 2002; DCE 1999]**

(a) Benzyl alcohol (b) Nitro benzene

(c) Benzene (d) Diazonium salt

35. Which of the following compound is the strongest base **[BHU 1999]**

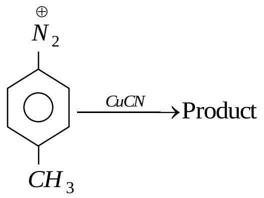
(a) Ammonia (b) Aniline

(c) Methylamine (d) N-methyl aniline

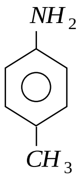
36. Nitrobenzene combines with hydrogen in the presence of platinum to produce **[BHU 1999]**

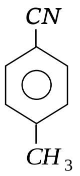
(a) Toluene (b) Benzene

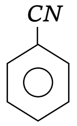
(c) Aniline (d) Azobenzene

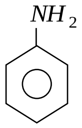
37. 

The product is **[RPET 2000]**

(a) 

(b) 





(c) (d)

38. Ethyl amine on heating with CS_2 in presence of $HgCl_2$ forms **[MP PET 2000]**

(a) C_2H_5NCS (b) $(C_2H_5)_2S$

(c) $(C_2H_5)_2CS$ (d) $C_2H_5(CS)_2$

39. Which of the following reacts with $NaNO_2 + HCl$ to give phenol **[MP PMT 2000]**

(a) $C_6H_5CH_2NHCH_3$ (b) $(CH_3)_2NH$

(c) CH_3NH_2 (d) $C_6H_5NH_2$

40. Which of the following reactions give $RCONH_2$ **[Roorkee 2000]**

(a) $R-C\equiv N + H_2O \xrightarrow{HCl}$

(b) $RCOONH_4 \xrightarrow{\text{heat}}$

(c) $R-COCl + NH_3 \longrightarrow$

(d) $(RCO)_2O + NH_3 \longrightarrow$

41. When chlorobenzene is treated with NH_3 in presence of Cu_2O in xylene at 570 K. The product obtained is **[Pb. PMT 2000]**

(a) Benzylamine (b) Diazonium salt

(c) Schiff's base (d) Aniline

42. Nitrobenzene can be prepared from benzene by using a mixture of conc. HNO_3 and conc. H_2SO_4. In the nitrating mixture, HNO_3 acts as a **[BHU 2001]**

(a) Base (b) Acid

(c) Catalyst (d) Reducing agent

43. The rate determining step for the preparation of nitrobenzene from benzene is **[AIIMS 2001]**

(a) Removal of $\overset{+}{N}O_2$ (b) Removal of $\overset{+}{N}O_3$

(c) Formation of $\overset{+}{N}O_2$ (d) Formation of $\overset{+}{N}O_3$

44. In this reaction $C_6H_5NH_2 + HCl + NaNO_2 \rightarrow X$. Product X is **[RPMT 2002; AFMC 2002]**

(a) Aniline hydrochloride

(b) Nitro aniline

(c) Benzenediazonium chloride

(d) None of these

45. The diazonium salts are the reaction products in presence of excess of mineral acid with nitrous acid and **[MP PET 2002]**

(a) Primary aliphatic amine

(b) Secondary aromatic amine

(c) Primary aromatic amine

(d) Tertiary aliphatic amine

46. In acid medium nitrobenzene is reduced to aniline as shown in the reaction

$C_6H_5-NO_2 + 6[H] \rightarrow C_6H_5-NH_2 + 2H_2O$

The reducing agent used in this reaction is .... **[Orissa JEE 2002]**

(a) $LiAlH_4$ (b) Sn/HCl

(c) Na/alcohol (d) H_2/Ni

47. When aniline is treated with sodium nitrite and hydrochloric acid at 0°C, it gives **[Orissa JEE 2003]**

(a) Phenol and N_2 (b) Diazonium salt

(c) Hydrazo compound (d) No reaction takes place

48. $CH_3NO_2 \xrightarrow{Sn+HCl} CH_3X$, the '$X$' contain **[CPMT 2003]**

(a) $-NH_2$ (b) $-COOH$

(c) $-CHO$ (d) $(CH_3CO)_2O$

49. In the series of reaction $C_6H_5NH_2 \xrightarrow[0-5°C]{NaNO_2/HCl} X \xrightarrow[CH_2O]{HNO_2} Y + N_2 + HCl$ X and Y are respectively **[EAMCET 2003]**

(a) $C_6H_5-N=N-C_6H_5, C_6H_5N_2^{\oplus}Cl^{\ominus}$

(b) $C_6H_5N_2^{\oplus}Cl^{\ominus}, C_6H_5-N=N-C_6H_5$

(c) $C_6H_5N_2^{\oplus}Cl^{\ominus}, C_6H_5NO_2$

(d) $C_6H_5NO_2, C_6H_6$

50. Aromatic nitriles ($ArCN$) are not prepared by reaction **[AIIMS 2004]**

(a) $ArX + KCN$ (b) $ArN_2^{+} + CuCN$

(c) $ArCONH_2 + P_2O_5$ (d) $ArCONH_2 + SOCl_2$

51. An organic amino compound reacts with aqueous nitrous acid at low temperature to produce an oily nitroso amine. The compound is :

(a) CH_3NH_2 (b) $CH_3CH_2NH_2$

(c) $CH_3CH_2NH.CH_2CH_3$ (d) $(CH_3CH_2)_3$

52. Azo-dyes are prepared from : **[BHU 2004; Pb. CET 2001]**

(a) Aniline (b) Salicylic acid

(c) Benzaldehyde (d) Chlorobenzene

53. Gabriel's phthalimide synthesis is used for the preparation of **[CPMT 1982; DPMT 1983]**

(a) Primary aromatic amine (b) Secondary amine

(c) Primary aliphatic amine (d) Tertiary amine

54. For the preparation of *p*-nitroiodobenzene from *p*-nitroaniline, the best method is **[Orissa JEE 2005]**

(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

55. KCN reacts readily to give a cyanide with **[J & K 2005]**

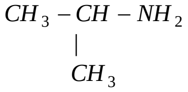
(a) Ethyl alcohol (b) Ethyl bromide

(c) Bromobenzene (d) Chlorobenzene

Properties of Nitrogen Containing Compounds

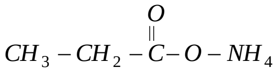
1. Which of the following amine will not react with nitrous acid to give nitrogen

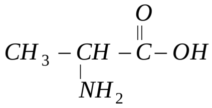
(a) CH_3NH_2 (b) $CH_3-CH_2-NH_2$

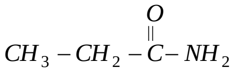
(c) 
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-NH_2$
(d) $(CH_3)_3N$

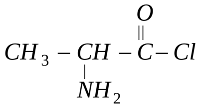
2. Which of the following compound is expected to be most basic **[NCERT 1982]**
(a) Aniline (b) Methylamine
(c) Hydroxylamine (d) Ethylamine

3. Which of the following compounds is an amino acid **[Manipal MEE 1995]**

(a) 
$CH_3-CH_2-\overset{\displaystyle O}{\overset{||}{C}}-O-NH_4$

(b) 
$CH_3-\underset{\displaystyle NH_2}{\underset{|}{CH}}-\overset{\displaystyle O}{\overset{||}{C}}-OH$

(c) 
$CH_3-CH_2-\overset{\displaystyle O}{\overset{||}{C}}-NH_2$

(d) 
$CH_3-\underset{\displaystyle NH_2}{\underset{|}{CH}}-\overset{\displaystyle O}{\overset{||}{C}}-Cl$

4. Nitro group in nitrobenzene is a **[MNR 1986]**
(a) Ortho director (b) Meta director
(c) Para director (d) Ortho and para director

5. The alkyl cyanides are
(a) Acidic (b) Basic
(c) Neutral (d) Amphoteric

6. 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

7. Aniline when treated with HNO_2 and HCl at 0^oC gives **[CPMT 1982, 89; RPMT 2000]**
(a) Phenol (b) Nitrobenzene
(c) A diazo compound (d) None of these

8. Nitrosobenzene can be isolated from nitrobenzene under **[DPMT 1982]**
(a) Metal and acid
(b) *Zn* dust and NH_4Cl
(c) Alkaline sodium arsenite
(d) Cannot be isolated

9. Alkyl cyanides when react with Grignard reagent, the product on hydrolysis found, is
(a) Aldehyde (b) Ketone
(c) Alcohol (d) Acid

10. The product formed when benzene is nitrated by fuming nitric acid is **[MP PMT 1979]**
(a) *m*-dinitrobenzene (b) Nitrobenzene
(c) *sym*-trinitrobenzene (d) None of these

11. Ethyl amine undergoes oxidation in the presence of $KMnO_4$ to form **[CPMT 1985]**
(a) An acid (b) An alcohol
(c) An aldehyde (d) A nitrogen oxide

12. Which of the following amines would undergo diazotisation
(a) Primary aliphatic amines (b)
(c) Both (a) and (b) (d) None of these

13. Reaction of primary amines with aldehyde yields **[NCERT 1984; Manipal MEE 1995]**
(a) Amides (b) Aldimines
(c) Nitriles (d) Nitro compounds

14. When acetamide is treated with HNO_2, the gas is evolved **[CPMT 1993]**
(a) H_2 (b) O_2
(c) N_2 (d) CH_4

15. Nitrobenzene on nitration gives **[NCERT 1978; CPMT 1989]**
(a) *o*-dinitrobenzene (b) *p*-dinitrobenzene
(c) *m*-dinitrobenzene (d) *o*- and *p*-nitrobenzene

16. Reduction of alkyl nitrites yields
(a) Alcohol (b) Base
(c) Amine (d) Acid

17. When primary amines are treated with *HCl*, the product obtained is
(a) An alcohol (b) A cyanide
(c) An amide (d) Ammonium salt

18. Which one is weakest base **[BHU 1982; RPMT 2000]**
(a) Ammonia (b) Methylamine
(c) Dimethylamine (d) Trimethylamine

19. Chloroform when treated with aniline and alcoholic *KOH* gives **[CPMT 1986; EAMCET 1992; MP PMT 1997; Pb. PMT 1999]**
(a) Phenyl cyanide (b) Phenyl isocyanide
(c) Chlorobenzene (d) Phenol

20. Which of following do not react with HNO_2
(a) Primary nitroalkanes (b) Secondary nitroalkanes
(c) Tertiary nitroalkanes (d) All of these

21. Primary amines can be distinguished from secondary and tertiary amines by reacting with **[CPMT 198**
(a) Chloroform and alcoholic *KOH*
(b) Methyl iodide
(c) Chloroform alone
(d) Zinc dust

[MP PMT 1980]

22. Which of following is not an usual method for preparation of primary amine
(a) Hofmann's method (b) Curtius reaction
(c) Schmidt reaction (d) Friedel-Craft's reaction

23. A solution of methyl amine
(a) Turns blue litmus red
(b) Turns red litmus blue
(c) Does not affect red or blue litmus
(d) Bleaches litmus

24. Mark the correct statement

[CPMT 1974; DPMT 1983; MP PMT 1994]

(a) Methyl amine is slightly acidic
(b) Methyl amine is less basic than NH_3
(c) Methyl amine is stronger base than NH_3
(d) Methyl amine forms salts with alkalies

25. The product of mustard oil reaction is
(a) Alkyl isothiocyanate (b) Dithio carbonamide
(c) Dithio ethylacetate (d) Thioether

26. Which of the following is azo- group
(a) $-N=$ (b) $-N=N-$
(c) $-NH-$ (d) $-CO-NH-$

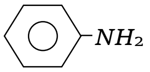
27. 'Oil of mirbane' is
(a) Aniline (b) Nitrobenzene
(c) *p*-nitroaniline (d) *p*-aminoazobenzene

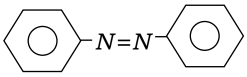
28. The maximum number of $-NO_2$ groups that can be introduced by nitration in benzene is usually
(a) 4 (b) 2
(c) 3 (d) 6

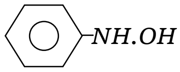
29. Nitrobenzene at room temperature is
(a) Gas (b) Liquid
(c) Solid (d) Solution

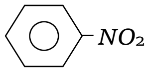
30. In the explosive amatol, TNT is mixed with**[CPMT 1988]**
(a) Ammonium citrate (b) Ammonium nitrate
(c) Ammonium oxalate (d) Ammonium sulphate

31. By reduction of nitrosobenzene which of the following is not obtained

(a) 

(b) 

(c) 

(d) 

32. By the presence of a halogen atom in the ring, basic properties of aniline is
(a) Increased (b) Decreased
(c) Unchanged (d) Doubled

33. In the mustard oil reaction, an amine is treated with
(a) Na/C_2H_5OH (b) Sn/HCl
(c) CS_2 (d) $K_2Cr_2O_7/H_2SO_4$

34. Primary nitro compounds when react with HNO_2 forms crystalline solids which on treatment with $NaOH$ gives
(a) Red solution (b) Blue solution
(c) White precipitate (d) Yellow colouration

35. 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

36. Which of the following possess powerful mustard smell (and are called mustard oils)
(a) Alkyl isocyanates (b) Alkyl cyanates
(c) Alkyl isothiocyanates (d) Alkyl thiocyanates

37. On heating acetamide in presence of P_2O_5, which of the following is formed**[MP PMT 1992; MP PET 1994;**
Kurukshetra CEE 1998]
(a) Ammonium acetate (b) Acetonitrile
(c) NH_3 (d) Methylamines

38. When chloroform reacts with ethyl amine in presence of alcoholic *KOH*, the compound formed is

[CPMT 1983; MP PMT 1993;
CBSE PMT 1997; BHU 1999; AIEEE 2002]

(a) Ethyl cyanide (b) Ethyl isocyanide
(c) Formic acid (d) An amide

39. When methyl cyanide is hydrolysed in presence of alkali, the product is **[MP PMT 1993; BCECE 2005]**
(a) Acetamide (b) Methane
(c) CO_2+H_2O (d) Acetic acid

40. Hofmann's hypobromite reaction affords a method of

[MP PMT 1993]

(a) Preparing a tertiary amine
(b) Preparing a mixture of amines
(c) Stepping down a series
(d) Stepping up a series

41. The compound which on reaction with aqueous nitrous acid on HNO_2 at low temperature produces an oily nitrosoamine is**[IIT 1981; CPMT 1989; MP**
Kurukshetra CEE 1998; MP PMT 2001]
(a) Diethylamine (b) Ethylamine
(c) Aniline (d) Methylamine

42. Identify the product Z in the series

$$CH_3CN \xrightarrow{Na+C_2H_5OH} X \xrightarrow{HNO_2} Y \xrightarrow[H_2SO_4]{K_2Cr_2O_7} Z$$

[AIIMS 1983; JIPMER 2001]

(a) CH_3CHO (b) CH_3CONH_2
(c) CH_3COOH (d) CH_3CH_2NHOH

43. The end product of the reactions is

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

[CPMT 1988, 89, 93; DCE 1999; JIPMER 2000]

