



**CLASSROOM STUDY
PACKAGE**

CHEMISTRY

**NITROGEN CONTAINING
COMPOUNDS**

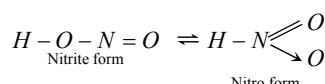
JEE EXPERT

NITROGEN CONTAINING COMPOUNDS

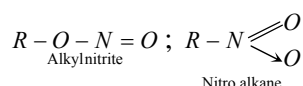
The important nitrogen containing organic compounds are alkyl nitrites (RONO), nitroalkanes (RNO₂), aromatic nitro compounds (ArNO₂), alkyl cyanides (RCN), alkyl isocyanides (RNC), amines (–NH₂), aryl diazonium salts (ArN₂Cl), amides (–CONH₂) and oximes (>C=N OH).

Alkyl nitrites and nitro alkanes:

Nitrous acid exists in two tautomeric forms.



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



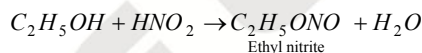
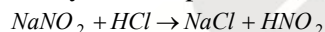
It is important to note that nitro alkanes are better regarded as nitro derivatives of alkanes, while alkyl nitrites are regarded as alkyl esters of nitrous acid.

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

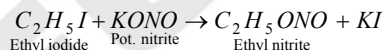
Ethyl nitrite (C₂H₅ONO)

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

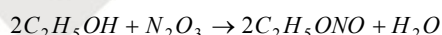
(a) By adding concentrated HCl or H₂SO₄ to aqueous solution of sodium nitrite and ethyl alcohol at very low temperature (0°C).



(b) From Ethyl iodide



(c) By the action of N₂O₃ on ethyl alcohol.

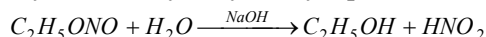


(ii) Physical properties

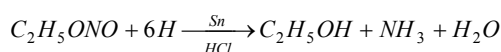
- (a) At ordinary temperature it is a gas which can be liquified on cooling to a colourless liquid, (boiling point 17°C) having characteristic smell of apples.
(b) It is insoluble in water but soluble in alcohol and ether.

(iii) Chemical properties

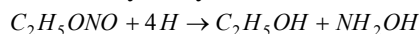
(a) Hydrolysis : It is hydrolysed by aqueous alkalies or acids into ethyl alcohol.



(b) Reduction :



Small amount of hydroxylamine is also formed.



(iv) **Uses**

(a) Ethyl nitrite dilates 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).

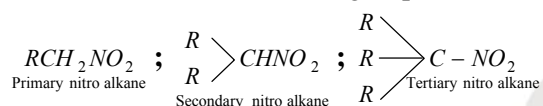
(b) Its 4% alcoholic solution (known as **sweet spirit of nitre**) is used in medicine as a diuretic.

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

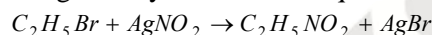
□ **Isoamyl nitrite** is used as an antispasmodic in angina pectoris and as a restorative in cardiac failure.

(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.

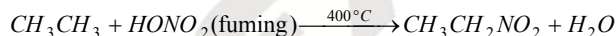
(ii) **General methods of preparation**

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



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)

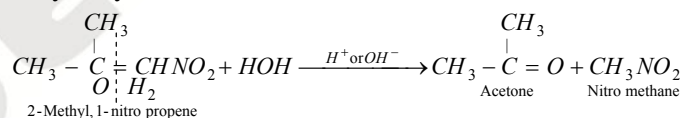


With higher alkanes, a mixture of different nitro alkanes is formed which can be separated by **fractional distillation**.

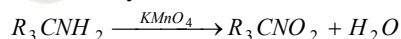
(c) By the action of sodium nitrite on α -halo carboxylic acids



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



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

(iii) **Physical properties**

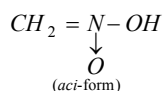
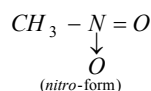
(a) Nitro alkanes are colourless, pleasant smelling liquids.

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

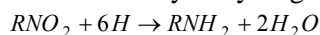
(c) Their boiling points are much higher than isomeric alkyl nitrites due to polar nature.

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

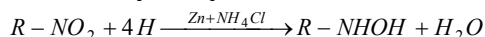
□ 1° and 2° - Nitro alkanes are known to exist as tautomeric mixture of nitro-form and aci-form.

(iv) **Chemical properties**

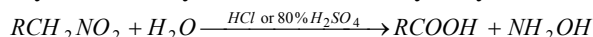
(a) Reduction : Nitro alkanes are reduced to corresponding primary amines with Sn and HCl or Fe and HCl or catalytic hydrogenation using nickel as catalyst.



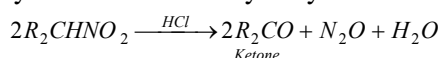
However, when reduced with a neutral reducing agent (**Zinc dust + NH₄Cl**), nitro alkanes form **substituted hydroxylamines**.



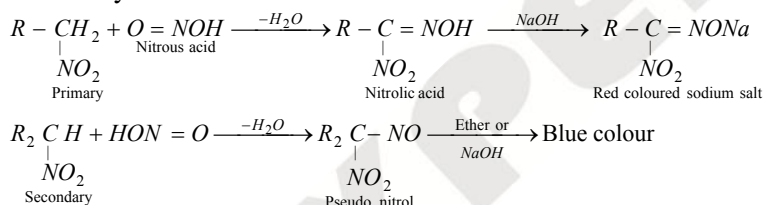
(b) Hydrolysis : Primary nitro alkanes on hydrolysis form hydroxylamine and carboxylic acid.



secondary nitro alkanes on hydrolysis form ketones.

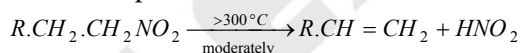


(c) Action of nitrous acid : Nitrous acid reacts with primary, secondary and tertiary nitro alkanes differently.

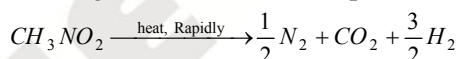


Tertiary nitro alkanes do not react with nitrous acid.

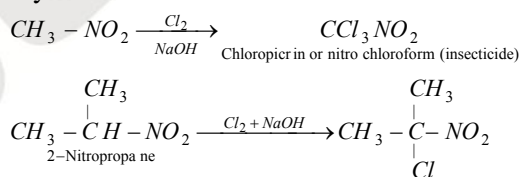
(d) Thermal decomposition : .



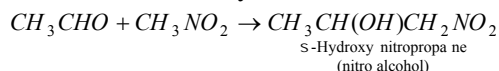
On rapid heating nitro alkanes decompose with great violence.



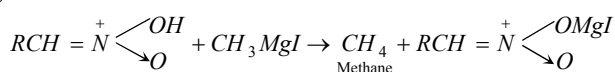
(e) Halogenation : Primary and secondary nitro alkanes are readily halogenated in the α -position by treatment with chlorine or bromine.



(f) Condensation with aldehyde :



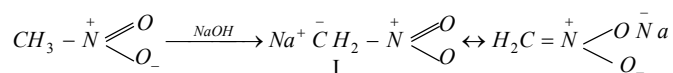
(g) Reaction with grignard reagent : The aci-form of nitroalkane reacts with Grignard reagent forming alkane.



□ The nitrogen of $-\text{NO}_2$ 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.



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

- Strong electron withdrawing effect of the $-\text{NO}_2$ group.
- 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,

- As solvents for polar substances such as cellulose acetate, synthetic rubber etc.
- As an explosive.
- For the preparation of amines, hydroxylamines, chloropicrin etc.

Table : 1. Distinction between Ethyl nitrite and Nitro ethane:

Test	Ethyl nitrite ($\text{C}_2\text{H}_5\text{ONO}$) (Alkyl nitrite, RONO)	Nitro ethane ($\text{C}_2\text{H}_5\text{NO}_2$) (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 . $\text{C}_2\text{H}_5\text{ONO} + 4\text{H} \rightarrow \text{C}_2\text{H}_5\text{OH} + \text{NH}_2\text{OH}$ $\text{RONO} + 6\text{H} \rightarrow \text{ROH} + \text{NH}_3 + \text{H}_2\text{O}$	Gives corresponding primary amine. $\text{C}_2\text{H}_5\text{NO}_2 + 6\text{H} \rightarrow \text{C}_2\text{H}_5\text{NH}_2 + 2\text{H}_2\text{O}$ $\text{RNO}_2 + 6\text{H} \rightarrow \text{RNH}_2 + 2\text{H}_2\text{O}$
Action of NaOH (alkalies).	Readily hydrolysed to give corresponding alcohol and sodium nitrite (decomposition). $\text{C}_2\text{H}_5\text{ONO} + \text{NaOH} \rightarrow \text{C}_2\text{H}_5\text{OH} + \text{NaNO}_2$ $\text{RONO} + \text{NaOH} \rightarrow \text{ROH} + \text{NaNO}_2$	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. $\text{CH}_3 - \text{CH} = \overset{+}{\text{N}} \begin{array}{c} \text{OH} \\ \parallel \\ \text{O}^- \end{array} \xrightarrow{\text{NaOH}} \text{CH}_3 - \text{CH} = \overset{+}{\text{N}} \begin{array}{c} \text{ONa} \\ \parallel \\ \text{O}^- \end{array}$
Action of HNO_2 ($\text{NaNO}_2 + \text{HCl}$)	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 :

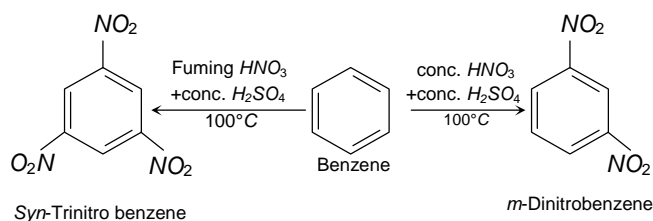
Aromatic nitro compounds are the derivatives of aromatic hydrocarbons in which one or more hydrogen atom (s) of the benzene nucleus has been replaced by nitro ($-\text{NO}_2$) group.

(1) Preparation

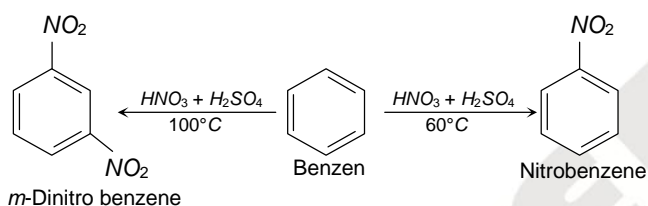
(i) **Nitration (Direct method)** : The number of $-\text{NO}_2$ groups introduced in benzene nucleus

depends upon the nature and concentration of the nitrating agent, temperature of nitration and nature of the compound to be nitrated.