(a) Ethyl cyanide (b) Ethyl amine
(c) Methyl amine (d) Acetamide

44. Primary and secondary amines are distinguished by

[AMU 1988; MP PMT 1996]

(a) Br_2/KOH (b) $HClO_4$
(c) HNO_2 (d) NH_3

45. Which one of the following will give a primary amine on hydrolysis **[BHU 1982]**
(a) Nitroparaffin (b) Alkyl cyanide
(c) Oxime (d) Alkyl isocyanide

46. Methyl amine reacts with HNO_2 giving**[RPMT 1997]**
(a) $CH_3O-N=O$ (b) CH_3-O-CH_3
(c) CH_3OH (d) (a) and (b) both

47. Nitrobenzene on reduction by zinc and NH_4Cl gives **[CPMT 1989, 94; BHU 1996; Pb. PMT 1999]**
(a) Aniline (b) Nitrosobenzene
(c) Hydrazobenzene (d) Phenylhydroxyl amine

48. The decreasing order of the basic character of the three amines and ammonia is **[MP PET/PMT 1988; KCET 1990]**
(a) $NH_3 > CH_3NH_2 > C_2H_5NH_2 > C_6H_5NH_2$
(b) $C_2H_5NH_2 > CH_3NH_2 > NH_3 > C_6H_5NH_2$
(c) $C_6H_5NH_2 > C_2H_5NH_2 > CH_3NH_2 > NH_3$
(d) $CH_3NH_2 > C_2H_5NH_2 > C_6H_5NH_2 > NH_3$

49. Correct order of increasing basicity is **[CBSE PMT 1992]**
(a) $NH_3 < C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2 < (C_2H_5)_3N$
(b) $C_6H_5NH_2 < NH_3 < (C_2H_5)_3N < (C_2H_5)_2NH < C_2H_5NH_2$
(c) $C_6H_5NH_2 < NH_3 < C_2H_5NH_2 < (C_2H_5)_3N < (C_2H_5)_2NH$
(d) $C_6H_5NH_2 < (C_2H_5)_3N < NH_3 < C_2H_5NH_2 < (C_2H_5)_2NH$

50. Among the following compounds nitrobenzene, benzene, aniline and phenol, the strongest basic behaviour in acid medium is exhibited by **[KCET 1993]**
(a) Phenol (b) Aniline
(c) Nitrobenzene (d) Benzene

51. Aniline on treatment with excess of bromine water gives **[AFMC 1990; MP PMT 1991; RPMT 1997]**
(a) Aniline bromide (b) *o*-bromoaniline
(c) *p*-bromoaniline (d) 2, 4, 6-tribromoaniline

52. Unpleasant smelling carbylamines are formed by heating alkali and chloroform with **[KCET 1987, 2000, 01]**
(a) Any amine (b) Any aliphatic amine
(c) Any aromatic amine (d) Any primary amine

53. When an organic compound was treated with sodium nitrite and hydrochloric acid in the ice cold, nitrogen gas was evolved copiously. The compound is **[KCET 1986]**
(a) A nitro compound
(b) A primary amine
(c) An aliphatic primary amine
(d) An aromatic primary amine

54. Aniline reacts with alkyl halide to give **[KCET 1984]**
(a) Amino compound
(b) Tertiary compound
(c) Quaternary ammonium compound
(d) Azomethane

55. Aniline on treatment with conc. $HNO_3 +$ conc. H_2SO_4 mixture yields **[AIIMS 1992]**
(a) *o*- and p-nitroanilines (b) *m*-nitroanilines
(c) A black tarry matter (d) No reaction

56. Which statement is not correct **[MP PMT 1995]**
(a) Amines form hydrogen bond
(b) Ethyl amine has higher boiling point than propane
(c) Methyl amine is more basic than ammonia
(d) Dimethyl amine is less basic than methyl amine

57. Which of the following is not used as an explosive **[MP PET 1996]**
(a) Trinitrotoluene (b) Trinitrobenzene
(c) Picric acid (d) Nitrobenzene

58. Primary amines react with nitrous acid to yield
(a) Insoluble nitrite salts (b) Yellow oily layer
(c) Nitrogen gas (d) Azo dye

59. Which of the following has the smell of bitter almonds
(a) Nitromethane (b) Nitroethane
(c) Nitrobenzene (d) Aniline

60. The reaction of HNO_2 with '*A*' gives quaternary ammonium salt. A is **[MP PMT 1997]**
(a) Methyl amine (b) Dimethyl amine
(c) Trimethyl amine (d) Aniline

61. Reaction of nitrous acid with aliphatic primary amine in the cold gives **[MP PET/PMT 1998; CBSE PMT 1994]**
(a) A diazonium salt (b) An alcohol
(c) A nitrite (d) A dye

62. In presence of acid, hydrolysis of methyl cyanide gives **[MP PET/PMT 1998]**
(a) Acetic acid (b) Methylamine
(c) Methyl alcohol (d) Formic acid

63. The amine which does not react with acetyl chloride is **or** Which of the following cannot be acetylated **[MP PET 1999; MP PMT 1999]**
(a) CH_3NH_2 (b) $(CH_3)_2NH$
(c) $(CH_3)_3N$ (d) None of these

64. The fusion of sodium with amine gives mainly **[MP PMT 1999; CPMT 2002]**
(a) $NaCN$ (b) NaN_3
(c) $NaSCN$ (d) $NaNO_2$

65. Which of the following is most basic **[MP PMT 1999]**
(a) $C_6H_5NH_2$ (b) $(CH_3)_2NH$
(c) $(CH_3)_3N$ (d) NH_3

66. In reaction
$CH_3CN + 2H \xrightarrow[\text{Ether}]{HCl} X \xrightarrow{\text{Boiling } H_2O} Y$; the term Y is **[CBSE PMT 1999]**
(a) Acetone (b) Ethylamine
(c) Acetaldehyde (d) Dimethylamine

67. The following compound can be classified as *N*-*N* dimethyl propanamine, *N*-methyl aniline and aniline **[Bihar MEE 1996]**
(a) Primary, secondary, tertiary
(b) Primary, tertiary, secondary
(c) Secondary, tertiary, primary

(d) Tertiary, primary, secondary

(e) None of these

68. Which of the following compounds does not react with $NaNO_2$ and HCl **[KCET 1996]**

(a) C_6H_5OH (b) $C_6H_5NH_2$

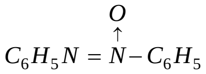
(c) $(CH_3)_3CNO_2$ (d) $(CH_3)_3CHNO_2$

69. In the reduction of nitrobenzene, which of the following is the intermediate

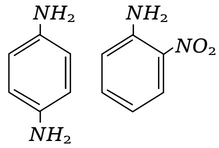
(a) $C_6H_5N=O$

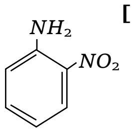
(b) $C_6H_5NH-NH-C_6H_5$

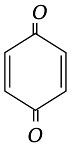
(c) $C_6H_5-N=N-C_6H_5$

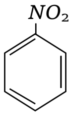
(d) 
$C_6H_5N=\overset{\overset{O}{\uparrow}}{N}-C_6H_5$

70. Aniline when treated with conc. HNO_3 gives **[KCET 1996]**

(a) 

(b) 

(c) 

(d) 

71. Which one of the following is not a base **[EAMCET 1997]**

(a) N_2H_4 (b) NH_2OH

(c) $(CH_3)_3N$ (d) HN_3

72. *p*-Nitrobromobenzene can be converted to *p*-nitroaniline by using $NaNH_2$. The reaction proceeds through the intermediate named **[Orissa JEE 2005]**

(a) Carbocation (b) Carbanion

(c) Benzyne (d) Dianion

73. If methyl is alkyl group, then which order of basicity is correct **[RPMT 1997]**

(a) $R_2NH > RNH_2 > R_3N > NH_3$

(b) $R_2NH > R_3N > RNH_2 > NH_3$

(c) $RNH_2 > NH_3 > R_2NH > R_3N$

(d) $NH_3 > RNH_2 > R_2NH > R_3N$

74. Which of the following has the minimum heat of dissociation **[Roorkee Qualifying 1998]**

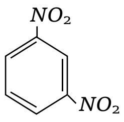
(a) $(CH_3)_3N \rightarrow BF_3$

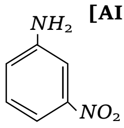
(b) $(CH_3)_3N \rightarrow B(CH_3)F_2$

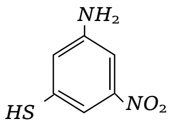
(c) $(CH_3)_3N \rightarrow B(CH_3)_2F$

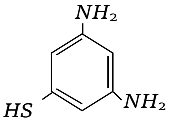
(d) $(CH_3)_3N \rightarrow B(CH_3)_3$

75. The major product (70% to 80%) of the reaction between *m*-dinitrobenzene with NH_4HS is **[AIIMS 1997]**

(a) 

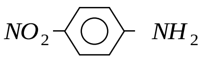
(b) 

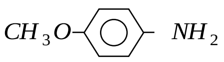


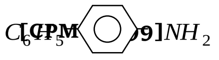


(c) (d)

76. Which one is less alkaline **[CPMT 1997]**

(a) 

(b) 

(c) 

(d) All of these

77. In the diazotisation of aniline with sodium nitrite and hydrochloric acid, an excess of hydrochloric acid is used primarily to **[Pb. PMT 1998]**

(a) Suppress the concentration of free aniline available for coupling

(b) Suppress hydrolysis of phenol

(c) Insure a stoichiometric amount of nitrous acid

(d) Neutralize the base liberated

78. A primary amine can be converted to an alcohol by the action of **[CET Pune 1998]**

(a) Alkali (b) Nitrous acid

(c) Reducing agent (d) Oxidising agent

79. Arrange the following in increasing order of basicity $CH_3NH_2, (CH_3)_2NH, C_6H_5NH_2, (CH_3)_3N$ **[AFMC 1997]**

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

(b) $(CH_3)_3N > (CH_3)_2NH > CH_3NH_2 > C_6H_5NH_2$

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

(d) $C_6H_5NH_2 > (CH_3)_3N > CH_3NH_2 > (CH_3)_2NH$

80. In the reaction

$CH_3CN + CH_3MgI \rightarrow A \xrightarrow{H_2O/H^+} B$

The compound *B* is **[KCET 1999]**

(a) Acetic acid (b) Acetone

(c) Acetaldehyde (d) Ethyl alcohol

81. CH_3CN is known as acetonitrile because **[AMU 1999]**

(a) It contains an aceto group

(b) On hydrolysis it gives acetic acid

(c) Both (a) and (b)

(d) None of these

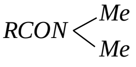
82. What is formed, when nitrobenzene is reduced using zinc and alkali **[BHU 2000; AIIMS 2000; CBSE PMT 2000; MH CET 2003]**

(a) Phenol (b) Aniline

(c) Nitrosobenzene (d) Hydrazobenzene

83. $RCOCl + 2Me_2NH \rightarrow A + Me_2\overset{+}{N}H_2Cl^-$

Here *A* is **[RPET 2000]**

(a) 
$RCON\begin{matrix}Me\\Me\end{matrix}$

(b) $RCONH_2$

(c) $RCONHMe$ (d) $(RCO)_2NH$

84. Decreasing order of basicity is **[RPET 2000]**

(1) CH_3CONH_2 (2) $CH_3CH_2NH_2$

(3) Ph–CH_2CONH_2

(a) 1 > 2 > 3 (b) 2 > 1 > 3

(c) 3 > 2 > 1 (d) None of these

85. Among the following, the strongest base is **[UPSEAT 2000; IIT-JEE (Screening) 2000]**

(a) $C_6H_5NH_2$ (b) $p-NO_2C_6H_4NH_2$

(c) $m-NO_2-C_6H_4NH_2$ (d) $C_6H_5CH_2NH_2$

86. Aniline and methyl amine can be differentiated by **[DPMT 2000]**

(a) Reaction with chloroform and aqueous solution of KOH

(b) Diazotisation followed by coupling with phenol

(c) Reaction with HNO_2

(d) None of these

87. The amine which can react with $C_6H_5-SO_2-Cl$ to form a product insoluble in alkali shall be **[AMU 2000]**

(a) Primary amine

(b) Secondary amine

(c) Tertiary amine

(d) Both primary and secondary amines

88. A mixture of benzene and aniline can be separated by **[KCET (Engg.) 2001]**

(a) Hot water (b) dil. HCl

(c) dil. $NaOH$ (d) Alcohol

89. Nitrobenzene on further excessive nitration gives **[AFMC 2001]**

(a) Trinitrobenzene (b) *m*-dinitrobenzene

(c) *p*-dinitrobenzene (d) All of these

90. The compound A with following sequence of reaction gave benzoic acid

$A \xrightarrow{NaNO_2/HCl} B \xrightarrow{KCN} C \xrightarrow{H_3O^+}$ benzoic acid. The compound A is **[AMU 2001]**

(a) Nitrobenzene (b) Aniline

(c) Benzaldehyde (d) Amides

91. Which of the following chemicals are used to manufacture methyl isocyanate that caused "Bhopal Tragedy"

(i) Methylamine (ii) Phosgene

(iii) Phosphine (iv) Dimethylamine

[AIIMS 2005]

(a) (i) and (iii) (b) (iii) and (iv)

(c) (i) and (ii) (d) (ii) and (iv)

92. An isocyanide on hydrolysis gives **[AMU 2001]**

(a) An amide

(b) A carboxylic acid and ammonia

(c) A N-substituted amide

(d) A 1°-amine and formic acid

93. Methyl isocyanide on hydrolysis gives **[UPSEAT 2001]**

(a) CH_3NH_2 (b) $HCOOH$

(c) CH_3COOH (d) Both (a) and (b)

94. Pure aniline is a **[UPSEAT 2001]**

(a) Colourless solid

(b) Brown coloured solid

(c) Colourless liquid

(d) Brown coloured liquid

95. Reduction of methyl isocyanide gives **[RPMT 2002]**

(a) Ethylamine (b) Methylamine

(c) Dimethylamine (d) Trimethylamine

96. Reaction of aniline with benzaldehyde is **[RPMT 2002]**

(a) Polymerisation (b) Condensation

(c) Addition (d) Substitution

97. In the reaction $C_6H_5CHO + C_6H_5NH_2 \rightarrow C_6H_5N = HCC_6H_5 + H_2O$, the compound $C_6H_5N = CHC_6H_5$ is known as **[RPMT 2000; AIIMS 2002; AMU 2001]**

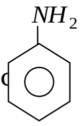
(a) Aldol (b) Schiff's reagent

(c) Schiff's base (d) Benedict reagent

98. The unshared pair of electrons on a cyanide ion can acts as **[Kerala (Med.) 2002]**

(a) Isocyanide centre (b) Amido centre

(c) Cationic centre (d) Nucleophilic centre

99. Electrophilic substitution of  with bromine gives **[Kerala (Med.) 2002]**

(a) 1, 4, 6-tribromo aniline

(b) 2, 4, 6-tribromo aniline

(c) 4-bromo aniline

(d) 3-bromo aniline

100. Mustard gas is obtained by **[MP PET 2002]**

(a) The action of dilute acids on mustard seeds

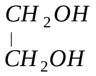
(b) Treating ethylene with mustard oil

(c) Treating sulphur chloride with ethylene

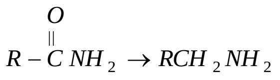
(d) None of these

101. Which of the following is capable of forming a zwitter ion **[JIPMER 2002]**

(a) C_6H_5-OH (b) $C_6H_4(NH_2)_2$

(c) 
CH_2OH-CH_2OH (d) H_2N-CH_2-COOH

102. Which one of the following reducing agents is likely to be the most effective in bringing about the following change


$R-\overset{O}{\overset{\|}{C}}NH_2 \rightarrow RCH_2NH_2$ **[AMU 2002]**

(a) H_2-Ni (b) $NaBH_4$

(c) $LiAlH_4$ (d) Na-alcohol

103. During acetylation of amines what is replaced by acetyl groups **[UPSEAT 2002]**

(a) Hydrogen atom attached to nitrogen atom

(b) One or more hydrogen atoms attached to carbon atom

(c) One or more hydrogen atoms attached to nitrogen atom

(d) Hydrogen atoms attached to either carbon atom or nitrogen atom

104. Hydrolysis of acetonitrile in acidic medium produces **[CPMT 2003; RPMT 2003]**

(a) CH_3CH_2OH (b) CH_3COOH

(c) CH_3NC (d) CH_3COOCH_3

105. Which has a pyramidal structure **[UPSEAT 2003]**

(a) Trimethylamine (b) Methanol

(c) Acetylene (d) Water

106. Ethyl amine on acetylation gives **[BHU 2002; BVP 2003]**

(a) N-ethyl acetamide

(b) Acetamide

(c) Methyl acetamide

(d) None

107. The refluxing of $(CH_3)_2NCOCH_3$ with acid gives **[BHU 2002; BVP 2003]**

(a) $(CH_3)_2NH + CH_3COOH$

(b) $(CH_3)_2NCOOH + CH_4$

(c) $2CH_3OH + CH_3CONH_2$

(d) $2CH_3NH_2 + CH_3COOH$

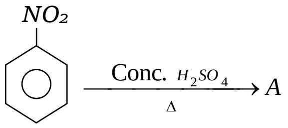
108. *p*-chloro aniline and anilinium hydrogen chloride can be distinguished by **[UPSEAT 2003]**

(a) Sandmaeyer reaction

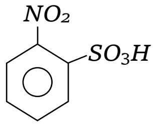
(b) Carbyl amine reaction

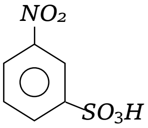
(c) Hinsberg's reaction

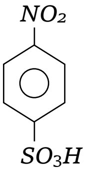
(d) $AgNO_3$

109. 

Product '*A*' in above reaction is

(a) 

(b) 

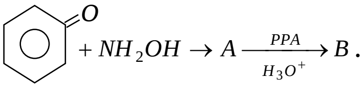
(c) 

(d) None of these

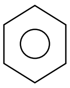
110. Product obtained by electrolytic reduction of nitrobenzene in presence of H_2SO_4 is **[RPMT 2003]**

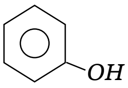
(a) *o*-amino phenol (b) *m*-amino phenol

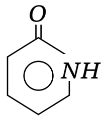
(c) *p*-amino phenol (d) None of these

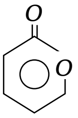
111. 

The product '*B*' is **[RPMT 2003]**

(a) 

(b) 

(c) 

(d) 

112. Identify the product *Z* in the following reaction

$C_6H_5NH_2 \xrightarrow{(AC)_2O} X \xrightarrow{Br_2/CCl_4} Y \xrightarrow{HOH} Z$ **[Kerala (Med.) 2003]**

(a) *p*-Bromoaniline (b) *p* - Bromoacetophenone

(c) *o*-Bromoacetophenone (d)*o*-Bromoacetonilide

113. Benzaldehyde condenses with *N*, *N*-dimethylaniline in presence of anhydrous $ZnCl_2$ to give **[Kerala (Med.) 2003]**

(a) Michler's ketone (b) Azo dye

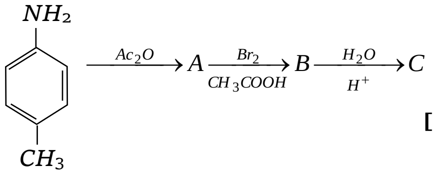
(c) Malachite green (d) Buffer yellow

114. The correct order of reactivity towards the electrophilic substitution of the compounds aniline (I) benzene (II) and nitrobenzene (III) is **[CBSE PM**

(a) I > II > III (b) III > II > I

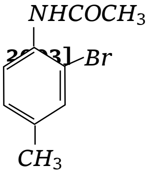
(c) II > III > I (d) I < II > III

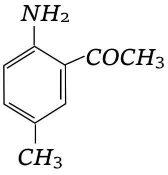
115. The final product *C*, obtained in this reaction

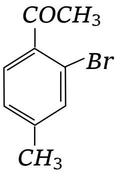


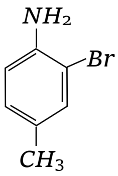
would be **[CBSE PMT 2003]**

[RPMT 2003]

(a) 

(b) 

(c) 

(d) 

116. The correct order of increasing basic nature for the bases NH_3, CH_3NH_2 and $(CH_3)_2NH$ is **[AIEEE 2003]**

(a) $CH_3NH_2 < NH_3 < (CH_3)_2NH$

(b) $(CH_3)_2NH < NH_3 < CH_3NH_2$

(c) $NH_3 < CH_3NH_2 < (CH_3)_2NH$

(d) $CH_3NH_2 < (CH_3)_2NH < NH_3$

117. Nitrobenzene gives *N*-phenylhydroxylamine by

[AIIMS 2003]

(a) Sn/HCl (b) $H_2/Pd-C$

(c) $Zn/NaOH$ (d) Zn/NH_4Cl

118. Among the following the weakest base is **[AIIMS 2003]**

(a) $C_6H_5CH_2NH_2$ (b) $C_6H_5CH_2NHCH_3$

(c) $O_2N\,CH_2NH_2$ (d) $CH_3NH\,CHO$

119. The correct order of basicity of amines in water is :

[Pb. CET 2003]

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

120. Complete the following reaction : **[MHCET 2004]**

$R\ NH_2 + H_2SO_4 \rightarrow$

(a) $[R\ NH_3]^+HSO_4^-$ (b) $[R\ NH_3]_2^+SO_4^{2-}$

(c) $R\ NH_2.H_2SO_4$ (d) No reaction

121. Which of the following compound reacts with chloroform and a base to form phenyl isocyanide ?**[MHCET 2003]**

(a) Phenol (b) Aniline

(c) Benzene (d) Nitro benzene

122. Which one doesn't liberate NH_3 when undergoes hydrolysis **[Orissa JEE 2005]**

(a) Acetanilide (b) Acetonitrile

(c) Acetamide (d) Phenyl isocyanide

123. A nitrogen containing organic compound gave an oily liquid on heating with bromine and potassium hydroxide solution. On shaking the product with acetic anhydride, an antipyretic drug was obtained. The reactions indicate that the starting compound is **[KCET 2004]**

(a) Aniline (b) Benzamide

(c) Acetamide (d) Nitrobenzene

124. Benzamide on reaction with $POCl_3$ gives**[IIT-JEE 2004]**

(a) Aniline (b) Chlorobenzene

(c) Benzyl amine (d) Benzonitrile

125. Among the following which one does not act as an intermediate in Hofmann rearrangement **[AIIMS 2005]**

(a) $RNCO$ (b) $RCO\ \ddot{N}$

(c) $RCO\ \ddot{N}\ HBr$ (d) RNC

126. Aniline reacts with which of these to form Schiff base

[AFMC 2004]

(a) Acetic acid (b) Benzaldehyde

(c) Acetone (d) NH_3

127. Which of the following does not reduce Tollen's reagent

[Kerala PMT 2004]

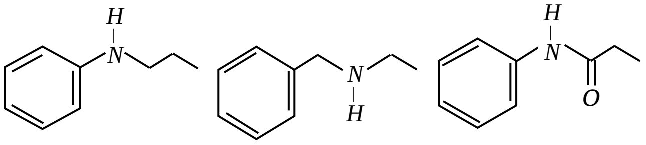
(a) CH_3CHO (b) C_6H_5NHOH

(c) $HCOOH$ (d) $C_6H_5NO_2$

(e) None of these

128. Which one of the following compound is most basic ?

[UPSEAT 2004]



(A) (B) (C)

(a) (A) (b) (B)

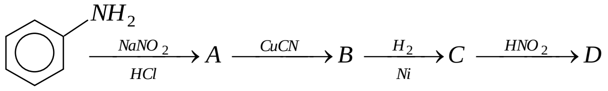
(c) (C) (d) All are equally basic

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

(a) Hinsberg method (b) Hofmann method

(c) Wurtz reaction (d) Curtius reaction

130. Aniline in a set of reactions yielded a product D.



The structure of product D would be **[CBSE PMT 2005]**

(a) $C_6H_5CH_2NH_2$ (b) $C_6H_5NH\,CH_2CH_3$

(c) C_6H_5NHOH (d) $C_6H_5CH_2OH$

131. Electrolytic reduction of nitrobenzene in weakly acidic medium gives **[CBSE PMT 2005]**

(a) Aniline (b) Nitrosobenzene

(c) *N*-Phenylhydroxylamine (d) *p*-Hydroxylaniline

132. Among the following compounds $C_3H_7NH_2$, $NH_3, CH_3NH_2, C_2H_5NH_2$ and $C_6H_5NH_2$, the least basic compound is

(a) $C_3H_7NH_2$ (b) NH_3

(c) CH_3NH_2 (d) $C_6H_5NH_2$

(e) $C_2H_5NH_2$

133. The reduction of which of the following compound would yield secondary amine ?

(a) Alkyl nitrite

(b) Carbylamine

(c) Primary amine

(d) Secondary nitro compound

134. Azo dye is prepared by the coupling of phenol and :

[Pb. CET 2000]

(a) Diazonium chloride

(b) *o*-nitro aniline

(c) Benzoic acid

(d) Chlorobenzene

135. $C_6H_5NH_2 \xrightarrow{NaNO_2HCl} X \xrightarrow{Cu_2(CN)_2} Y \xrightarrow{H_2O/H^+} Z$

Z is identified as : **[Pb. PMT 2004]**

(a) $C_6H_5-NH-CH_3$

(b) C_6H_5-COOH

(c) $C_6H_5-CH_2-NH_2$

(d) $C_6H_5-CH_2-COOH$

136. When acetamide reacts with Br_2 and caustic soda, then we get :

(a) Acetic acid (b) Bromoacetic acid

(c) Methyl amine (d) Ethyl amine

137. In the reaction

$$CH_3CN+2H\xrightarrow[\text{Ether}]{HCl}X\xrightarrow[H_2O]{\text{Boiling}}Y;$$

the term *Y* is: **[BHU 2004]**

(a) Acetone (b) Ethyl amine

(c) Acetaldehyde (d) Dimethyl amine

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

(a) A Schiff's base (b) An enamine

(c) An imine (d) An amine

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

In the given reaction what will be the product **[BHU 2005]**

(a) $R-N=C=O$ (b) $R-\overset{+}{N}\equiv C^{-}$

(c) $R-C\equiv N$ (d) None of these.

140. Which of the following is secondary pollulant. **[BHU 2005]**

(a) CO_2 (b) N_2O

(c) *PAN* (d) SO_2

141. Nitration of aniline also gives *m*-nitro aniline, in strong acidic medium because

(a) In electrophilic substitution reaction amino group is meta directive

(b) Inspite of substituents nitro group always goes to *m*- position

(c) In strong acidic medium, nitration of aniline is a nucleophic substitution reaction

(d) In strong acidic medium aniline present as anilinium ion

(e) Strong acid, gives nitrate anion, which attacks at *m*-position

142. Identify the product in following order

3,4,5-Tribromoaniline $\xrightarrow[\text{(ii)}H_3PO_2]{\text{(i)diazotization}}$? **[Kerala CET 2005]**

(a) 3, 4,5 –Tribromobenzene

(b) 1, 2, 3 – Tribromobenzene

(c) 2, 4, 6 – Tribromobenzene

(d) 3, 4, 5 – Tribromo nitro benzene

(e) 3, 4, 5 – Tribromo phenol

143. The correct order of basicity in amines

(i) $C_4H_5NH_2$ (ii) CH_3NH_2

(iii) $(CH_3)_2NH$ (iv) $(CH_3)_3N$

[Kerala CET 2005]

(a) (i) < (iv) < (ii) < (iii) (b) (iv) < (iii) < (ii) < (i)

(c) (i) < (ii) < (iii) < (iv) (d) (ii) < (iii) < (iv) < (i)

(e) (iv) < (iii) < (ii) < (i)

Tests for Nitrogen Containing Compounds

[CPMT 2004]

1. When acetamide reacts with Br_2 and caustic soda, then we get

[DPMT 1983; BHU 1997; Orissa JEE 2002; CPMT 1971, 78, 79, 81, 85, 2000, 03; MP PMT 1989; MP PET 1995, 2002]

(a) Acetic acid (b) Bromoacetic acid

(c) Methyl amine (d) Ethane

2. In organic compounds, nitrogen is tested in Lassaigne's test as

(a) $NaNH_2$ (b) $NaCN$

(c) $NaNO_2$ (d) $NaNO_3$

3. Liebermann's nitroso reaction is used for testing

(a) Primary amines (b) Secondary amines

(c) Tertiary amines (d) All the above

4. A nauseating smell in the carbylamine test for primary amines is due to the formation of **[MP PET 1993]**

(a) Isocyanide (b) Chloroform

(c) Cyanide (d) DDT

5. A positive carbylamine test is given by **[IIT-JEE 1999]**

(a) *N*, *N*-dimethylaniline

(b) 2, 4-dimethylaniline

(c) *N*-methyl-*o*-methylaniline

(d) *p*-methylbenzylamine

6. The colour of *p*-amino azobenzene is **[BHU 1997]**

(a) Orange **[Kerala CET 2005]** (b) Congo red

(c) Bismark brown (d) Indigo

7. When primary amine is heated with CS_2 in presence of excess mercuric chloride, it gives isothiocyanate. This reaction is called **[KCET 1998; CPMT 19**

(a) Hofmann bromide reaction

(b) Hofmann mustard oil reaction

(c) Carbylamine reaction

(d) Perkin reaction

8. Diazo-coupling is useful to prepare some **[CPMT 1999]**

(a) Dyes (b) Proteins

(c) Pesticides (d) Vitamins

9. Carbylamine test is used in the detection of **[DCE 1999]**

(a) Aliphatic 2° amine

(b) Aromatic 1° amine

(c) Aliphatic 1° amine

(d) Both aliphatic and aromatic 1° amines

10. Which of the following substance does not give iodoform test

(a) C_6H_5CN (b) RNH_2

(c) CH_3OH (d) All

11. Which one of the following compounds when heated with KOH and a primary amine gives carbylamine test

[Orissa JEE 2005]