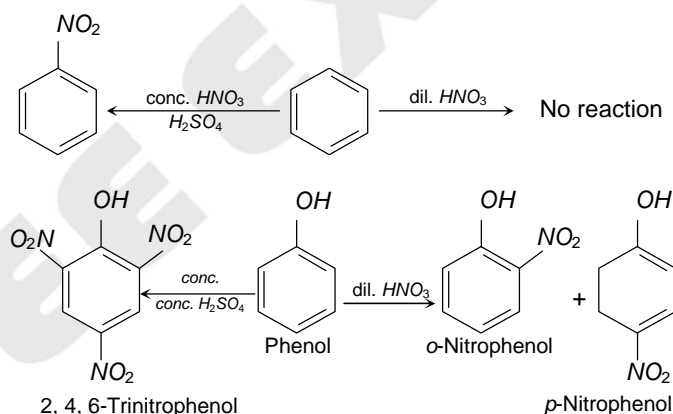
(a) The nature of the nitrating agent : For example,



(b) Temperature of nitration : For example,

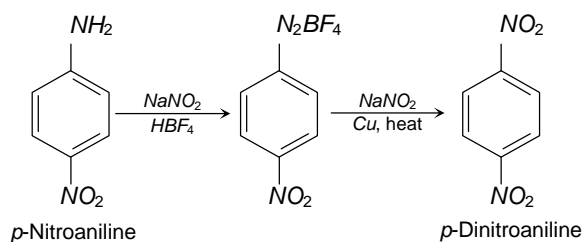


(c) Nature of the compound to be nitrated : Presence of electron-releasing group like $-\text{OH}$, $-\text{NH}_2$, $-\text{CH}_3$, $-\text{OR}$, etc., in the nucleus facilitates nitration. Thus aromatic compounds bearing these groups (i.e. phenol, aniline, toluene, etc.) can be nitrated readily as compared 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 $-\text{NO}_2$, $-\text{SO}_3\text{H}$ requires powerful nitrating agent (like fuming HNO_3 + $\text{conc. H}_2\text{SO}_4$) 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.

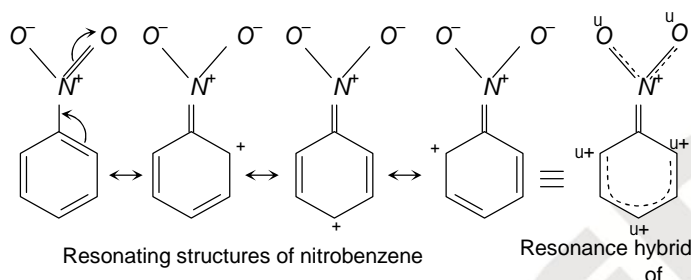


(2) **Physical properties**

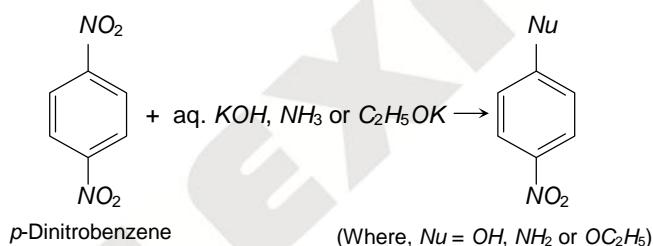
- (i) Aromatic nitro compounds are insoluble in water but soluble in organic solvents.
 (ii) They are either pale yellow liquids or solids having distinct smells. For example, nitro benzene (oil of Mirabane) is a pale yellow liquid having a smell of bitter almonds.

(3) **Chemical properties**

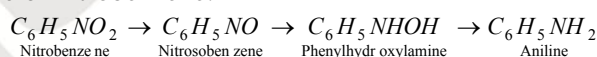
- (i) Resonance in nitrobenzene imparts a partial double bond character to the bond between carbon of benzene nucleus and nitrogen of the $-\text{NO}_2$ group with the result the $-\text{NO}_2$ group is firmly bonded to the ring and therefore cannot be replaced other groups, i.e., it is very inert.



- (ii) **Displacement of the $-\text{NO}_2$ group :** Although $-\text{NO}_2$ group of nitrobenzene cannot be replaced by other groups, but if a second $-\text{NO}_2$ group is present on the benzene ring of nitrobenzene in the o- or p- position, it can be replaced by a nucleophile. For example,

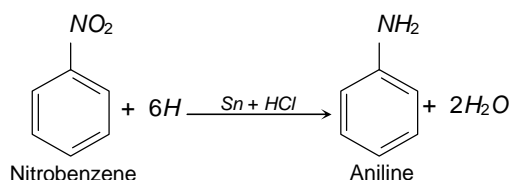


- (iii) **Reduction :** Aromatic nitro compounds can be reduced to a variety of product as shown below in the case of nitrobenzene.

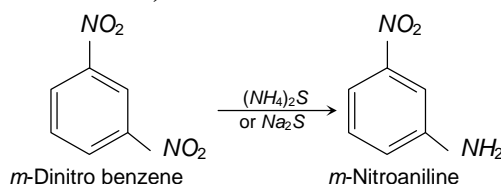


The nature of the final product depends mainly on the nature (acidic, basic or neutral) of the reduction medium and the nature of the reducing agent.

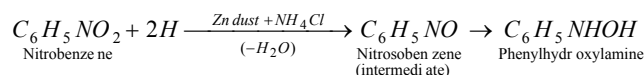
- (a) Reduction in acidic medium



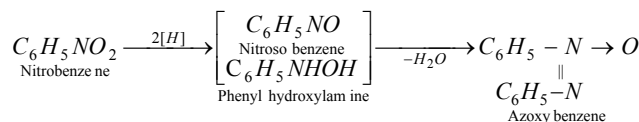
Reduction of dinitrobenzene with ammonium sulphide reduces only one $-\text{NO}_2$ group (**selective reduction**)



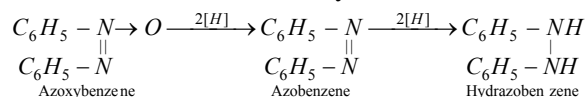
(b) Reduction in neutral medium :



(c) Reduction in alkaline medium :

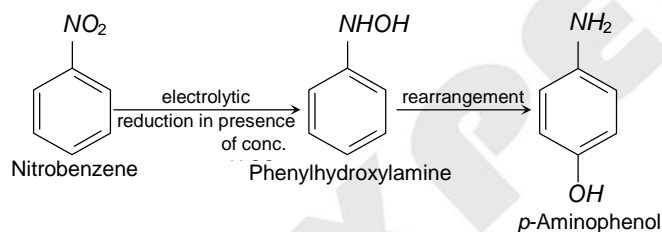


Azobenzene on further reduction yields azobenzene and hydrazobenzene.



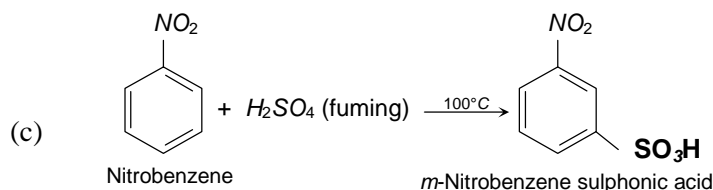
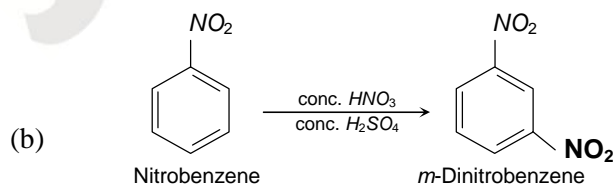
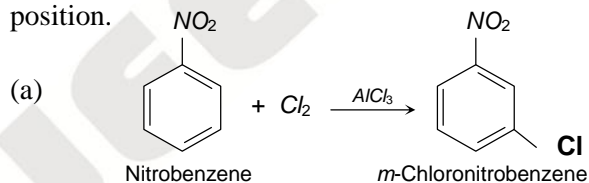
(d) Electrolytic reduction :

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

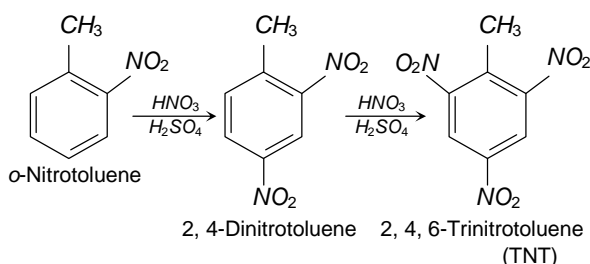


- Alkaline medium of electrolytic reduction gives all the **mono- and di-nuclear reduction products** mentioned above in point (c).

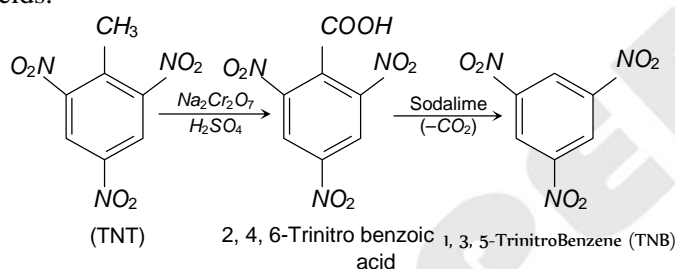
(iv) **Electrophilic substitution** : Since $-\text{NO}_2$ group is deactivating and m-directing, electrophilic substitution (halogenation, nitration and sulphonation) in simple aromatic nitro compounds (e.g. nitrobenzene) is very difficult as compared to that in benzene. Hence vigorous reaction conditions are used for such reaction and the new group enters the m-position.



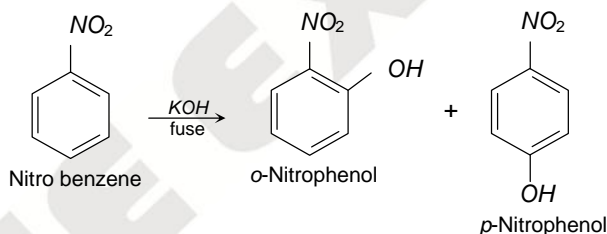
Although nitrobenzene, itself undergoes electrophilic substitution under drastic conditions, nitrobenzene having activating groups like alkyl, $-OR$, $-NH_2$ etc. undergoes these reactions relatively more readily.



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.