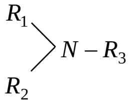
(a) $CHCl_3$ (b) CH_3Cl

(c) CH_3OH (d) CH_3CN

Critical Thinking

Objective Questions

1. The compound



$R_1, R_2 > N-R_3$

forms nitroso amines when the substituents are

[Roorkee 1999]

(a) $R_1=CH_3, R_2=R_3=H$

(b) $R_1=R_2=H,\ R_3=C_2H_5$

(c) $R_1=H,\ R_2=R_3=CH_3$

(d) $R_1=CH_3,\ R_2=C_2H_5,\ R_3=H$

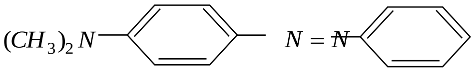
2. The action of nitrous acid on ethyl amine gives

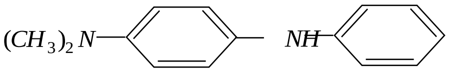
[DPMT 1982; CPMT 1971, 89, 94; MP PET 1993, 2001; RPMT 1997; Pb. PMT 1999]

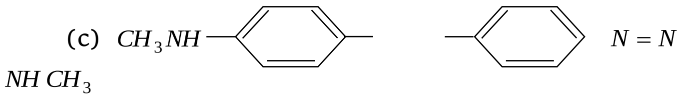
(a) Ethane (b) Ammonia

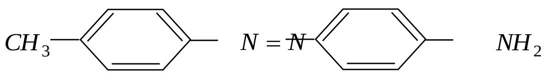
(c) Ethyl acohol (d) Nitroethane

3. Aniline when diazotized in cold and then treated with dimethyl aniline gives a coloured product. Its structure would be **[CBSE PMT 2004]**

(a) 

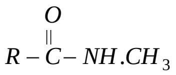
(b) 

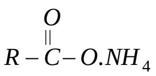
(c) 

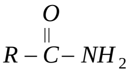
(d) 

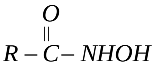
4. Indicate which nitrogen compound amongst the following would undergo Hofmann's reaction (i.e. reaction with Br_2 and strong KOH) to furnish the primary amine ($R-NH_2$)

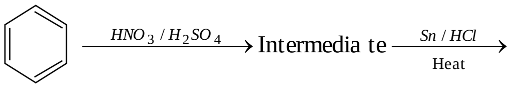
[CBSE PMT 1989]

(a) 
$R-\overset{O}{\overset{\|}{C}}-NH.CH_3$

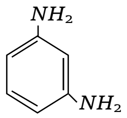
(b) 
$R-\overset{O}{\overset{\|}{C}}-O.NH_4$

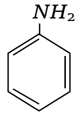
(c) 
$R-\overset{O}{\overset{\|}{C}}-NH_2$

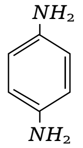
(d) 
$R-\overset{O}{\overset{\|}{C}}-NHOH$

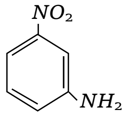
5. 

[BHU 1995]

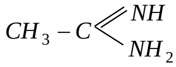
(a) 

(b) 

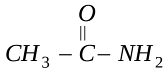
(c) 

(d) 

6. The correct order of basicities of the following compounds is


$CH_3-C{<}^{NH}_{NH_2}$ $\quad CH_3-CH_2-NH_2 \quad (CH_3)_2NH$

1 2 3


$CH_3-\overset{O}{\overset{\|}{C}}-NH_2$

4 **[IIT-JEE (Screening) 2001]**

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

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

7. Which of the following would be most reactive towards nitration **[AMU 2000; UPSEAT 2002]**

(a) Benzene (b) Nitro benzene

(c) Toluene (d) Chloro benzene

8. Aniline reacts with acetaldehyde to form

[MHCET 2004; AFMC 2004]

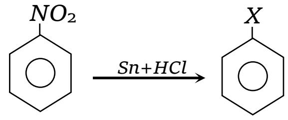
(a) Schiff's base (b) Carbylamine

(c) Immine (d) None of these

9. *p*-chloroaniline and anilinium hydrochloride can be distinguished by **[IIT-JEE 1998]**

(a) Sandmeyer reaction (b) $NaHCO_3$

(c) $AgNO_3$ (d) Carbylamine test

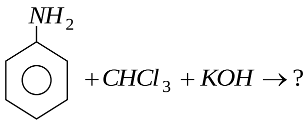
10. 

In the above reaction 'X' stands for

[CPMT 1986, 2001; MP PET 1992; KCET (Engg./Med.) 2000]

(a) NH_2 (b) $SnCl_2$

(c) Cl (d) $NH_4^+Cl^-$

11. 

[BHU 2000; Pb. PMT 2000; Kerala 2003]

(a) Phenyl isocyanide (b) Benzyl amine

(c) Benzyl chloride (d) None of these

12. The order of basic strength among the following amines in benzene solution is**[AIIMS 1991; RPMT 2002]**

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

13. The refluxing of $(CH_3)_2NCOCH_3$ with acid gives **[KCET 1996]**

(a) $2CH_3NH_2 + CH_3COOH$

(b) $2CH_3OH + CH_3COOH$

(c) $(CH_3)_2NH + CH_3COOH$

(d) $(CH_3)_2NCOOH + CH_4$

14. Order of basicity of ethyl amines is**[MP PMT/PET 1988]**

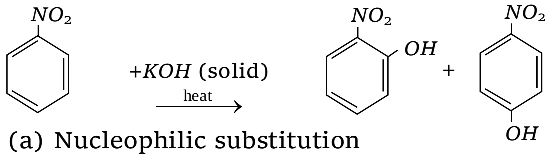
(a) Secondary > Primary > Tertiary

(b) Primary > Secondary > Tertiary

(c) Secondary > Tertiary > Primary

(d) Tertiary > Primary > Secondary

15. The following reaction is **[KCET 1996]**



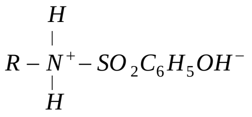
(a) Nucleophilic substitution

(b) Electrophilic substitution

(c) Free radical substitution

(d) None of these

16. RNH_2 reacts with $C_6H_5SO_2Cl$ in aqueous KOH to give a clear solution. On acidification a precipitate is obtained which is due to the formation of **[Roorkee 2000]**

(a) 
$R-\overset{H}{\underset{H}{N^+}}-SO_2C_6H_5OH^-$

(b) $R-N^-SO_2C_6H_5K^+$

(c) $R-NHSO_2C_6H_5$

(d) $C_6H_5SO_2NH_2$

17. If N and S are present in an organic compound during Lassaigne test, then both changes into**[CPMT 1997]**

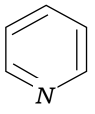
(a) Na_2S and $NaCN$

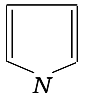
(b) $NaSCN$

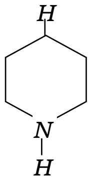
(c) Na_2SO_3 and $NaCN$

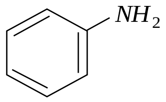
(d) Na_2S and $NaCNO$

18. The strongest base among the following is **[AIIMS 2004; BHU 2004]**

(a) 

(b) 

(c) 

(d) 

19. 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**[AFMC 1998; AIIMS**

(a) Perkin's reaction

(b) Fittig's reaction

(c) Sandmeyer's reaction

(d) Liebermann's nitroso reaction

20. A primary amine is formed an amide by the treatment of bromine and alkali. The primary amine has : **[BHU 2004]**

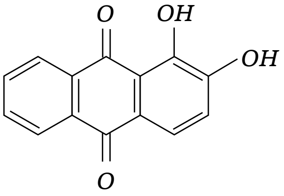
(a) 1 carbon atom less than amide

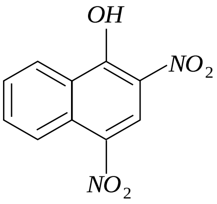
(b) 1 carbon atom more than amide

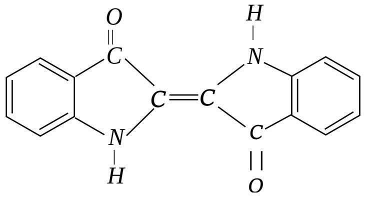
(c) 1 hydrogen atom less than amide

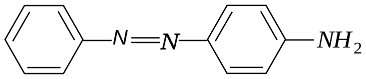
(d) 1 hydrogen atom more than amide

21. The structural formula of Indigo dye is :**[DPMT 2004]**

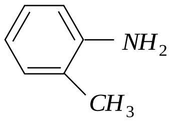
(a) 

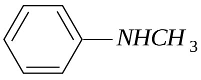
(b) 

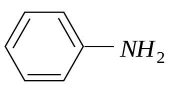
(c) 

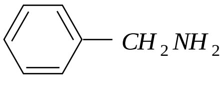
(d) 

22. Which of the following is the strongest base ?**[AIEEE 2004**

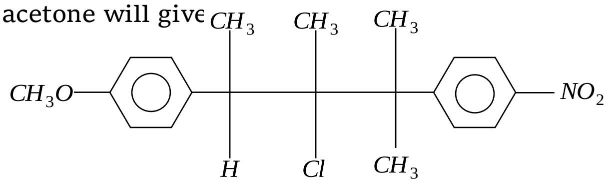
(a) 

(b) 

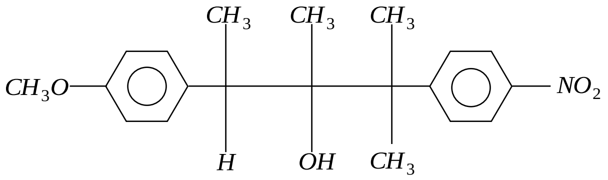
(c) 

(d) 

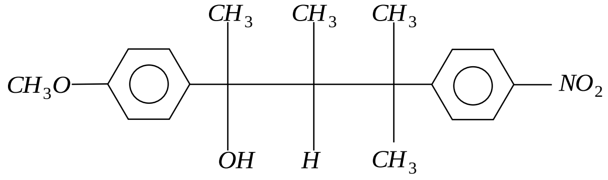
23. The following compound on hydrolysis in aqueous acetone will give



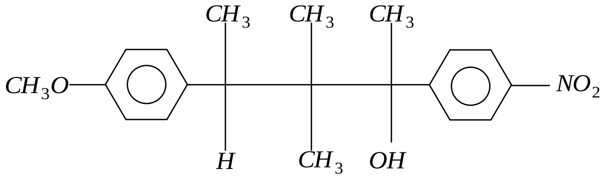
(K:)



(L:)



(M:)



(a) Mixture of (K) and (L) (b) Mixture of (K) and (M)

(c) Only (M) (d) Only (K)

Assertion & Reason

For AIIMS Aspirants

Read the assertion and reason carefully to mark the correct option out of the options given below :

(a) If both assertion and reason are true and the reason is the correct explanation of the assertion.
(b) If both assertion and reason are true but reason is not the correct explanation of the assertion.
(c) If assertion is true but reason is false.
(d) If the assertion and reason both are false.
(e) If assertion is false but reason is true.

1. Assertion : Benzene diazonium chloride does not give tests for nitrogen:
Reason : N_2 gas lose takes place during heating
[AIIMS 1999]

2. Assertion : Amines are basic in nature.
Reason : Presence of lone pair of electron on nitrogen atom. **[AIIMS 1999]**

3. Assertion : Methyl isocyanide reacts with ozone to form methyl isocyanate.
Reason : Methyl isocyanate was responsible for Bhopal tragedy.

4. Assertion : Alkyl cyanide can be prepared by carbylamine reaction
Reason : Ethyl amine when heated with chloroform in presence of alcoholic KOH, cyanide is formed.

5. Assertion : CN^- ion is an ambident nucleophile.
Reason : Nucleophiles are electron rich species.

6. Assertion : Sulphanilic acid exists as dipolar ion whereas *p*-aminobenzoic acid does not.
Reason : Carboxyl group being more acidic than $-SO_3H$ group can easily transfer a H^+ to the amino group.

7. Assertion : Nitrating mixture used for carrying our nitration of benzene consists of conc. HNO_3 + conc. H_2SO_4.
Reason : In presence of H_2SO_4, HNO_3 acts as a base and produces NO_2^+ ions.

8. Assertion : In order to convert R–Cl to pure R–NH_2, Gabriel pthalimide synthesis can be used.
Reason : With proper choice of alkyl halides, pthalimide synthesis can be used to prepare 1°, 2° or 3° amines.

9. Assertion : Ammonolysis of alkyl halides involves the reaction between alkyl halides and alcoholic ammonia.
Reason : Reaction can be used to prepare only 2° amines.

10. Assertion : Nitroalkanes, but not nitroarenes can be distilled at normal atmospheric pressure.
Reason : Nitroalkanes are sparingly soluble in water while nitroarenes are insoluble.

11. Assertion : In Hofmann bromide reaction, the amine formed has one carbon atom less than the parent 1° amide.
Reason : *N*-methyl acetamide undergoes Hofmann bromamide reaction.

12. Assertion : Nitrobenzene does not undergo Friedel Craft alkylation.
Reason : Nitrobenzene is used as solvent in laboratory and industry.

13. Assertion : Ammonia is less basic than water.
Reason : Nitrogen is less electronegative than oxygen.

14. Assertion : The reaction between a diazo salt and an aromatic amine or a phenol, giving an aminoazo or hydroxyazo compounds is called coupling reaction.

Reason : Condensation of diazonium salt with phenol is carried out in weakly acidic medium.

15. Assertion : Carbylamine reaction involves the reaction between 1° amine and chloroform in basic medium.

Reason : In carbylamine reaction, $-NH_2$ group is converted into $-NC$ group.

16. Assertion : Me_3N reacts with BF_3 whereas Ph_3N does not.

Reason : The electron pair on nitrogen atom in Ph_3N is delocalised in the benzene ring and is not available to boron in BF_3

17. Assertion : *p*-Anisidine is weaker base than aniline.

Reason : $-OCH_3$ group in anisidine exerts $-R$ effect.

18. Assertion : Lower aldehydes and ketones are soluble in water but the solubility decreases as the molecular mass increases.

Reason : Distinction between aldehydes and ketones can be made by Tollen's test.

[AIIMS 1999]

19. Assertion : Aniline hydrogen sulphate on heating forms a mixture of ortho and para aminobenzene sulphonic acids.

Reason : The sulphonic acid group is electron withdrawing. **[AIIMS 1996]**

20. Assertion : $p-O_2N-C_6H_5COCH_3$ is prepared by Friedel Crafts acylation of nitrobenzene.

Reason : Nitrobenzene easily undergoes electrophilic substitution reaction.**[AIIM**

21. Assertion : Alkyl isocyanides in acidified water give alkyl formamides.

Reason : In isocyanides, carbon first acts as a nuclephile and then as an electrophile.