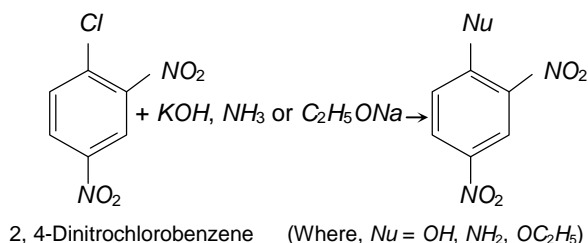


(v) **Nucleophilic Substitution** : Benzene is inert to nucleophiles, but the presence of $-NO_2$ group in the benzene ring activates the latter in o- and p-positions to nucleophiles.



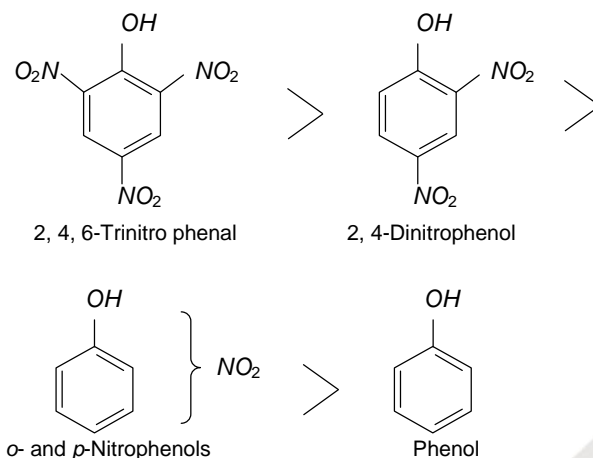
(vi) **Effect of the $-NO_2$ group on other nuclear substituents**

(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 ($KOH, NH_3, NaOC_2H_5$).

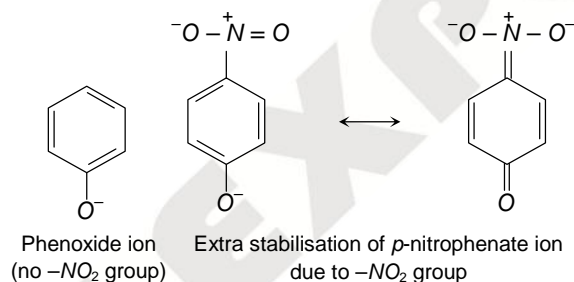


(b) Effect on phenolic $-OH$ group : The acidity of the phenolic hydroxyl group is markedly increased by the presence of $-NO_2$ group in o- and p-position.

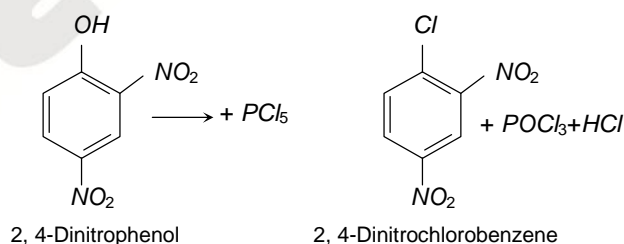
The decreasing order of the acidity of nitrophenols follows following order



Increased acidity of o- and p-nitrophenols is because of the fact that the presence of electron-withdrawing –NO₂ 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.



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 PCl₅ gives poor yield of chlorobenzene.

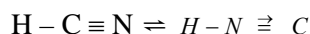


(4) Uses

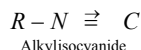
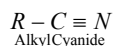
- (i) On account of their high polarity, aromatic nitro compounds are used as solvents.
- (ii) Nitro compounds like TNT, picric acid, TNB etc. are widely used as **explosives**.
- (iii) These are used for the synthesis of aromatic amino compounds.
- (iv) Nitro benzene is used in the preparation of shoe polish and scenting of cheap soaps.

Cyanides and Isocyanides

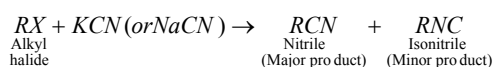
Hydrogen cyanide is known to exist as a tautomeric mixture.



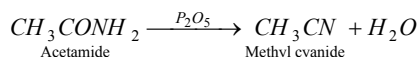
Hence, it forms two types of alkyl derivatives which are known as alkyl cyanides and alkyl isocyanides.

**(1) Alkyl Cyanides****(i) Methods of preparation**

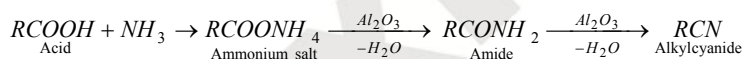
(a) From alkyl halides : The disadvantage of this method is that a mixture of nitrile and isonitrile is formed.



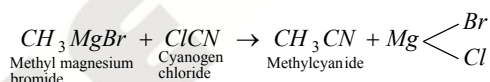
(b) From acid amides : $RCNH_2 \xrightarrow[-H_2O]{P_2O_5} RCN$



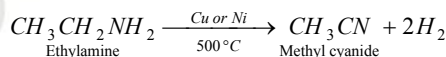
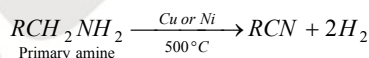
Industrially, alkyl cyanides are prepared by passing a mixture of carboxylic acid and ammonia over alumina at 500°C.



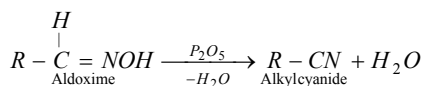
(c) From Grignard reagent



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



(e) From oximes :

**(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.

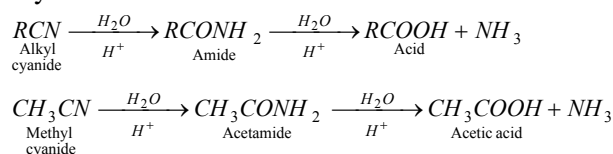
(c) They are soluble in water. The solubility decreases with the increase in number of carbon atoms in the molecule.

(d) They are soluble in organic solvents.

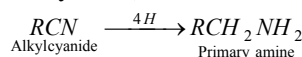
(e) They are poisonous but less poisonous than HCN

(iii) Chemical properties

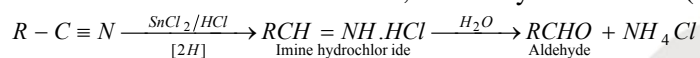
(a) Hydrolysis



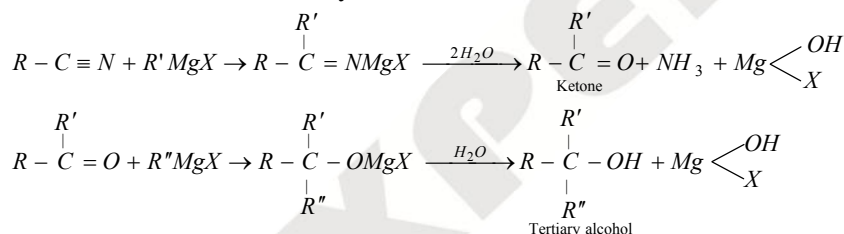
(b) Reduction : When reduced with hydrogen in presence of Pt or Ni, or LiAlH_4 (Lithium aluminium hydride) or sodium and alcohol, alkyl cyanides yield primary amines.



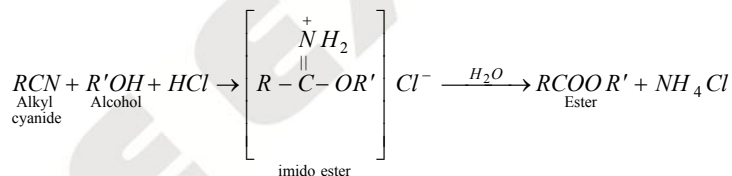
However, when a solution of alkyl cyanides in ether is reduced with stannous chloride and hydrochloric acid and then steam distilled, an aldehyde is formed (**Stephen's reaction**).



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



(d) Alcohololysis :

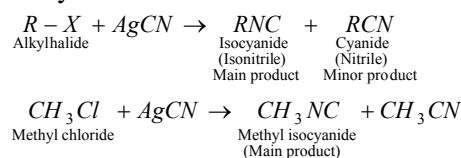


(iv) Uses : Alkyl cyanides are important intermediates in the organic synthesis of a large number of compounds like acids, amides, esters, amines etc.

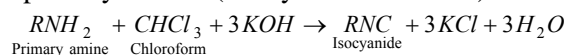
(2) Alkyl Isocyanides

(i) Methods of preparation

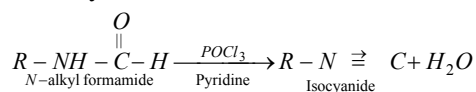
(a) From alkyl halides :



(b) From primary amines (Carbylamine reaction) :



(c) From N-alkyl formamides :

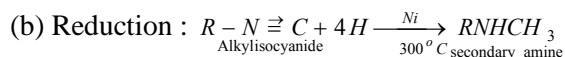
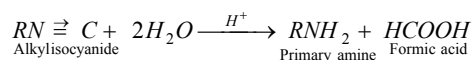


(ii) **Physical properties**

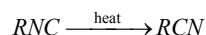
- (a) Alkyl isocyanides are colourless, unpleasant smelling liquids.
 (b) They are insoluble in water but freely soluble in organic solvents.
 (c) Isonitriles are much more poisonous than isomeric cyanides.

(iii) **Chemical properties**

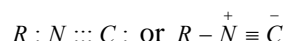
(a) Hydrolysis :



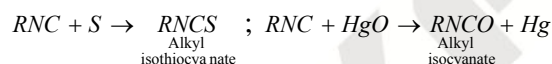
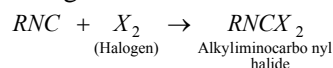
(c) Action of heat : When heated for sometime at 250°C, a small amount of isonitrile changes into isomeric nitrile.



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



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



(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.

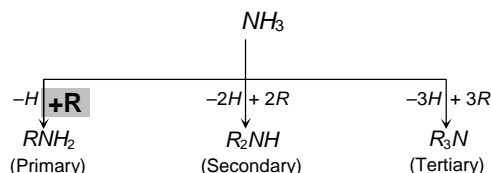
Table : 2 Comparison of Alkyl Cyanides and Alkyl Isocyanides:

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

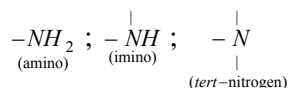
Amines

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

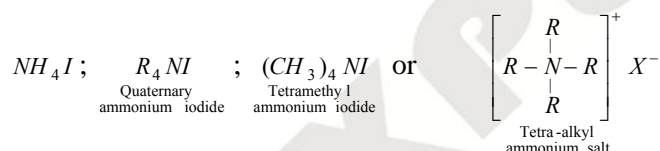


Amines are classified as primary, secondary or tertiary depending on the number of alkyl groups attached to nitrogen atom.