[AIIMS 2005]

Answers

Introduction of Nitrogen Containing Compounds

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

Preparation of Nitrogen Containing Compounds

1	c	2	d	3	b	4	b	5	b
6	b	7	c	8	a	9	c	10	a
11	d	12	d	13	b	14	b	15	d
16	c	17	a	18	b	19	a	20	c
21	b	22	a	23	a	24	a	25	b
26	b	27	c	28	d	29	c	30	a
31	a	32	a	33	a	34	d	35	c
36	c	37	b	38	a	39	d	40	b,c
41	d	42	b	43	c	44	c	45	c
46	b	47	b	48	a	49	c	50	a
51	c	52	a	53	c	54	a	55	b

Properties of Nitrogen Containing Compounds

1	d	2	d	3	b	4	b	5	a
6	c	7	c	8	d	9	b	10	c
11	c	12	b	13	b	14	c	15	c
16	a	17	d	18	a	19	b	20	c
21	a	22	d	23	b	24	c	25	a
26	b	27	b	28	c	29	b	30	b
31	d	32	a	33	c	34	a	35	b
36	c	37	b	38	b	39	d	40	c
41	a	42	c	43	b	44	c	45	d
46	d	47	d	48	b	49	d	50	b
51	d	52	d	53	c	54	c	55	c
56	d	57	d	58	c	59	c	60	c
61	b	62	a	63	c	64	a	65	b
66	c	67	e	68	c	69	a	70	c
71	d	72	c	73	a	74	b	75	b
76	a	77	a	78	b	79	c	80	b
81	b	82	d	83	a	84	b	85	d
86	b	87	b	88	b	89	b	90	b
91	c	92	d	93	d	94	c	95	c
96	b	97	c	98	c	99	b	100	c
101	d	102	a	103	c	104	b	105	a
106	a	107	a	108	d	109	b	110	c
111	c	112	a	113	c	114	a	115	d
116	c	117	d	118	b	119	a	120	b
121	b	122	d	123	b	124	d	125	d
126	b	127	d	128	b	129	c	130	d

131	a	132	d	133	b	134	a	135	b
136	c	137	c	138	b	139	b	140	c
141	d	142	b	143	a				

Tests for Nitrogen Containing Compounds

1	c	2	b	3	b	4	a	5	b
6	a	7	b	8	a	9	d	10	d
11	a								

Critical Thinking Questions

1	c	2	c	3	a	4	c	5	b
6	b	7	b	8	a	9	bc	10	a
11	a	12	b	13	c	14	a	15	a
16	c	17	b	18	c	19	d	20	a
21	c	22	d	23	a				

Assertion & Reason

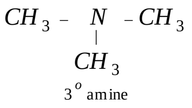
1	a	2	a	3	b	4	d	5	b
6	c	7	a	8	c	9	c	10	b
11	c	12	b	13	e	14	c	15	a
16	a	17	d	18	b	19	d	20	d
21	a								

Answers and Solutions

Introduction of Nitrogen Containing Compounds

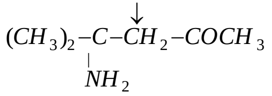
4. (d) C_3H_9N can form all the 3 amines.

$CH_3CH_2CH_2-NH_2$ (1° amine), $CH_3-CH_2-NH-CH_3$ (2° amine)



$CH_3-\underset{\underset{CH_3}{|}}{N}-CH_3$ (3° amine)

5. (c) $(CH_3)_2C=O+H.CH_2-COCH_3+NH_3$

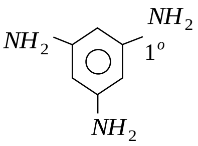


$$\downarrow$$
$$(CH_3)_2-\underset{\underset{NH_2}{|}}{C}-CH_2-COCH_3$$

diacetoneamine

8. (d) Allyl isocyanide. $CH_2=CH-CH_2-N\equiv C$

9. (c)



1^o amine

12. (b) $CH_3CH_2-O-N=O$ is a nitrite derivative, hence it is not a nitro derivative.

13. (b) CH_3CN is called acetonitrile....

15. (b) Four 1^o amines are possible

$CH_3CH_2CH_2CH_2NH_2, (CH_3)_2CHCH_2NH_2,$

$CH_3CH(NH_2)CH_2CH_3, (CH_3)_3CNH_2$

Preparation of Nitrogen Containing Compounds

1. (c) Hofmann's bromamide reaction

$\underset{\text{Acetamide}}{CH_3-CO-NH_2}+Br_2+4KOH\xrightarrow{H_2O}$

$\underset{\text{Methyl amine}}{CH_3NH_2}+K_2CO_3+2KBr+2H_2O$

2. (d) $CH_3CONH_2\xrightarrow{NaOBr}CH_3NH_2$.

3. (b) $\underset{\text{Acetamide}}{CH_3CONH_2}+Br_2+4NaOH\rightarrow$

$\underset{\text{Methylamine}}{CH_3NH_2}+Na_2CO_3+2NaBr+2H_2O$

4. (b) $\underset{(2c)}{CH_3-CO-NH_2}\xrightarrow[\text{Hofmann's bromamide}]{NaOH\ /\ Br_2}\underset{(1c)}{CH_3-NH_2}$

5. (b) $CH_3C\equiv N+4[H]\xrightarrow[\text{Reduction}]{Na+C_2H_5OH}CH_3CH_2NH_2$

6. (b) $\underset{\text{Propionamide}}{CH_3-CH_2-CO-NH_2}+Br_2+4KOH\rightarrow$

$CH_3CH_2NH_2+K_2CO_3+2KBr+2H_2O$

7. (c) $C_2H_5I+NH_3\rightarrow HI+C_2H_5-NH_2$

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

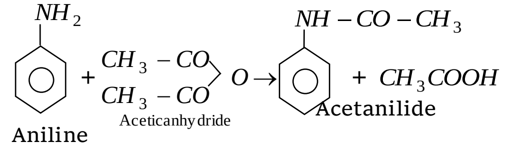
9. (c) $\underset{\text{Nitro ethane}}{CH_3-CH_2-NO_2}+6[H]\xrightarrow{Sn\ /\ HCl}$

$\underset{\text{Ethyl amine}}{CH_3-CH_2-NH_2}+2H_2O$

11. (d) $CH_3I\xrightarrow[\Delta]{NH_3}\underset{\text{Methylamine}}{CH_3NH_2}\xrightarrow{CH_3I}\underset{\text{Dimethyl amine}}{(CH_3)_2NH}$

$\xrightarrow{CH_3I}\underset{\text{Trimetyhlamine}}{(CH_3)_3N}$

12. (d)

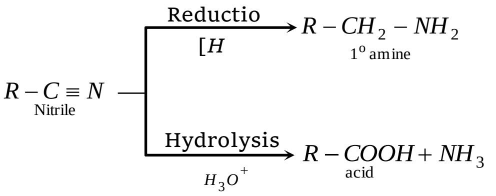


16. (c) $CH_3-N\overset{\rightarrow}{=}C+4[H]\xrightarrow{\text{Reduction}}\underset{2^o\text{ amine}}{CH_3-NH-CH_3}$

17. (a) $\underset{\text{Nitromethane}}{CH_3NO_2}+3Cl_2+3NaOH\rightarrow$

$\underset{\text{(chloropicrin)}}{CCl_3-NO_2}+3NaCl+3H_2O.$

18. (b)



19. (a) $C_2H_5OH+NH_3\xrightarrow{\text{alumina}}C_2H_5NH_2+H_2O$.

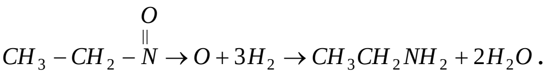
20. (c) $R-CN+H_2O\xrightarrow{H_2O/H^+}RCOOH+NH_3$

It yield amine when reduced as –

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

21. (b) $CH_3CONH_2\xrightarrow{P_2O_5}CH_3CN\xrightarrow{4H}CH_3CH_2NH_2$

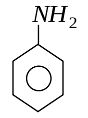
22. (a)



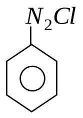
$CH_3-CH_2-\overset{\overset{O}{||}}{N}\rightarrow O+3H_2\rightarrow CH_3CH_2NH_2+2H_2O$.

23. (a) $\underset{\text{Methyl amine}}{CH_3NH_2}\xrightarrow{NO_2}CH_3OH+N_2+H_2O$

24. (a) $\underset{1^o-\text{amine}}{R-NH_2}+CHCl_3+3KOH\rightarrow R-NC+3KCl+3HO$



Aniline



Benzene diazonium

25. (b) $\xrightarrow[0^o - 5^o C]{NaNO_2 / HCl}$ $+ \ 2H_2O$.

26. (b) $CH_3CH_2COOH \xrightarrow{SOCl_2} CH_3CH_2COCl + SO_2 + HCl$

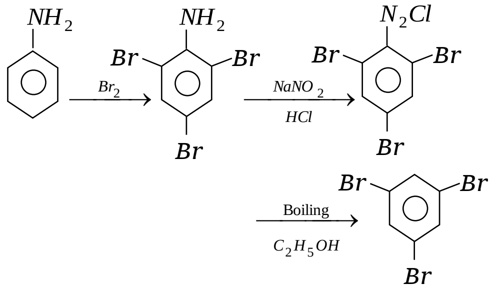
$CH_3CH_2COCl + NH_3 \rightarrow CH_3CH_2CONH_2 + HCl$

$CH_3CH_2CONH_2 + Br_2 / NaOH \rightarrow \underset{\text{Ethyl amine}}{CH_3CH_2NH_2} + CO_2$

27. (c) $CH_3COOH \xrightarrow{PCl_5} CH_3COCl \xrightarrow{NH_3} CH_3CONH_2$

$\xrightarrow{NaOBr} CH_3NH_2$

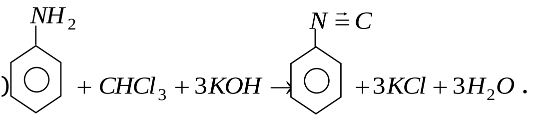
28. (d)



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

32. (a) $CH_3CONH_2 \xrightarrow{Na + ROH} CH_3CH_2OH + H_2O$

33. (a)



35. (c) Methyl amine is the strongest base.

36. (c) $\underset{\text{Nitrobenzene}}{C_6H_5NO_2} + 6H \xrightarrow{\text{pt} / H_2} \underset{\text{Aniline}}{C_6H_5NH_2} + 2H_2O$

38. (a) $C_2H_5NH_2 + CS_2 + HgCl_2 \rightarrow C_2H_5NCS + 2HCl + HgS$.

39. (d) $C_6H_5NH_2 \xrightarrow[HCl]{NaNO_3} C_6H_5N_2Cl \xrightarrow{H_2O}$

$C_6H_5OH + N_2 + HCl$

41. (d) $\underset{\text{chlorobenzene}}{2C_6H_5Cl} + 2NH_3 \xrightarrow[\text{in xylene} 570^o K]{H_2O}$

$\underset{\text{(Aniline)}}{C_6H_5NH_2} + Cu_2Cl_2 + H_2O$

44. (c) $C_6H_5NH_2 + HCl + NaNO_2 \rightarrow C_6H_5N_2Cl$

46. (b) $C_6H_5NO_2 + 6H \xrightarrow{Sn + HCl} C_6H_5 - NH_2 + 2H_2O$

47. (b) $C_6H_5NH_2 \xrightarrow{NaNO_2 + HCl \ 0^o C} C_6H_5N_2Cl$

48. (a) $CH_3NO_2 + 6H \xrightarrow[HCl]{Sn} CH_3NH_2 + 2H_2O$

49. (c) $C_6H_5NH_2 \xrightarrow[0^o C - 5^o C]{NaNO_2 / HCl} \underset{(X)}{C_6H_5N_2^+Cl^-} \xrightarrow[H_2O]{HNO_2}$

$\underset{(Y)}{C_6H_5NO_2} + N_2 + HCl$

50. (a) Halogen have –*I* and +*M* effect by which its electron delocalized in benzene ring by resonance & due to its –*I* effect its bonded with benzene ring and cannot be substitute by CN^- & show the inertness against KCN while other option gives Aromatic nitrile

$ArN_2^+ + CuCN \rightarrow ArCN + N_2 + Cu^+$

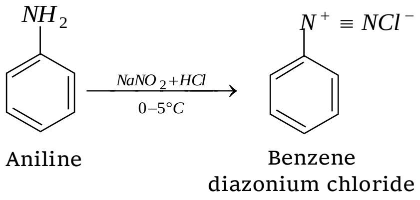
$ArCONH_2 \xrightarrow[-H_2O]{P_2O_5} ArCN$

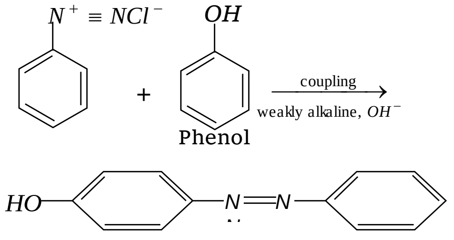
$ArCONH_2 + SOCl_2 \rightarrow ArCN + SO_2 + 2HCl$

51. (c) Secondary amines gives oily nitrosomine with nitrous acid.

$(CH_3CH_2)_2 NH + HONO \rightarrow \underset{\text{oily}}{(CH_3CH_2)_2 N.NO} + H_2O$

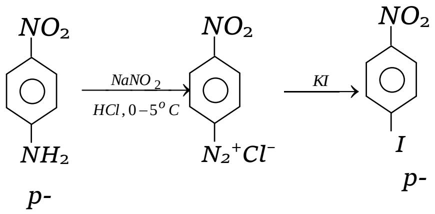
52. (a) When aniline is treated with HNO_2 at 0–5°*C* then diazonium salt is formed and by the coupling of diazonium salt and phenol azo dyes are prepared.





Azo dye

54. (a) *p*-nitrobenzene from *p*-nitroaniline.



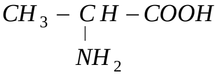
55. (b) $C_2H_5Br + KCN \xrightarrow{\text{alcohol}} C_2H_5CN + KBr$

Properties of Nitrogen Containing Compounds

1. (d) Tertiary amine does not react with nitrous acid because in it α-H atom is absent.

2. (d) Due to +ve I.E. of alkyl group, *N*-atom of amines acquires patrial –ve charge and thus electron pair is easily donated.

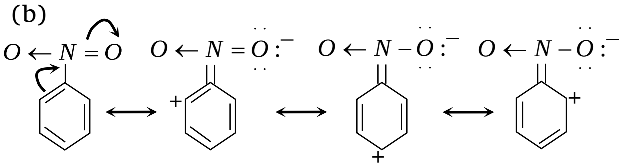
3. (b)



$CH_3 - \underset{NH_2}{\underset{|}{C}H} - COOH$

The compounds in which both amino $(-NH_2)$ as well as acidic ($-COOH$) group is present is called amino acid.

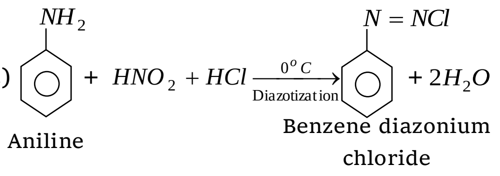
4. (b)



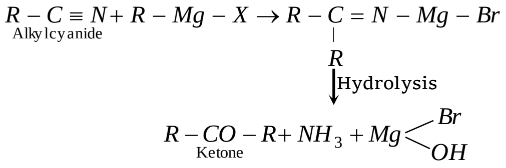
Presence of $-NO_2$ group decreases electron density at *o*- and *p*- positions. Hence, incoming electrophile goes to m position. Therefore it is m-directing group.

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

7. (c)

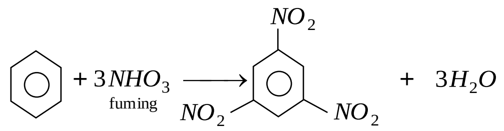


9. (b)



$$\underset{\text{Alkylcyanide}}{R-C\equiv N}+R-Mg-X\rightarrow R-\underset{\underset{R}{|}}{C}=N-Mg-Br$$
$$\Big\downarrow\text{Hydrolysis}$$
$$\underset{\text{Ketone}}{R-CO-R}+NH_3+Mg\begin{smallmatrix}Br\\OH\end{smallmatrix}$$

10. (c)



sym-trinitro benzene

11. (c) $\underset{\text{Ethylamine}}{CH_3-CH_2-NH_2}\xrightarrow[{[O]}]{KMnO_4}\underset{\text{Aldimine}}{CH_3-CH=NH}$

$$\xrightarrow{H_3O^+}\underset{\text{Acetaldehyde}}{CH_3-CHO}$$

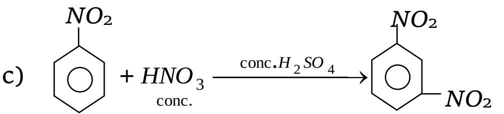
12. (b) Only primary aromatic amines can undergo diazotisation.

13. (b) $\underset{1^o\text{ amine}}{R-CH_2-NH_2}+\underset{\text{aldehyde}}{O=CH-R}\rightarrow$

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

14. (c) $\underset{\text{Acetamide}}{CH_3-CO-NH_2}+HNO_2\rightarrow\underset{\text{Acetic acid}}{CH_3COOH}+N_2\uparrow+H_2O$

15. (c)



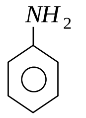
$-NO_2$ group is meta directing group.

16. (a) $\underset{\text{Alkyl nitrite}}{R-O-N=O}+6[H]\xrightarrow{Sn/HCl}\underset{\text{Alcohol}}{ROH}+NH_3+H_2O$

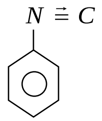
17. (d) $CH_3-CH_2-NH_2+HCl\rightarrow\underset{\text{Ethyl ammonium chloride}}{CH_3CH_2-NH_3^+Cl^-}$

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

18. (a) $\underset{\substack{2^o\text{ amine is}\\ \text{most basic}}}{(CH_3)_2NH}>\underset{1^o\text{ amine}}{CH_3NH_2}>\underset{3^o\text{ amine}}{(CH_3)_3N}>\underset{\substack{\text{Ammonia is}\\ \text{least basic}}}{\ddot{N}H_3}$



Aniline



Phenyl isocyanide

19. (b) $+CHCl_3+3KOH\rightarrow\qquad+3KCl+3H_2O$

20. (c) Because in tertiary nitroalkanes $\alpha-H$ atom is absent.

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

22. (d) Friedel-craft's reaction is used for the preparation of alkyl benzene or acetophenone. It is not a method to prepare amine.

23. (b) $\underset{\text{(Litmus paper)}}{\text{Red}}\xrightarrow{CH_3NH_2}\text{Blue}$

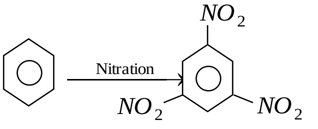
This litmus paper test shows basic nature of amine.

24. (c) Presence of alkyl group increases electron density on nitrogen atom due to +I effect. Thus basic nature increases.

25. (a) Mustard oil reaction

$$\underset{\text{Ethyl amine}}{CH_3-CH_2-NH_2}+CS_2\xrightarrow{HgCl_2}$$
$$\underset{\text{Ethyl isothiocyanate}}{CH_3-CH_2-N=C=S}+H_2S$$

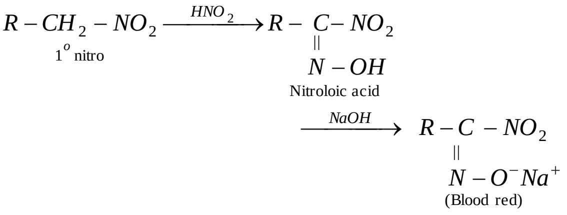
28. (c)



1, 3, 5-trinitrobenzene

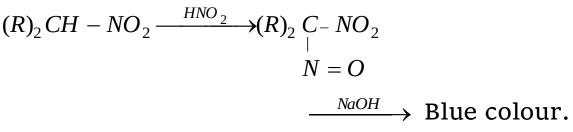
3- nitro group can be introduced.

34. (a)



$$\underset{1^o\text{ nitro}}{R-CH_2-NO_2}\xrightarrow{HNO_2}\underset{\text{Nitroloic acid}}{R-\underset{\underset{N-OH}{||}}{C}-NO_2}$$
$$\xrightarrow{NaOH}\underset{\text{(Blood red)}}{R-\underset{\underset{N-O^-Na^+}{||}}{C}-NO_2}$$

35. (b)



$$(R)_2CH-NO_2\xrightarrow{HNO_2}(R)_2\underset{\underset{N=O}{|}}{C}-NO_2$$
$$\xrightarrow{NaOH}\text{Blue colour.}$$

37. (b) $\underset{\text{Acetamide}}{CH_3CONH_2}\xrightarrow{P_2O_5}\underset{\text{Acetonitrile}}{CH_3-C\equiv N}+H_2O$.

38. (b) $CHCl_3+C_2H_5NH_2+3KOH\rightarrow$

$$\underset{\text{Ethyl isocyanide}}{C_2H_5N\overset{\rightarrow}{=}C}+3KCl+3H_2O$$

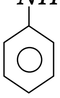
39. (d) $\underset{\text{Methylcyanide}}{CH_3-C\equiv N}+2H_2O\rightarrow\underset{\text{Aceticacid}}{CH_3COOH}+NH_3$

40. (c) $\underset{(2c)}{CH_3CONH_2}+Br_2+4KOH\rightarrow$

$$\underset{(1c)}{CH_3NH_2}+K_2CO_3+3KBr+2H_2O$$

41. (a) $(C_2H_5)_2NH+(\text{aq.})HONO\rightarrow\underset{\text{Diethyl nitrosoamine}}{(C_2H_5)_2N-N=O}+H_2O$

42. (c) $CH_3-C\equiv N\xrightarrow[\text{Reduction}]{Na+EtOH}CH_3-CH_2-NH_2$



$\xrightarrow{HNO_2} CH_3CH_2-OH \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3COOH$

43. (b) $\underset{\text{Ethyl amine}}{C_2H_5NH_2} \xrightarrow{HNO_2} \underset{\text{Ethyl alcohol}}{C_2H_5OH} \xrightarrow{PCl_5} C_2H_5Cl$

$\xrightarrow{NH_3} \underset{\text{Ethyl amine}}{C_2H_5NH_2}$

44. (c) $\underset{1^o}{CH_3CH_2-NH_2}+HNO_2 \rightarrow \underset{\text{Alcohol}}{CH_3CH_2-OH}+N_2+H_2O$

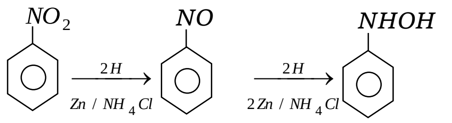
$\underset{2^o}{(CH_3CH_2)_2NH}+HNO_2 \rightarrow \underset{\text{Nitroso amine}}{(CH_3CH_2)_2N-N=O}+H_2O$

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

46. (d)

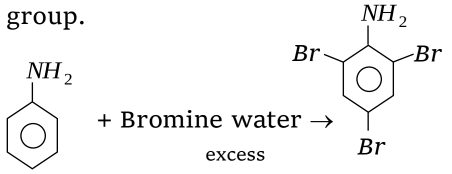
$CH_3NH_2+2HNO_2 \rightarrow CH_3-O-N=O+N_2+2H_2O$

$2CH_3NH_2+2HNO_2 \rightarrow CH_3-O-CH_3+2N_2+3H_2O$

47. (d) 

Phenyl hydroxyl

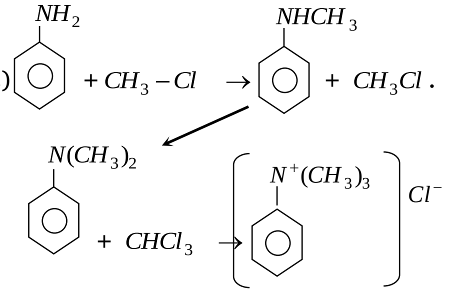
50. (b) Because the N atom in aniline has a lone pair to donate and also due to +I effect of $-NH_2$ group.

51. (d) 

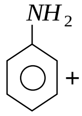
52. (d) $R-NH_2+CHCl_3+3NaOH \rightarrow RN\equiv C+3NaCl+3H_2O$

The unpleasant smell is due to the formation of isocyanide.

53. (c) $RNH_2+NaNO_2+HCl \rightarrow R-OH+NaCl+N_2+H_2O$

54. (c) 

Quaternary ammonium salt

55. (c) 

$+\ HNO_3/H_2SO_4 \rightarrow$ A black mass.

Nitration of aniline without protecting the amino group is not possible because HNO_3 is a strong oxidising agent which oxidises aniline.

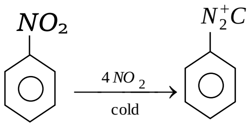
56. (d) $\begin{matrix}CH_3\searrow\\ CH_3\nearrow\end{matrix}\overset{\cdot\cdot}{NH}$ and $CH_3 \rightarrow \overset{\cdot\cdot}{NH_2}$.

In methyl amine only one electron releasing group is present but in dimethyl amine two electron releasing groups are present which increase the basicity higher in dienethyl amine.

57. (d) Nitro compounds are not explosive but stable compound.

58. (c) $CH_3-NH_2+HNO_2 \rightarrow CH_3OH+N_2+H_2O$

60. (c) $R_3N+HONO \rightarrow R_3N.HONO$ called as Quaternary ammonium salt.

61. (b) 

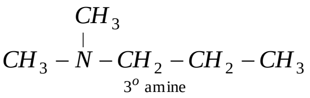
But $R-NH_2 \xrightarrow[\text{cold}]{4NO_2} R-OH+N_2+H_2O$

62. (a) $CH_3CN \xrightarrow{H_2O/H^+} CH_3COOH+NH_3$

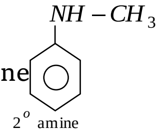
63. (c) 3^o amine cannot be Acetylated because replacable H-atom is absent.

67. (e) Because

N-N dimethyl propanimine

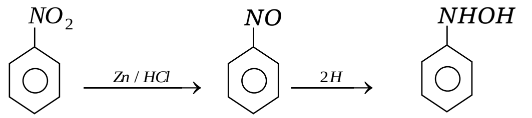


$\underset{3^o\text{ amine}}{CH_3-\overset{\overset{CH_3}{|}}{N}-CH_2-CH_2-CH_3}$

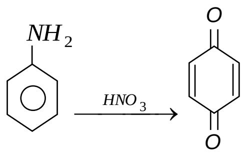
N-Methyl aniline 

aniline → 1^o amine.

68. (c) Replacable H^- is absent.

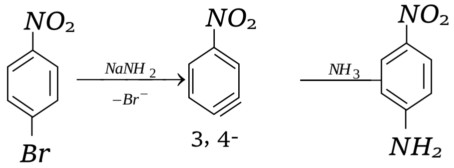
69. (a) 

Nitro benzene Nitro benzene N-phenyl hydroxylamine

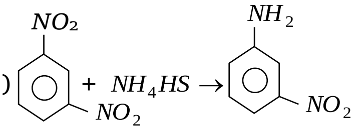
70. (c) 

Because oxidation of aniline occur in absence of making effect.

P - Benzoquinone

72. (c) 

73. (a) $R_2NH > RNH_2 > R_3N > NH_3$.

75. (b) 

76. (a) Because of presence of electron withdrawing group - NO_2.

77. (a) To supress the concentration of the aniline available for coupling other rise coupling occurs.

78. (b) $R-NH_2+HNO_2 \to \underset{\text{alcohol}}{R-OH}+N_2+H_2O$.

79. (c) $C_6H_5NH_2<(CH_3)_3N<CH_3NH_2<(CH_3)_2NH$

80. (b) $CH_3CN+CH_3MgI \to \underset{\text{(A)}}{(CH_3)_2CNMgI} \xrightarrow[-NH_3]{H_2O/H^+}$

$$\underset{\text{(B)}}{CH_3COCH_3}+Mg\Big<\begin{matrix}OH\\ I\end{matrix}$$

82. (d) $C_6H_5-NO_2 \xrightarrow[Zn/NaOH]{10[H]} \underset{\text{Hydrazo benzene}}{C_6H_5NH-NHC_6H_5}+4H_2O$

83. (a) $RCOCl+2Me_2NH \to RCON\Big<\begin{matrix}Me\\ Me\end{matrix}+Me_2+\overset{+}{N}H_2Cl^-$

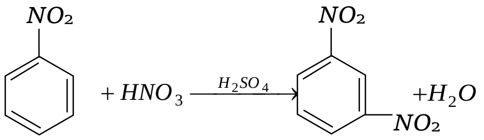
Me = Methyl.

86. (b) Phenol react with aniline to give diazonium salt by coupling but Methyl amine not react with phenol.

87. (b) $C_6H_5SO_2Cl$ is called Hinsberg's reagent they react with sec amine to form a product in soluble in alkalies. This reaction used to separate 1^o, 2^o and 3^o amine from their mixture.

88. (b) A mixture of benzene and aniline can be separated by dil. *HCl*.

89. (b)



m-

90. (b)

$$\underset{\substack{\text{(A)}\\ \text{Aniline}}}{C_6H_5NH_2} \xrightarrow[0^oC]{NaNO_2+HCl} \underset{\text{(B)}}{C_6H_5N_2Cl} \xrightarrow{KCN} \underset{\text{(C)}}{C_6H_5CN} \xrightarrow{H_3O} \underset{\text{(D)}}{C_6H_5COOH}$$

91. (c) Methyl isocyanate is industrially prepared by the action of methyl amine with phosgene.