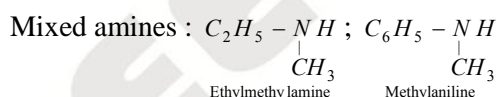
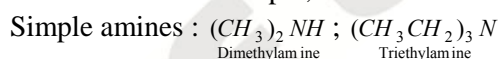
The characteristic groups in primary, secondary and tertiary amines are:



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



- (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,

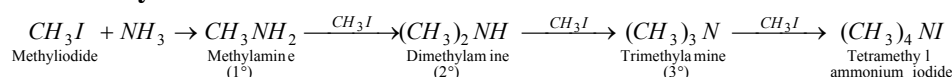


The aliphatic amines have pyramidal shape with one electron pair. In amines, N undergoes **sp³ hybridisation**.

- (2) **General methods of preparation**

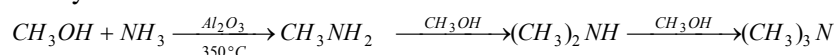
(i) **Methods yielding mixture of amines (Primary, secondary and tertiary)**

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



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.

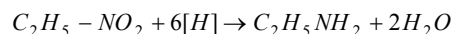
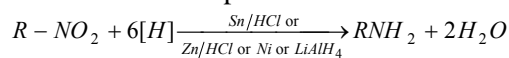
(b) Ammonolysis of alcohols :



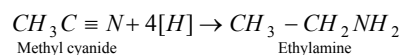
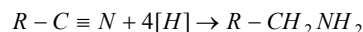
Primary amine may be obtained in a good yield by using a excess of ammonia.

(ii) **Methods yielding primary amines**

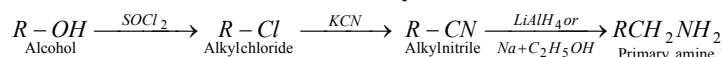
(a) Reduction of nitro compounds



(b) Reduction of nitriles (Mendius reaction)

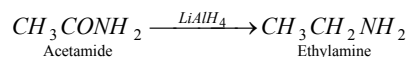


The start can be made from alcohol or alkyl halide.

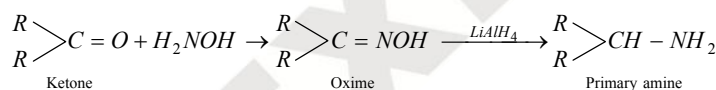
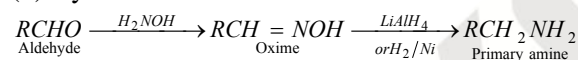


This sequence gives an amine containing one more carbon atom than alcohol.

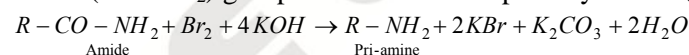
(c) By reduction of amides with $LiAlH_4$



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



(e) Hofmann's bromamide reaction or degradation (Laboratory method) : By this method the amide ($-CONH_2$) group is converted into primary amino ($-NH_2$) group.

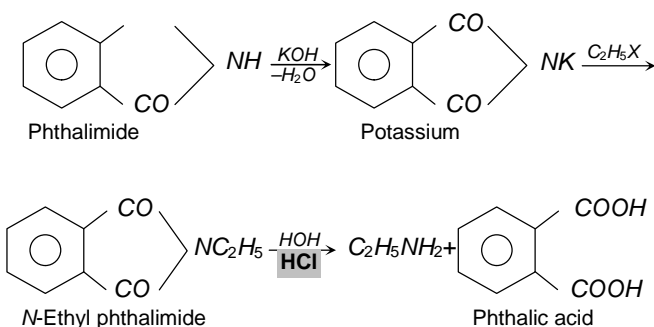


This is the most convenient method for preparing primary amines.

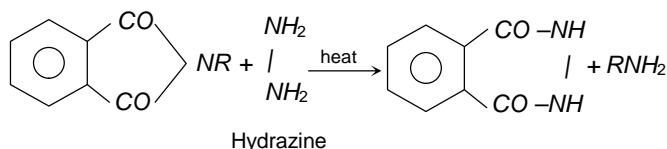
This method gives an **amine containing one carbon atom less than amide**.

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

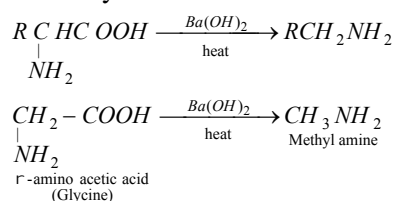
- Phthalimide is reacted with KOH to form potassium phthalimide.
- The potassium salt is treated with an alkyl halide.
- The product N-alkyl phthalimide is put to hydrolysis with hydrochloric acid when primary amine is formed.



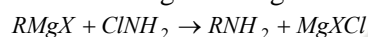
When hydrolysis is difficult, the N-alkyl phthalimide can be treated with hydrazine to give the required amine.



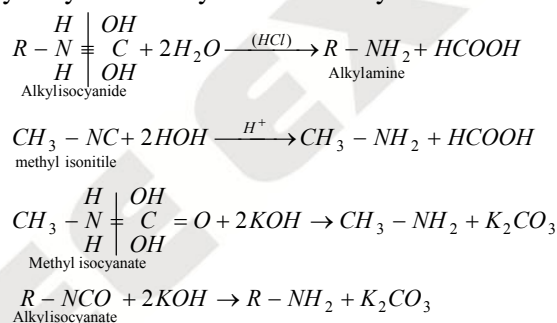
(g) By decarboxylation of α -amino acids



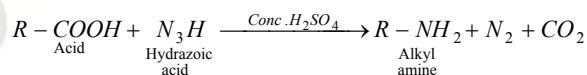
(h) By means of a Grignard reagent and chloramine :



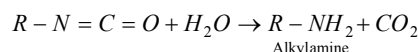
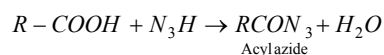
(i) By hydrolysis of Isocyanides or Isocyanates



(j) By Schmidt reaction :

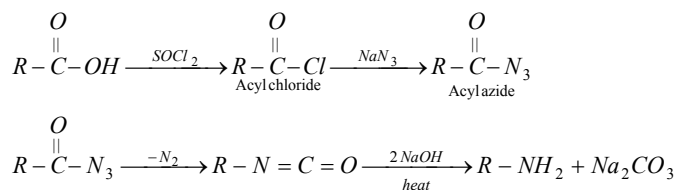


In this reaction the acyl azide ($\text{R}-\text{CON}_3$) and alkyl isocyanate ($\text{R}-\text{NCO}$) are formed as an intermediate.

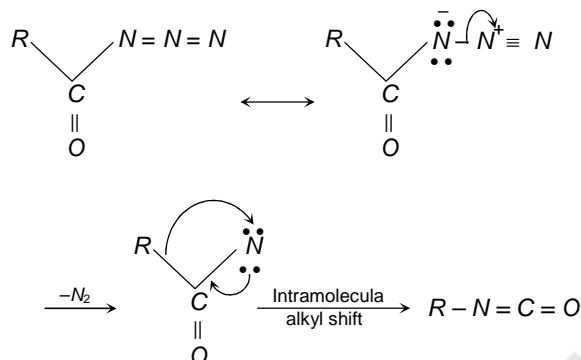


The overall reaction which proceeds by the elimination of nitrogen from acyl azide followed by acidic or alkaline hydrolysis to yield primary amine containing one carbon less, is called **Curtius Degradation**.

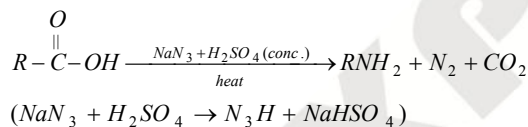
The method uses acid chloride to prepare primary amine through acyl azide.



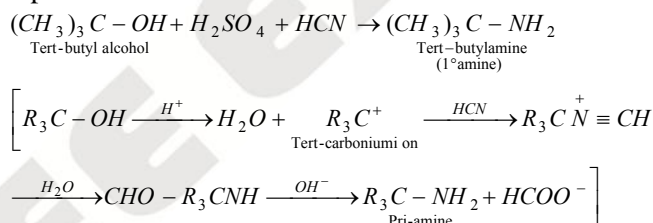
The mechanism of **curtius rearrangement** is very similar to Hofmann degradation.



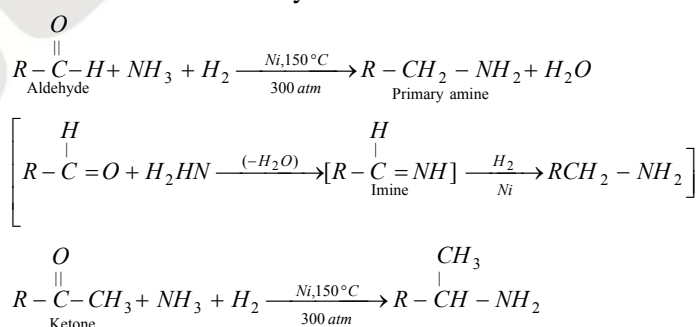
Schmidt reaction converts $\text{R}-\text{COOH}$ to $\text{R}-\text{NH}_2$, which is a modification of curtius degradation. In this reaction a carboxylic acid is warmed with sodium azide (Na^+N_3^-) and conc. H_2SO_4 . The carboxylic acid is directly converted to the primary amine without the necessity of isolating alkyl azide.



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

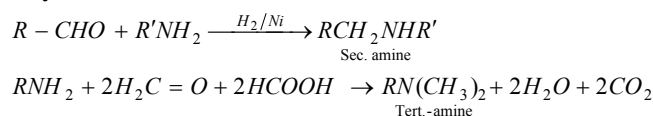


(l) Reductive amination of aldehydes and ketones :

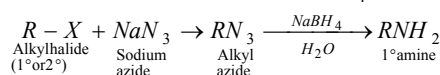


This reaction probably takes place through the formation of an imine (Schiff's base).

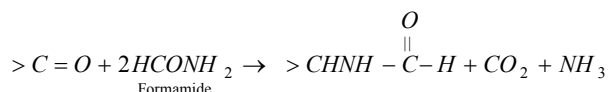
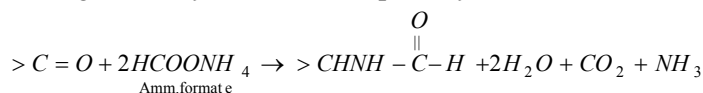
The primary amine can also be converted into sec. or tert. amines by the following steps



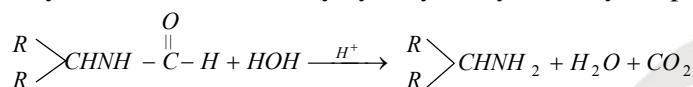
(m) By reduction of azide with NaBH_4



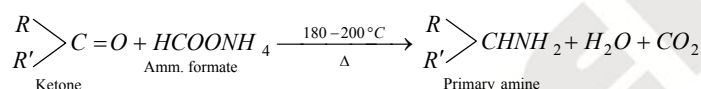
(n) By Leuckart reaction : Aldehydes or ketones react with ammonium formate or with formamide to give formyl derivative of primary amine.