$CH_3NH_2 + COCl_2 \xrightarrow{-HCl} [CH_3NH-CO-Cl]$

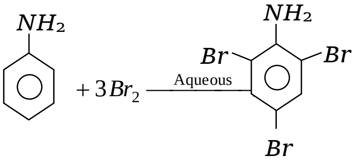
$\xrightarrow[-HCl]{\Delta} \underset{\text{methyl}}{CH_3-N=C=O}$

92. (d) $R-NC+2H_2O \to RNH_2+HCOOH$.

93. (d) $CH_3-NC+2H_2O \to CH_3NH_2+HCOOH$

95. (c) $CH_3NC+4H \xrightarrow[\text{ether}]{LiAlH_4} (CH_3)_2NH$.

99. (b)



2, 4, 6 tribromo

102. (a) $R-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow{H_2-Ni} R-CH_2-NH_2$

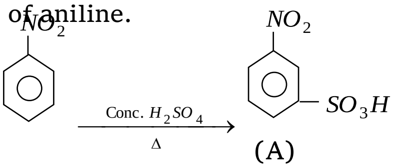
104. (b) $CH_3CN+2H_2O \xrightarrow{HCl} CH_3COOH+NH_3$

106. (a) $CH_3CH_2NH_2+CH_3COCl \to \underset{N\text{ Ethylacetanilide}}{CH_3CH_2NHCOCH_3}+HCl$

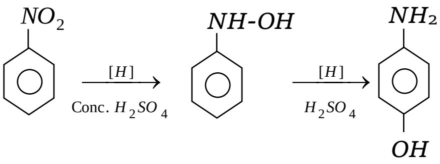
107. (a) $\begin{matrix}CH_3\\ CH_3\end{matrix}\!>NH+CH_3COOH \to \begin{matrix}CH_3\\ CH_3\end{matrix}\!>N-\overset{\overset{O}{\|}}{C}-CH_3$

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

109. (b)

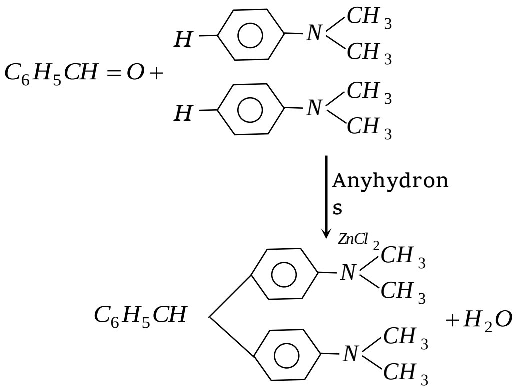


110. (c)



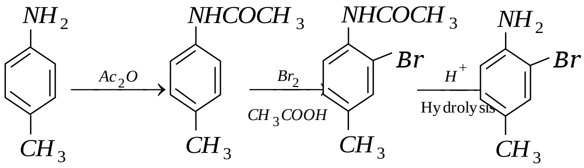
Nitrobenzene Phenyl hydroxyl amine *p*-amino phenol

113. (c)



Malachite

115. (d)



119. (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 stearic hinderence 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 :

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

120. (b) Amines are basic in nature, hence form salts with acid.

$$2RNH_2 + H_2SO_4 \rightarrow [RNH_3^+]_2SO_4^{2-}$$

121. (b) We know that

$$\underset{\text{Aniline}}{C_6H_5NH_2} + \underset{\text{Chloroform}}{CHCl_3} + 3KOH \rightarrow \underset{\text{phenyl isocyanide}}{C_6H_5NC} + 3KCl + 3H_2O$$

Thus in this reaction phenyl isocyanide is produced. this is called carbylamine reaction.

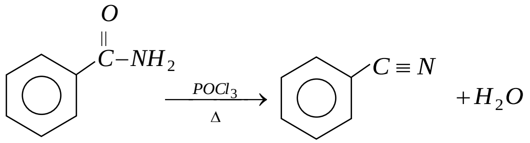
122. (d) Isocyanides on hydrolysis forms primary amines not ammonia

123.(b) $C_6H_5CONH_2 + Br_2 + KOH \rightarrow C_6H_5CONHBr + KBr + H_2O$

$$\downarrow KOH$$

$$K_2CO_3 + C_6H_5NH_2 \xleftarrow[2KOH]{} C_6H_5NCO + KBr + H_2O$$

$$C_6H_5NH_2 + (CH_3CO)_2O \rightarrow \underset{\text{Acetanilide}}{CH_3CONHC_6H_5} + CH_3COOH$$

124. (d) 

Benzonitril

125. (d) (i) $R\overset{\overset{O}{||}}{C}NH_2$ + Br₂ + KOH → RCONHBr + KBr + H₂O

(ii) RCONHBr + KOH → RNCO + KBr + H₂O

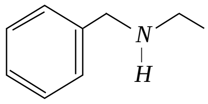
(iii) RNCO + 2KOH → RNH₂ + K₂CO₃

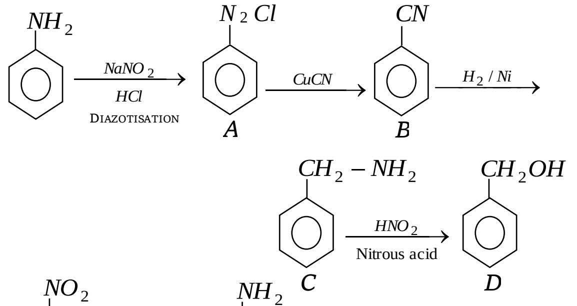
RCONH₂ + Br₂ + 4KOH → RNH₂ + 2KBr + K₂CO₃ +2H₂O

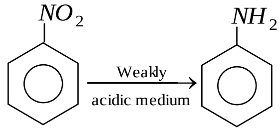
126. (b) Aniline reacts with benzaldehyde and forms Schiff's base (benzal aniline) or anils.

$$C_6H_5-NH_2 + O=CHC_6H_5 \xrightarrow[-H_2O]{\Delta} \underset{\text{Benzylidine aniline}}{C_6H_5N=CHC_6H_5}$$

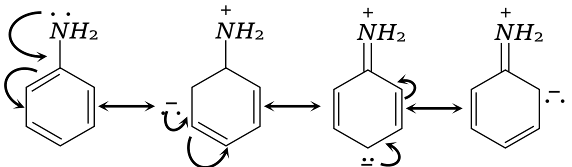
127. (d) $\underset{\text{Acetamide}}{CH_3CONH_2} + Br_2 + 4KOH \xrightarrow[-2H_2O]{} \underset{\text{(Methylamine)}}{CH_3NH_2} + 2KBr + 2K_2CO_3$

128. (b)  is most basic

130. (d) 

131. (a) 

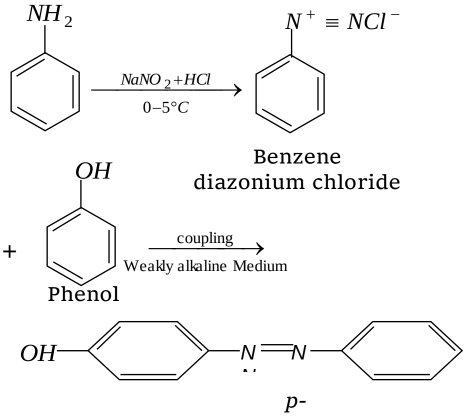
132. (d) $C_6H_5NH_2$ is least basic compound due to resonance by which the Lone pair of nitrogen takes part in resonance & due to unavailability of lone pair on *N* Aniline become less basic. The Lone pair of *N* is delocalized into benzene ring by resonance



133. (b) Carbylamine (or isocyanides) give secondary amine on reduction.

$$\underset{\text{Carbylamine}}{R-N \rightleftarrows C} \xrightarrow{Ni/H_2} \underset{\text{Secondary amine}}{R-NH-CH_3}$$

134. (a) Azo dye is prepared by the coupling of phenol and diazonium chloride.



135. (b) $C_6H_5NH_2 \xrightarrow{NaNO_2/HCl} \underset{(X)}{C_6H_5N_2Cl}$

$$\xrightarrow{Cu_2(CN)_2} \underset{(Y)}{C_6H_5CN} \xrightarrow{H_2O/H^+} \underset{\text{Benzoic acid}(Z)}{C_6H_5-COOH}$$

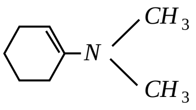
Thus product *Z* is identified as C_6H_5-COOH

136. (c) This is Hofman-bromide reaction. In this reaction one carbon less amines are formed from amides.

$$CH_3CONH_2 \xrightarrow{Br_2/KOH} CH_3NH_2$$

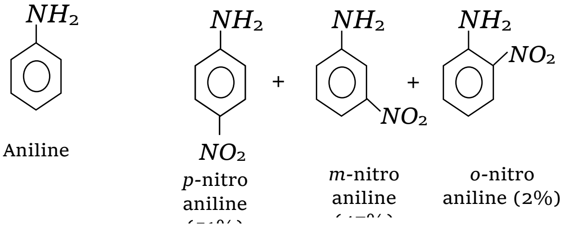
137. (c) $CH_3CN + 2H \xrightarrow[\text{Ether}]{HCl} HC \equiv CH$

$$\xrightarrow{\text{Boiling } H_2O} \underset{\text{Acetaldeyde}}{CH_3CHO}$$

138. (b) 

139. (b) *N*-alkyl formamides when dehydrated with POCl₃ in presence of pyridine give isocyanides.

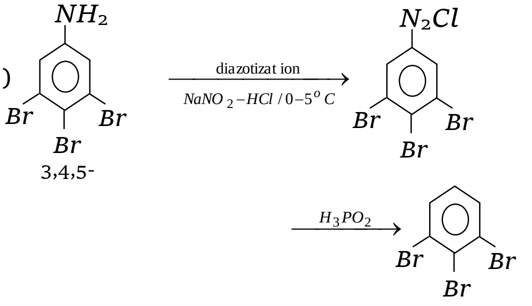
140. (c) Pollutants which are formed by reaction amongst the primary pollutants (persist in the environment in the form they are passed into it) are called as secondary pollutants. e.g. peroxyacyl nitrates (PAN) are formed through reaction between nitrogen oxides and hydrocarbons in the presence of sunlight.



141. (d) $\xrightarrow[H_2SO_4]{HNO_3}$

The reason for this is that, in acidic condition protonation of $-NH_2$ group gives anilinium ion $(+NH_3)$, which is of deactivating nature and of *m*-directive nature.

142. (b)



3,4,5-

1,2,3-

143. (a) Basicity order is

$C_4H_5NH_2 < (CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$

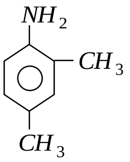
$(CH_3)_3N$ is less basic due to steric effect while $C_4H_5NH_2$ is less basic due to resonance.

Tests for Nitrogen Containing Compounds

1. (c) $\underset{\text{Acetamide}}{CH_3CONH_2} + Br_2 + 4NaOH \rightarrow$

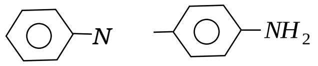
$\underset{\text{Methylamine}}{CH_3NH_2} + Na_2CO_3 + 2NaBr + 2H_2O$

5. (b)



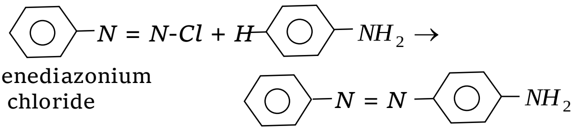
is a type of 1^o amine and hence gives +ve

6. (a)



Orange Colour

8. (a) Diazo-coupling is useful to prepare some dyes.



Benzenediazonium chloride

p-amino azo benzene (yellow dye)

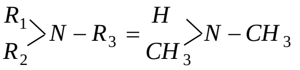
11. (a) $CHCl_3$ gives carbylamine test.

$RNH_2 + CHCl_3 + 3KOH(\text{alc.}) \xrightarrow{\Delta}$

$\underset{\text{alkyl isocyanide}}{RN \equiv C} + 3KCl + 3H_2O$

Critical Thinking Questions

1. (c) $R_1 = H$ and $R_2 = R_3 = CH_3$

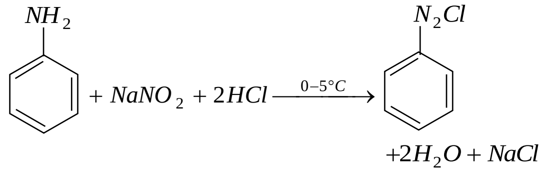


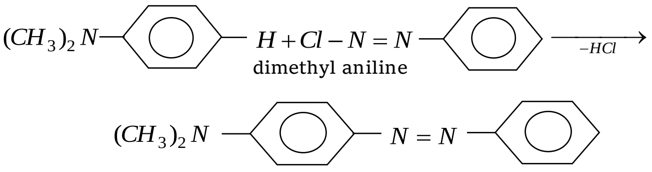
$$\begin{matrix}R_1\\R_2\end{matrix}>N-R_3 = \begin{matrix}H\\CH_3\end{matrix}>N-CH_3$$

Sec. amine reacts with Nitrous acid to form nitroso amine yellow liquid.

2. (c) $\underset{\text{Ethylamine}}{CH_3CH_2NH_2} + HNO_2 \rightarrow \underset{\text{Ethylalcohol}}{CH_3CH_2OH} + N_2 + H_2O$

3. (a)





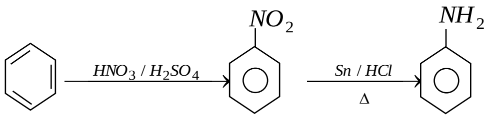
dimethyl aniline

4. (c) Hofmann degradation of amide

$R - CoNH_2 + Br_2 + 4KOH \longrightarrow$

$\underset{\text{primary amine}}{R - NH_2} + 2KBr + K_2CO_3 + 2H_2O$

5. (b)



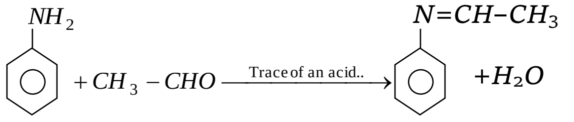
Nitrobenzene Aniline

6. (b) The relative basic charecter of $1^o,2^o$ and 3^o amines also depends upon the nature of the alkyl group.

R	Relative basic strength
$-CH_3$	$R_2NH > R-NH_2 > R_3N > NH_3$
$-C_2H_5$	$R_2NH > R-NH_2 > NH_3 > R_3N$
$-CHMe_2$	$R-NH_2 > NH_3 > R_2NH > R_3N$
$-CMe_3$	$NH_3 > R-NH_2 > R_2NH > R_3N$

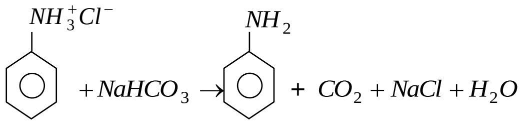
7. (b) The nitrogroup is very firmly linked to the benzene nucleus and does not undergo any displacement reaction. Nitro group deactivates the benzene nucleus.

8. (a)



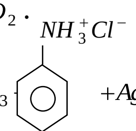
Anil or Schiff's

9. (bc) (1) With $NaHCO_3 \rightarrow$



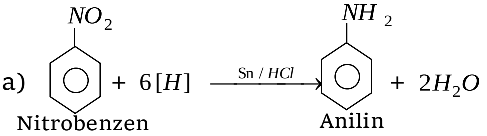
Anilinium hydrochloride is an acid salt and liberates CO_2 from $NaHCO_3$.

But p-chloro aniline is basic not acidic it does not liberate CO_2.

(2) With $AgNO_3$  $+AgNO_3 \rightarrow$

$NH_3^+NO_2^- + AgCl \downarrow$ (White ppt)

p-chloro aniline does not contain ionic chlorine to it does not give white ppt with $AgNO_3$

10. (a) 

11. (a) $C_6H_5-NH_2 + CHCl_3 + 3KOH \rightarrow \underset{\text{Phenyl Isocyanide}}{C_6H_5NC} + 3KCl + 3H_2O$

12. (b) $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N$

$K_b = 5.4\times10^{-4}$ $\quad 4.5\times10^{-4}$ $\quad 0.6\times10^{-4}$

13. (c) $(CH_3)_2NCOCH_3 + HCl/H_2O$

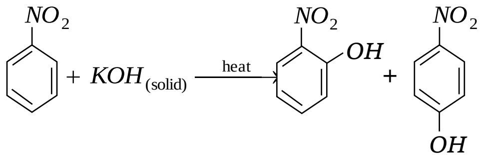
$\downarrow$

$(CH_3)_2NH + CH_3COOH$

14. (a) Order of basicity of amines

(i) $2^o > 1^o > 3^o$

(ii) $R_2NH > RNH_2 > ArCH_2-NH_2 > NH_3 > ArNH-R > ArNH_2 > ArNH-Ar$

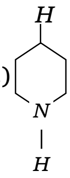
15. (a) 

Because OH^- is nucleophile.

16. (c) $C_6H_5SO_2Cl + RNH_2 \rightarrow RNHSO_2C_6H_5 \xrightarrow{KOH} \underset{\text{soluble in } KOH}{RNKSO_2C_6H_5}$

17. (b) When sulphur and nitrogen both are present in organic compound during Lassaigne's Test, both changes into "sodium thiocyanate". (NaSCN) which gives a blood red colouration with Ferric ion.

$3NaCNS + FeCl_3 \rightarrow \underset{\substack{\text{Ferric sulpho cyanide} \\ \text{(Blood red colour)}}}{Fe(CNS)_3} + 3NaCl$

18. (c) 

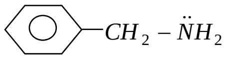
does not have aromaticity by which the Lone pair of electron of Nitrogen does not delocalised in benzene ring so it will be strong base on other hand rest 3 have aromaticity *i.e.,* they follow the huckel rule so the electron pair of Nitrogen delocalised in ring by resonance &

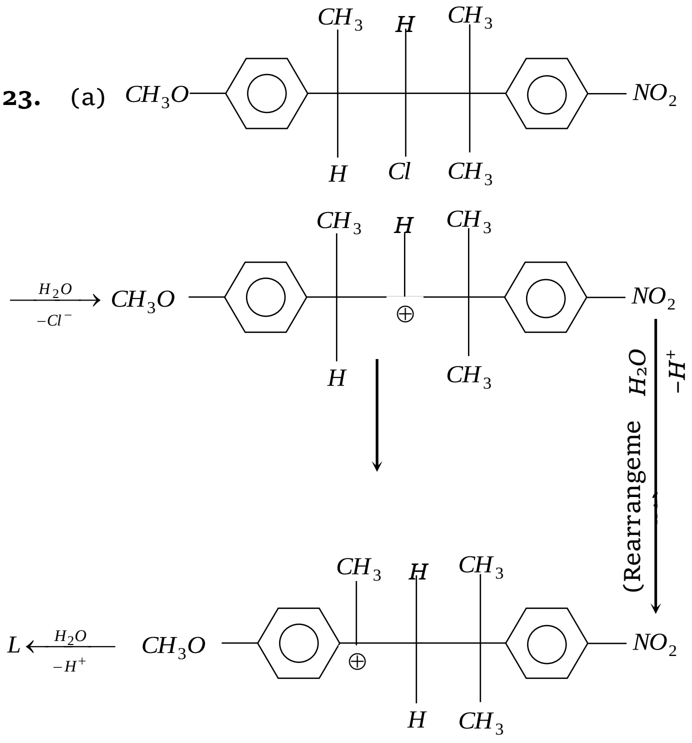
19. (d) Liebermann's Nitroso reaction.

20. (a) $\underset{\text{(Acetamide)}}{CH_3CONH_2} + Br_2 + 4KOH \xrightarrow[-2H_2O]{} \underset{\text{(Methylamine)}}{CH_3NH_2} + 2KBr + 2K_2CO_3$

21. (c) The class of Indigo dye is Indigoid or vat dye. Indigo dyes are insoluble in water.

22. (d) Lone pair of $\ddot{N}$ are not taking part in conjugation whereas in other parts lone pairs are taking part in conjugation



23. (a) 

Assertion and Reason

1. (a) It is true that benzene diazonium chloride does not respond Lassaigne test of nitrogen because benzene diazonium chloride losses N_2 on Slight heat and thus it can't react with sodium metal.

2. (a) Amines are basic due to the presence of a lone pair of electrons on nitrogen atom. The lone pair can be easily donated.

3. (b) The reason being that the terminal carbon atom in isocyanide has electron-deficient carbon having a sexlet of electrons and hence undergoes addition reactions with ozone.

4. (d) When primary amines are heated with chloroform in the presence of alcoholic *KOH*, isocyanides are formed. This reaction is known as carbylamine reaction. eg. ethyl amine gives ethyl isocyanide on treatment with $CHCl_3$ and alcoholic *KOH*.

$\underset{\text{Ethylamine}}{C_2H_5-NH_2} + \underset{\text{Chloroform}}{CHCl_3} + 3KOH(\text{alc}) \xrightarrow{\Delta}$

$C_2H_5-N \equiv C + 3KCl + 3H_2O$

5. (b) Nucleophilic species which have more than one site of reaction are called ambident nucleophiles.

$$:\overline{C} = N: \Leftrightarrow\ :C = \overline{N}:$$

6. (c) $-SO_3H$ group being more acidic than $-CO_2H$ group can easily transfer a proton to the amino group.

7. (a) $HNO_3 + 2H_2SO_4 \rightleftharpoons 2HSO_4^- + NO_2^+ + H_3\overset{+}{O}$

8. (c) Only primary aliphatic amines can be prepared by Gabriel phthalimide reaction.

9. (c) Reaction can be used to prepare 1°, 2°, 3° amines and finally quarternary ammonium salts.

10. (b) Nitroarene cannot be distilled under normal atmospheric pressure. This is because either they decompose or they explode on strong heating.

11. (c) Only 1° amines undergo Hofmann bromamide reaction. Since $CH_3CONHCH_3$ is a 2° amine therefore, it does not undergo Hofmann bromamide reaction.

12. (b) Nitrobenzene does not undergo Friedel Craft reaction because nitro group deactivate the ring towards electrophilic substitution and drastic conditions are needed to carry out the electrophilic substitution reactions.

13. (e) Ammonia is more basic than water. It is because nitrogen being less electronegative than oxygen has a greater tendency to donate electrons.

14. (c) Condensation of diazonium salt with phenol is carried out in weakly alkaline medium, $(pH = 9)$. This is due to the fact that in strongly acid medium the $-OH$ of a phenol remains unionised, and an amine forms a salt. Phenol exists as phenoxide ion and the latter is readily substituted by electrophiles than phenol itself. Thus, in phenol, coupling is carried out in alkaline medium.

15. (a) $RNH_2 + CHCl_3 + 3KOH\,(alc) \rightarrow R-N \overset{\rightarrow}{\equiv} C + 3KCl + 3H_2O$

17. (d) *p*-Anisidine is a stronger base than aniline.

$-OCH_3$ group in anisidine exerts +*R*– effect.

18. (b) Solubility of aldehydes and ketones decrease as the molecular mass increase.

20. (d) The nitro group strongly deactivates the benzene ring towards electrophilic substitution.

Nitrobenzene does not undergo Friedel-Craft acylation reaction.

21. (a) In an isocyanide, first an electrophile and then a nucleophile add at the carbon to form a species which usually undergoes further transformations.

$$R\overset{+}{N} \equiv \overset{-}{C} + E^+ \longrightarrow R\overset{+}{N} \equiv CE \xrightarrow{Nu} RN \equiv C(Nu)E$$

$$R\overset{+}{N} \equiv \overset{-}{C} + H_2O \longrightarrow RN = CHOH \longrightarrow \underset{\text{alkylformamide}}{RNHCHO}$$

Nitrogen Containing Compounds

SET Self Evaluation Test - 29

1. Melting points are normally the highest for **[AIIMS 2004]**

(a) Tertiary amides
(b) Secondary amides
(c) Primary amides
(d) Amines

2. Amines behave as **[Karnataka (Med.) 1999]**

(a) Lewis acids
(b) Lewis bases
(c) Aprotic acids
(d) Amphoteric compounds

3. Which of the following compound gives dye test **[MP PET/PMT 1998]**

(a) Aniline
(b) Methylamine
(c) Diphenylamine
(d) Ethylamine

4. In hydrolysis of aniline, the reagent used is **[AFMC 1995]**

(a) Dil. HCl
(b) Acetyl chloride
(c) CH_3OH
(d) None of these

5. A nitrogen containing organic compound on heating with chloroform and alcoholic KOH, evolved very unpleasant smelling vapour. The compound could be **[BHU 2002; BVP 2003]**

(a) *N, N*-dimethyl amine
(b) Nitrobenzene
(c) Aniline
(d) Benzamide

6. The reaction between a primary amine, chloroform and few drops of alcoholic KOH is known as **[MNR 1987; MP PMT 1994; Bihar MEE 1996; AIIMS 1998; MP PET 2002]**

(a) Cannizzaro reaction
(b) Carbylamine reaction
(c) Wurtz's reaction
(d) Reimer-Tiemann reaction

7. Nitrolim is **[BVP 2004]**

(a) $CaC_2 + N_2$
(b) $CaCN_2 + C$
(c) $Ca(CN)_2 + C$
(d) $Ca(CN)_2 + NH_4CN$

8. Phenyl isocyanides are prepared from which of the following reactions **[CBSE PMT 1999]**

(a) Rosenmund's reaction
(b) Carbylamine reaction
(c) Reimer-Tiemann reaction
(d) Wurtz reaction

9. On strong heating, ammonium acetate gives **[MNR 1995]**

(a) Acetamide
(b) Methyl cyanide
(c) Urea
(d) Formamide

10. Aniline is separated from a mixture by **[UPSEAT 2000, 01]**

(a) Fractional crystallization
(b) Fractional distillation
(c) Vacuum distillation
(d) Steam distillation

11. Molecular formula of chloropicrin is **[MH CET 2003]**

(a) $CHCl_3NO_2$
(b) CCl_3NO_3
(c) CCl_2NO_2
(d) CCl_3NO_2

12. In amines, the hybridisation state of N is **[CPMT 1999]**

(a) sp
(b) sp^2
(c) sp^3
(d) sp^2d

13. Foul smelling compound formed, during carbyl amine reaction is : **[Pb. CET 2001]**

(a) Alcohol
(b) Aldehyde
(c) Alkyl isocyanide
(d) Carboxylic acid

14. The end product of the reaction

$\text{ethyl amine} \xrightarrow{HNO_2} A \xrightarrow{PCl_5} B \xrightarrow{KCN} C$ is

(a) Ethyl amine

(b) Diethyl amine

(c) Propane nitrite

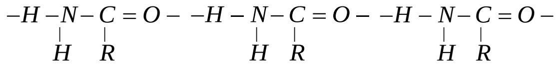
(d) Triethyl amine

(e) Methyl amine

Answers and Solutions

(SET -29)

1. (c) The higher boiling points of amide is because of Intermolecular hydrogen bonding



$$-H-\underset{H}{N}-\underset{R}{C}=O-\ -H-\underset{H}{N}-\underset{R}{C}=O-\ -H-\underset{H}{N}-\underset{R}{C}=O-$$

Due to intermolecular hydrogen bonding they have high boiling point than amine and amongst amide the order of Boiling point are

Primary > Sec > Tertiary

This is because of alkyl group by which the carbonyl oxygen do not form the hydrogen bond (other molecule) so primary amide have high boiling point and Tertiary amides does not have to form bond with *O* of other amide and have least B.P

2. (b) In amines nitrogen has a love pair of e^-. It can donate a election pair. So amines behaves as a lewis base.

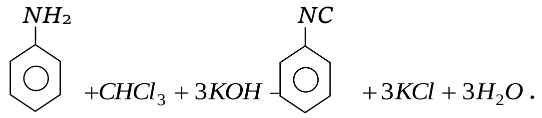
3. (a) Basically all the Azo dye are derivatives of aniline.

4. (a) All amines react with mineral acids such as HCl, H_2SO_4, HNO_3 etc. to form salts which are soluble in water.

5. (c) $C_6H_5NH_2 + CHCl_3 + 3\underset{\text{(Alc)}}{KOH} \to C_6H_5NC + 3KCl + 3H_2O$

6. (b) $CH_3NH_2 + CHCl_3 + 3KOH \to \underset{\text{Isocyanide}}{\overset{\oplus}{RN} \equiv \overset{\ominus}{C}} + 3KCl + 3H_2O$

7. (b) Nitrolim is a mixturee of calcium cyanamide and carbon.

8. (b) 

Carbyl amine reaction.

9. (b) $CH_3COONH_4 \xrightarrow{\Delta} CH_3CONH_2 \xrightarrow{\Delta} CH_3CN + H_2O$

10. (d) Steam distellation is used for separation of aniline from mixture. Aniline is insoluble in water but it is steam soluble.

11. (d) Molecular formula of chloropicrin is CCl_3NO_2

12. (c) It is similar that of NH_3 except *H*- is replaced by –*R* group.

$$\because \overset{..}{N}H_3 \to \frac{5+3}{2} \Rightarrow 4 \Rightarrow sp^3 .$$

13. (c) On heating $CHCl_3$ with ethanolic KOH and primary amine, isocyanide is formed and is readily detected by its offensive odour. This is called as carbyl amine test.

$CHCl_3$	+	3 KOH	+	RNH_2
Chloroform		Potassium hydroxide		Primary amine

$\xrightarrow{\Delta}$	RNC	+	3 KCl	+	H_2O_2
	Alkyl Isocyanide (Foul smell)		Potassium chloride		Water

14. (c) $C_2H_5NH_2 + HNO_2 \to \underset{(A)}{C_2H_5OH} + N_2 + H_2O$

$C_2H_5OH + PCl_5 \to \underset{(B)}{C_2H_5Cl} + POCl_3 + HCl$

$C_2H_5Cl + KCN \to \underset{(C)\text{Propane nitrile}}{C_2H_5CN} + KCl$

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