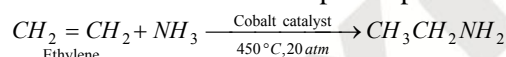
These formyl derivatives are readily hydrolysed by acid to yield primary amine.



This is called Leuckart reaction, i.e.,

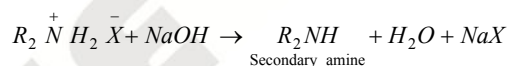
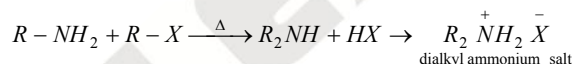


□ On commercial scale, ethylamine is obtained by heating a mixture of ethylene and ammonia at 450°C under 20 atmospheric pressure in presence of cobalt catalyst.



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

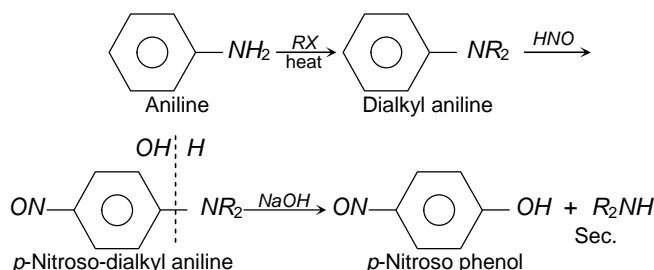
(a) Reaction of primary amines with alkyl halides



(b) Reduction of isonitriles : $R-\text{NC} + 4[\text{H}] \xrightarrow{\text{Pt}} \underset{\substack{\text{Sec. amine}}}{\text{RNHCH}_3}$

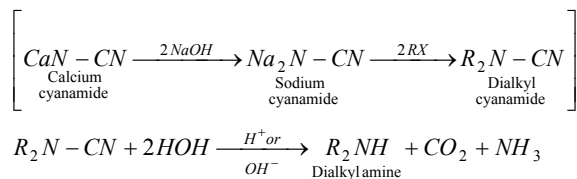
Secondary amine formed by this method always possesses one $-\text{CH}_3$ group linked directly to nitrogen.

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



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

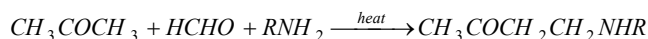
(d) Hydrolysis of dialkyl cyanamide



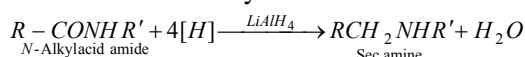
(e) Reduction of N-substituted amides : Reduction of N-substituted amides with LiAlH_4 yields secondary amines.

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**.

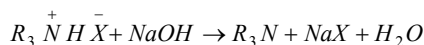
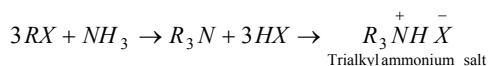


Which can be reduced to alkyl amines.

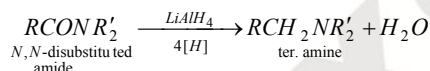


(iv) **Methods yielding tertiary amines**

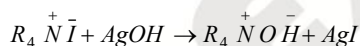
(a) Reaction of alkylhalides with ammonia



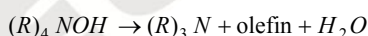
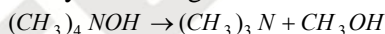
(b) Reduction of N, N-disubstituted amides : The carbonyl group is converted into $-\text{CH}_2$ group.



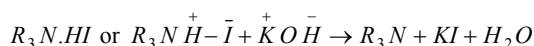
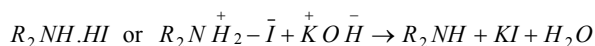
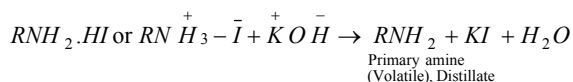
(c) Decomposition of tetra-ammonium hydroxides : The tetra-alkyl ammonium hydroxides are formed when corresponding halides are treated with moist silver oxide.



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.



(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.

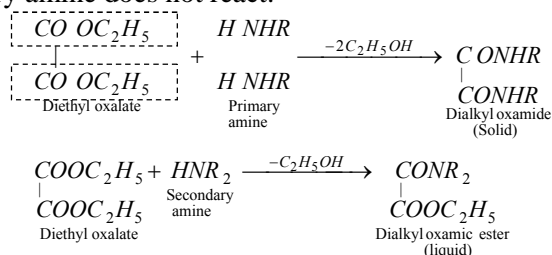


$\text{R}_4\text{N}^+\text{I}^-$ (non-volatile tetra-alkyl ammonium salt) has no reaction with KOH, however remains as residue.

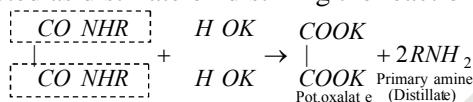
This mixture is separated into primary, secondary and tertiary amines by the application of following methods.

(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 $17^\circ C$, $(C_2H_5)_2NH$ is $56^\circ C$ and $(C_2H_5)_3N$ is $95^\circ C$ 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.

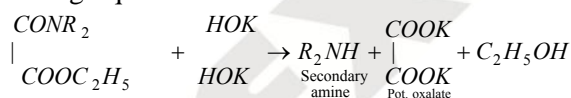


Primary amine is recovered when solid oxamide is heated with caustic potash solution and collected as distillate on distilling the reaction mixture.

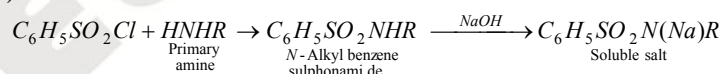


The liquid (mixture of oxamic ester+ tertiary amine) is subjected to fractional distillation when tertiary amine distils over.

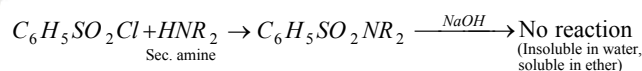
The remaining liquid is distilled with KOH to recover secondary amine.



(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).



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

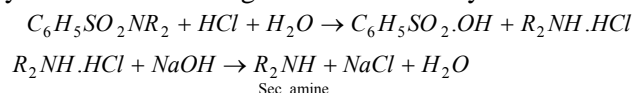


Tertiary amine does not react.

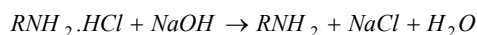
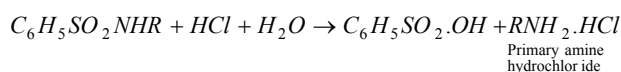
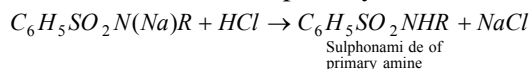
The above alkaline mixture of the amines is extracted with ether.

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.



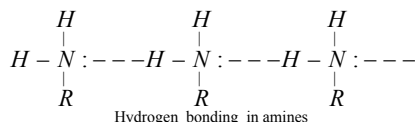
The aqueous layer is acidified and hydrolysed with dilute HCl. The hydrochloride formed is then distilled with NaOH when primary amine distils over.



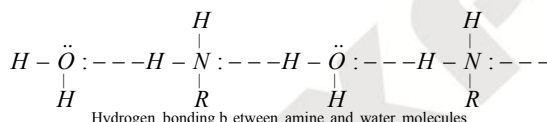
(4) **Physical properties**

(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**.



(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.



Solubility decreases with increase of molecular mass.

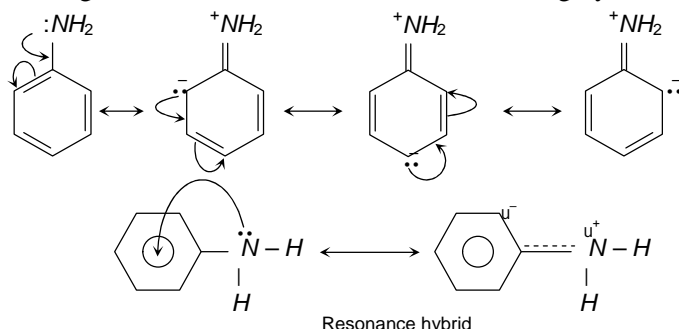
(5) **Chemical properties :** The main reactions of amines are due to the presence of a lone pair of electrons on nitrogen atom. Amines are **electrophilic reagents** as the lone pair of electrons can be donated to electron seeking reagents, (i.e., electrophiles).

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.

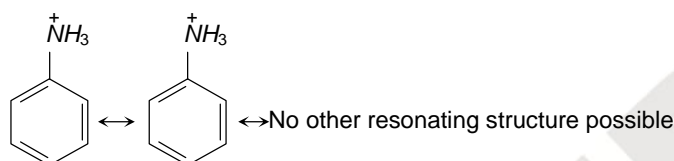
(i) The order of basic nature of various amines has been found to **vary with nature of alkyl groups**.

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.



But anilinium ion is less resonance stabilized than aniline.



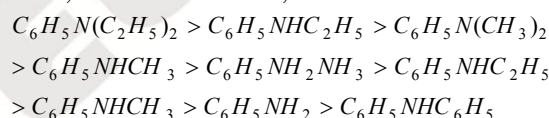
Thus, electron density is less on N atom due to which aniline or other aromatic amines are less basic than aliphatic amines.

However, any group which when present on benzene ring has electron withdrawing effect ($-\text{NO}_2$, $-\text{CN}$, $-\text{SO}_3\text{H}$, $-\text{COOH}$, $-\text{Cl}$, 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 ($-\text{NH}_2$, $-\text{OR}$, $\text{R}-$, etc.) increases basicity of aniline. Toluidine is more basic than aniline as $-\text{CH}_3$ group is electron repelling group ($+I$ group).

Further greater the value of K_b or lower the value of $\text{p}K_b$, stronger will be the base. The basic character of some amines have the following order,



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,



In Toluidines $-\text{p}$ -isomer $>$ $-\text{m}$ - $>$ $-\text{o}$ -

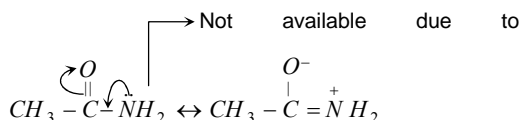
Chloroanilines $-\text{p}$ -isomer $>$ $-\text{m}$ - $>$ $-\text{o}$ -

Phenylene diamines $-\text{p}$ -isomer $>$ $-\text{m}$ - $>$ $-\text{o}$ -

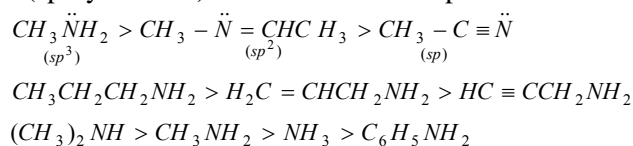
Nitroanilines $-\text{m}$ -isomer $>$ $-\text{p}$ - $>$ $-\text{o}$ -

❑ 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.

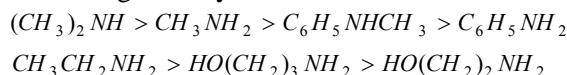
❑ Ethylamine and acetamide both contain an amino group but acetamide does not show basic nature. This is because lone pair of electrons on nitrogen is delocalised by resonance with the carbonyl group which makes it less available for protonation.



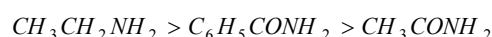
□ The compounds with least 's' character (sp^3 -hybridized) is most basic and with more 's' character (sp -hybridized) is least basic. Examples in decreasing order of basicity are,



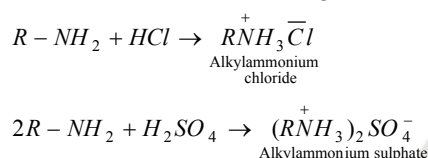
□ Electron withdrawing (C_6H_5-) groups decrease electron density on nitrogen atom and thereby decreasing basicity.



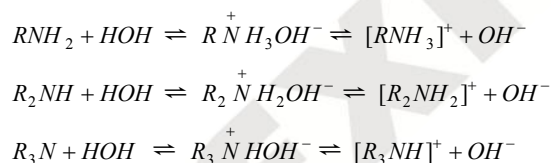
□ Electron withdrawing inductive effect of the $-OH$ group decreases the electron density on nitrogen. This effect diminishes with distance from the amino group.



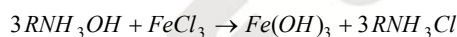
(iii) **Salt formation** : Amines being basic in nature, combine with mineral acids to form salts.



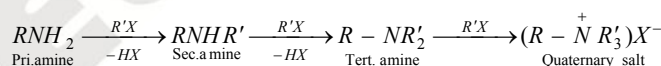
(iv) **Nature of aqueous solution** : Solutions of amines are alkaline in nature.



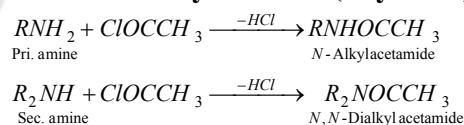
The aqueous solutions of amines behaves like NH_4OH and give ferric hydroxide precipitate with ferric chloride and blue solution with copper sulphate.



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



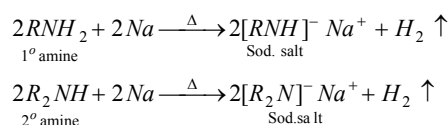
(vi) **Reaction with acetyl chloride (Acylation)**



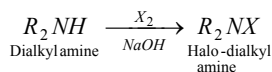
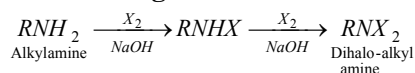
Tertiary amines do not react since they do not have replaceable hydrogen on nitrogen.

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

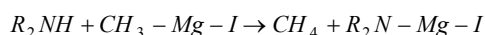
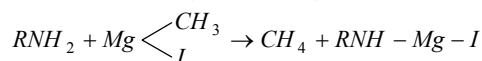
(vii) **Action of sodium**



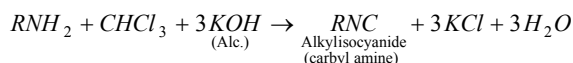
(viii) Action of halogens



(ix) Reaction with Grignard reagent



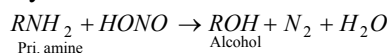
(x) **Carbylamine reaction** : This reaction is shown by only **primary amines**. This is a test of primary amines and is used to distinguish primary amines from secondary and tertiary amines.



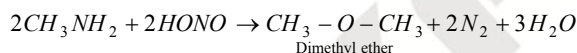
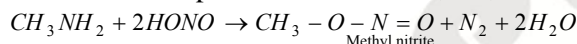
Isocyanides are bad smelling compounds and can be easily detected.

(xi) Reaction with nitrous acid

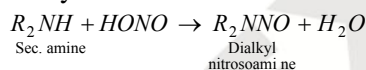
(a) Primary amines form alcohols with nitrous acid ($\text{NaNO}_2 + \text{HCl}$). Nitrogen is eliminated.



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

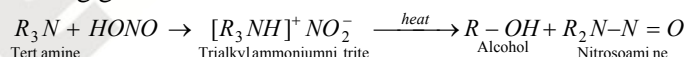


(b) Secondary amines form nitrosoamines which are water insoluble yellow oily liquids.



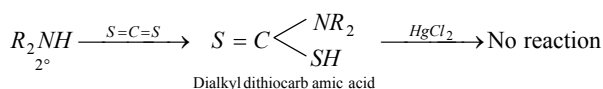
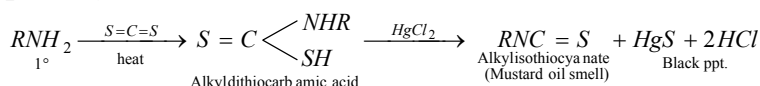
Nitrosoamine on warming with phenol and conc. H_2SO_4 give a brown or red colour which soon changes to blue green. The colour changes to red on dilution and further changes to blue or violet with alkali. This colour change is referred to **Liebermann's nitroso reaction** and is used for the test of secondary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

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



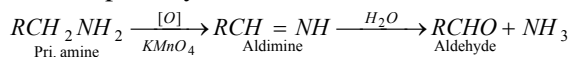
This reaction (nitrous acid test) is used to make distinction between primary, secondary and tertiary amines.

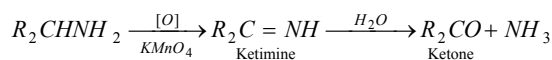
(xii) **Reaction with carbon di sulphide** : This **Hofmann's mustard oil reaction** is used as a test for primary amines.



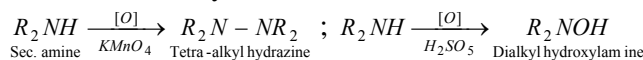
(xiii) **Oxidation** : All the three types of amines undergo oxidation. The product depends upon the nature of oxidising agent, class of amine and the nature of the alkyl group.

(a) Oxidation of primary amines

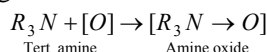




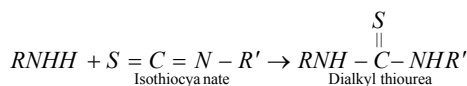
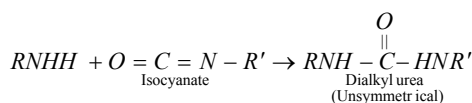
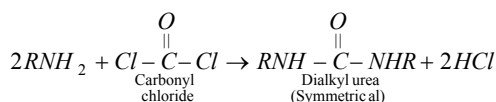
(b) Oxidation of secondary amines



(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.

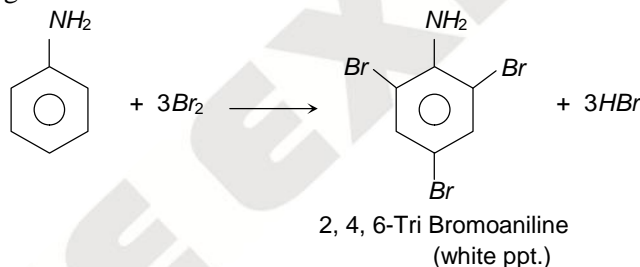


(xiv) Reaction with other electrophilic reagents



(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.

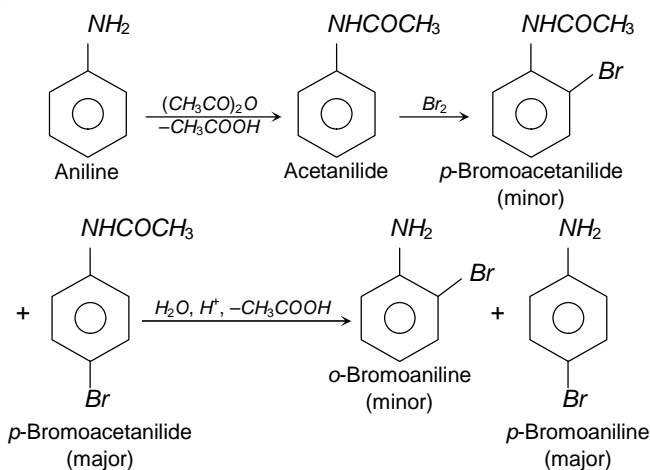
(a) Halogenation



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.

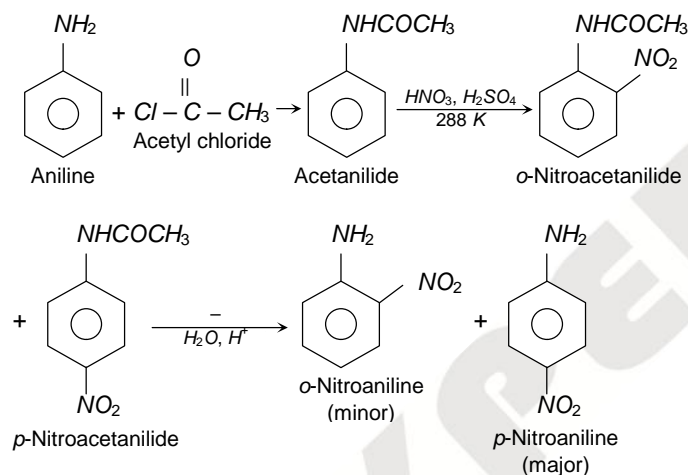


Acetylation deactivates the ring and controls the reaction to monosubstitution stage only because acetyl group is electron withdrawing group and therefore, the electron pair of N-atom is withdrawn towards the carbonyl group.

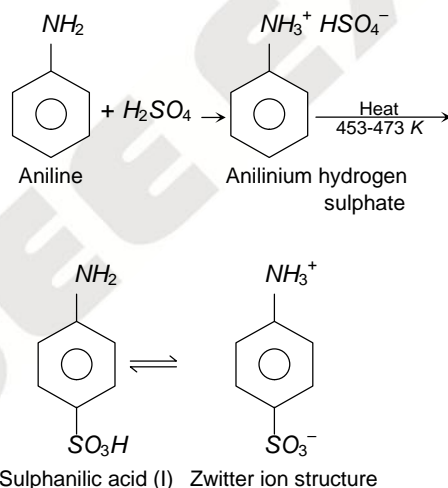
(b) Nitration : Aromatic amines cannot be nitrated directly because they are readily oxidized. This is because, HNO_3 is a strong oxidising agent and results in partial oxidation of the ring to form a black mass.

Therefore, to solve this problem, nitration is carried out by protecting the $-\text{NH}_2$ 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

- Ethylamine is used in solvent extraction processes in **petroleum refining** and as a **stabiliser** for **rubber latex**.
- The quaternary ammonium salts derived from long chain aliphatic tertiary amines are widely used as detergents.
- Aliphatic amines of low molecular mass are used as solvents.

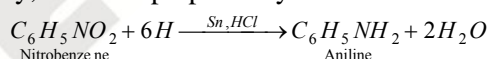
Table : 3 Distinction between primary, secondary and tertiary amines:

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 nitrosoamine 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:

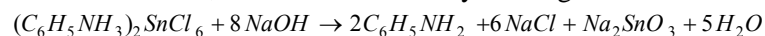
Aniline was first prepared by **Unverdorben (1826)** by **dry distillation of indigo**. In the laboratory, it can be prepared by the reduction of nitrobenzene with tin and hydrochloric acid.



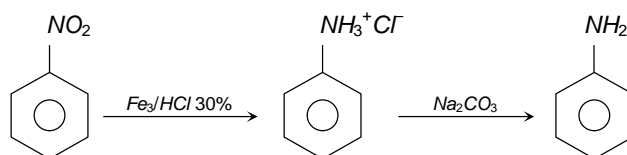
Aniline produced combines with $\text{H}_2\text{SnCl}_6 (\text{SnCl}_4 + 2\text{HCl})$ to form a double salt.



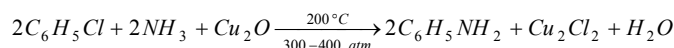
From double salt, aniline is obtained by treating with conc. caustic soda solution.



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.



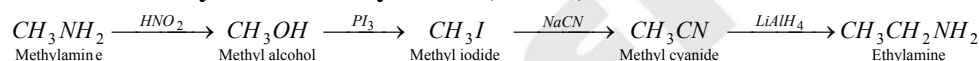
Properties Aniline when freshly prepared is a **colourless oily liquid (b.p. 184°C)**. It has a characteristic unpleasant odour and is not poisonous in nature. It is heavier than water and is only slightly soluble. It is soluble in alcohol, ether and benzene. Its colour changes to dark brown on standing.

It shows all the characteristic reactions discussed earlier.

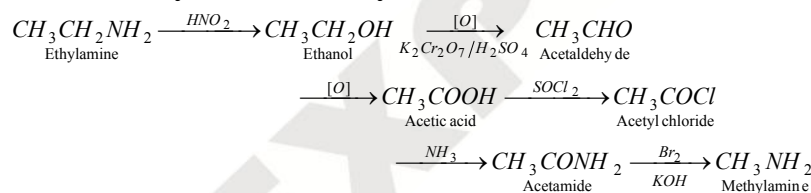
- Uses :**
- (1) It is used in the preparation of diazonium compounds which are used in dye industry.
 - (2) Anils (Schiff's bases from aniline) are used as antioxidants in rubber industry.
 - (3) It is used for the manufacture of its some derivatives such as acetamide, sulphanilic acid and sulpha drugs, etc.
 - (4) It is used as an accelerator in vulcanizing rubber.

Some important conversions:

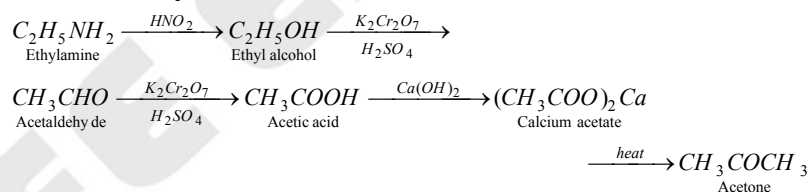
(1) Conversion of methylamine to ethylamine (Ascent)



(2) Conversion of ethylamine to methylamine (Descent)

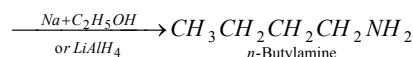
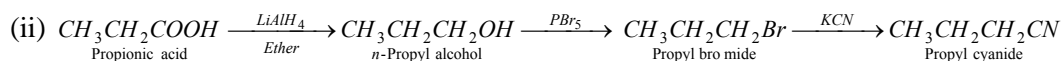
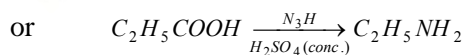


(3) Conversion of ethylamine to acetone

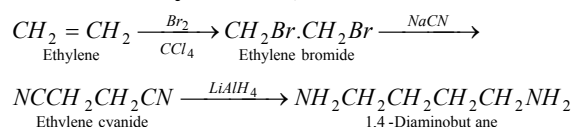


(4) Conversion of propionic acid to

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



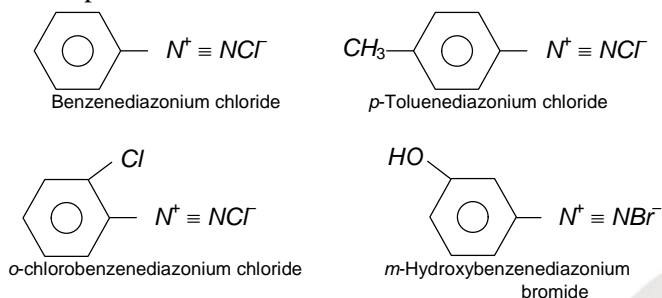
(5) Conversion of ethylene to 1,4-diaminobutane



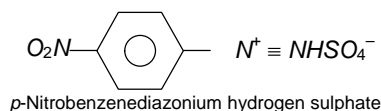
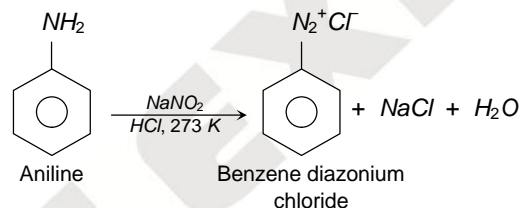
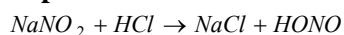
Diazonium salts :

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,



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

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

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

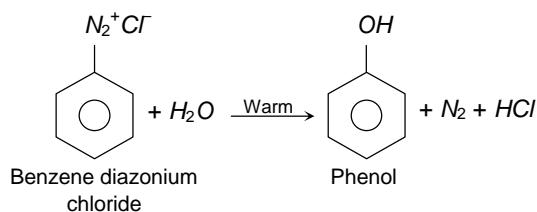
(3) Physical properties of diazonium salts

- (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.

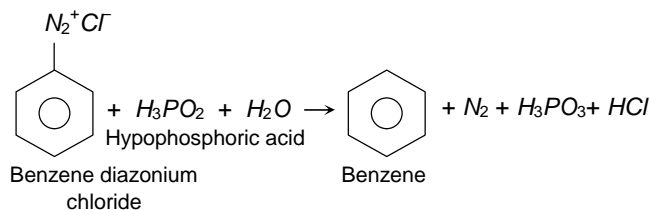
(4) Chemical properties of diazonium salts

(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.

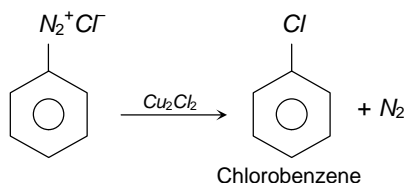
(a) Replacement by $-OH$ group



(b) Replacement by hydrogen

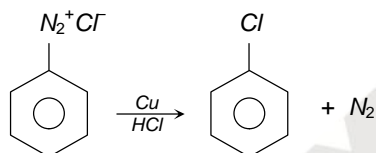


(c) Replacement by –Cl group

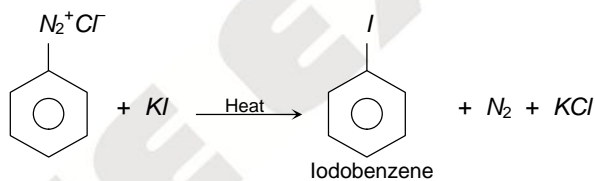


This reaction is called **Sandmeyer reaction**.

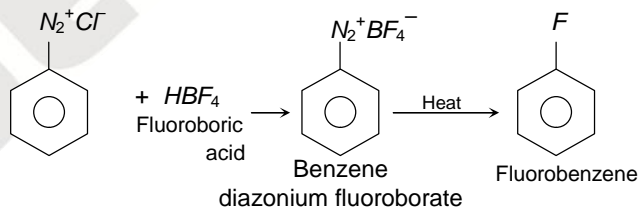
When the diazonium salt solution is warmed with copper powder and the corresponding halogen acid, the respective halogen is introduced. The reaction is a modified form of Sandmeyer reaction and is known as **Gattermann reaction**.



(d) Replacement by iodo (–I) group

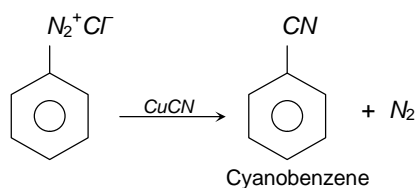


(e) Replacement by – F group

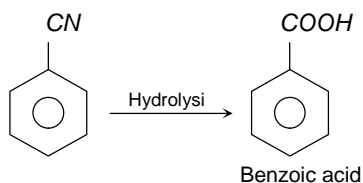


This reaction is called **Balz Schiemann reaction**.

(f) Replacement by Cyano (– CN) group

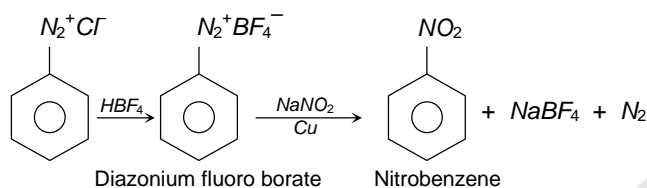


The nitriles can be hydrolysed to acids.

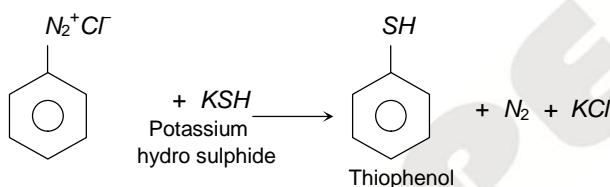


This method of preparing carboxylic acids is more useful than carbonation of Grignard reagents.

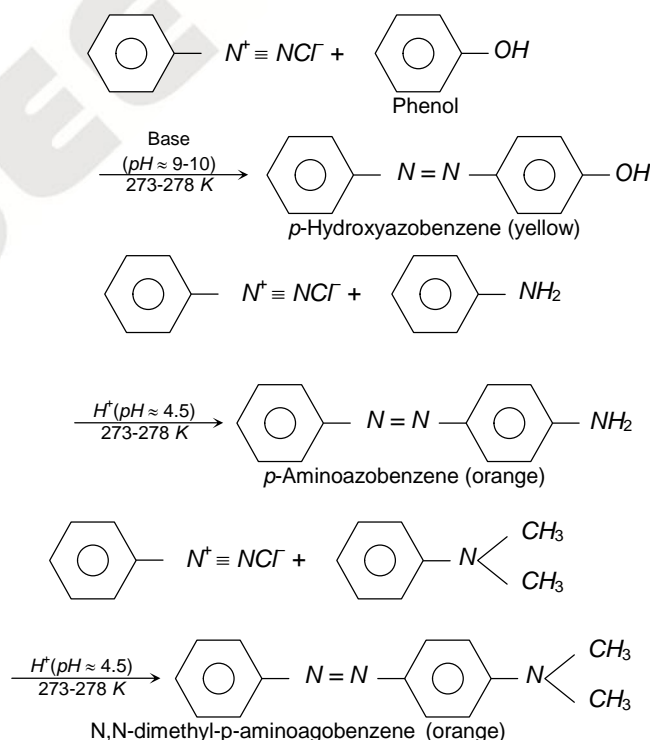
(g) Replacement by $-\text{NO}_2$ group



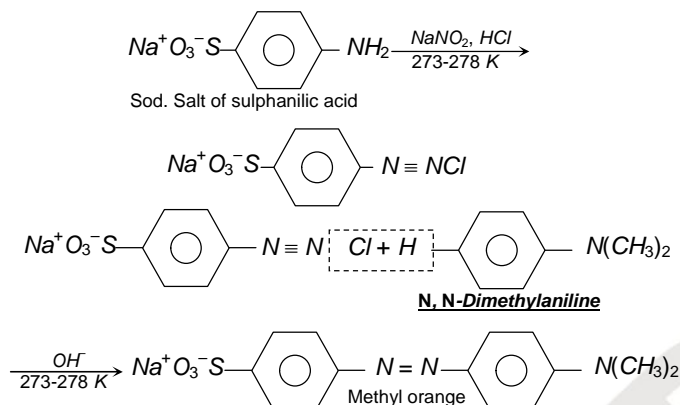
(h) Replacement by thio ($-\text{SH}$) group



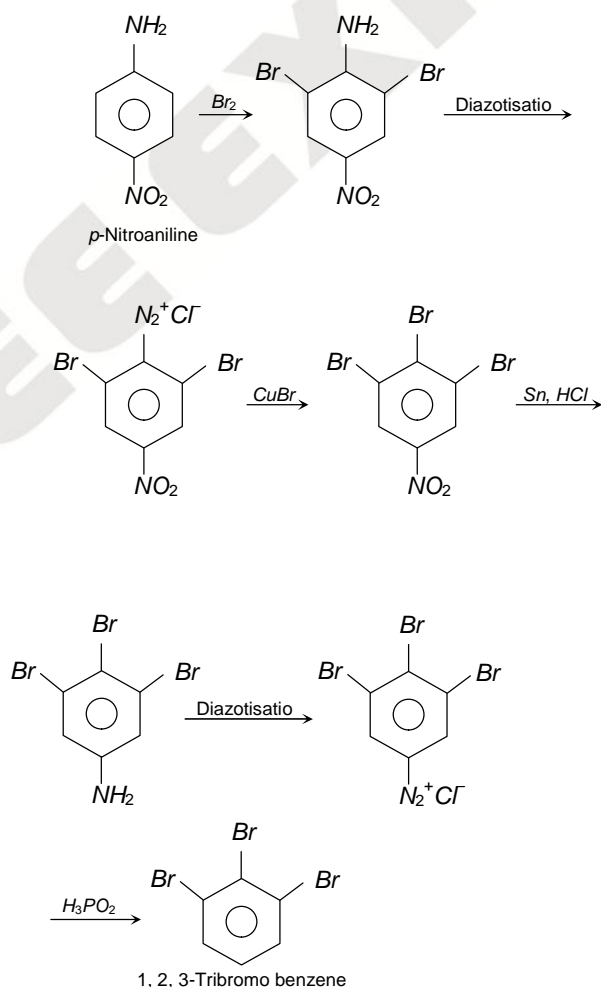
(ii) **Coupling reactions** : The diazonium ion acts as an electrophile because there is positive charge on terminal nitrogen. It can react with nucleophilic aromatic compounds ($\text{Ar}-\text{H}$) activated by electron donating groups ($-\text{OH}$ and $-\text{NH}_2$), which as strong nucleophiles 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 $-\text{N}=\text{N}-$ 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 :



(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 decreasing 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.
- ✍ Carbylamine test is specific for primary amines.

EXERCISE - I

OBJECTIVE QUESTIONS

Introduction of Nitrogen Containing Compounds :

- Cyanide ion is
(a) Nucleophilic (b) Electrophilic
(c) Strongly acidic (d) Non-reactive and neutral
- Compounds containing both amino and COOH groups are known as
(a) Diamines (b) Unknown (c) Amino acids (d) Enzymes
- Which of the following is 1° amine
(a) Ethylene diamine (b) Dimethyl amine (c) Trimethyl amine (d) *N*-methyl aniline
- C_3H_9N represents
(a) Primary amine (b) Secondary amine (c) Tertiary amine (d) All of these
- $(CH_3)_2\underset{\substack{| \\ NH_2}}{C}.CH_2.CO.CH_3$ is
(a) Diacetone (b) Acetoneamine (c) Diacetoneamine (d) Aminoacetone
- A secondary amine is
(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
- The structural formula of methyl aminomethane is
(a) $(CH_3)_2CHNH_2$ (b) $(CH_3)_3N$ (c) $(CH_3)_2NH$ (d) CH_3NH_2
- Allyl isocyanide has
(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
- Triaminobenzene is a
(a) 2° amine (b) 3° amine (c) 1° amine (d) Quarternary salt
- $CH_2 = CH - CH_2 - NH - CH_3$ is a
(a) Secondary amine (b) Primary amine (c) Tertiary amine (d) None of these
- Leakage of which gas was responsible for the Bhopal tragedy in 1984
(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
- (a) $C_6H_5NO_2$ (b) CH_3CH_2ONO (c) $CH_3CH - N \begin{array}{l} \nearrow O \\ \searrow O \end{array}$ (d) $C_6H_4(OH)NO_2$
13. Acetonitrile is:
- (a) C_2H_5CN (b) CH_3CN (c) CH_3COCN (d) $C_6H_5CH_2CN$
14. In alkyl cyanide alkyl group attached with
- (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

EXERCISE - II

Preparation of Nitrogen Containing Compounds:

1. Amides may be converted into amines by reaction named after
- (a) Perkin (b) Claisen (c) Hoffmann (d) Kolbe
2. Reaction $CH_3CONH_2 \xrightarrow{NaOBr}$ gives
- (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
- (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
- (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
- (a) Acetamide (b) Propionamide (c) Formamide (d) Methyl cyanide
7. Ethylamine can be obtained by the
- (a) Action of NH_3 on ethyl iodide (b) Action of NH_3 on ethyl alcohol
(c) Both (a) and (b) (d) None of the above
8. Aniline is usually purified by
- (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
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

$$R-\overset{\overset{O}{\parallel}}{C}-OH \xleftarrow{H_3O^+} X \xrightarrow{[H]} RCH_2NH_2; 'X' \text{ is}$$
 (a) Isonitrile (b) Nitrile (c) Nitrite (d) Oxime
19. When ethanol is mixed with ammonia and passed over alumina the compound formed is
(a) $C_2H_5NH_2$ (b) C_2H_4 (c) $C_2H_5OC_2H_5$ (d) CH_3OCH_3
20. Which of the following reactions does not yield an amine
(a) $RX + NH_3 \longrightarrow$ (b) $RCH = NOH + [H] \xrightarrow[C_2H_5OH]{Na}$
(c) $RCN + H_2O \xrightarrow{H^+}$ (d) $RCNH_2 + 4H \xrightarrow{LiAlH_4}$
21. Identify 'B' in the reaction
 Acetamide $\xrightarrow[\Delta]{P_2O_5} A \xrightarrow{4H} B$
 (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
 (a) $CH_3-CH_2-\overset{\overset{O}{\parallel}}{N} \rightarrow O$ (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
 (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
 (a) RNH_2 (b) R_2NH (c) R_3N (d) $R_4N^+Cl^-$
25. When aniline reacts with $NaNO_2$ and dil. HCl at $0^\circ - 5^\circ C$, the product formed is
 (a) Nitroaniline (b) Benzene diazonium chloride
 (c) Benzene (d) Trinitroaniline
26. Starting from propanoic acid, the following reactions were carried out

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

 What is the compound Z
 (a) $CH_3 - CH_2 - Br$ (b) $CH_3 - CH_2 - NH_2$
 (c) $CH_3 - CH_2 - C \begin{smallmatrix} O \\ \parallel \\ Br \end{smallmatrix}$ (d) $CH_3 - CH_2 - CH_2 - NH_2$
27. In the reaction

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

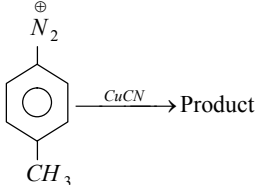
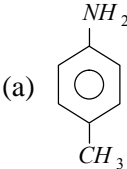
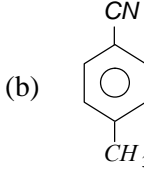
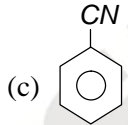
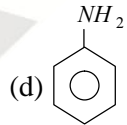
 the final product (C) is
 (a) Ammonium acetate (b) Acetamide (c) Amino methane (d) Ethanal
28. In the following reaction, X is

$$X \xrightarrow{\text{Bromination}} Y \xrightarrow{NaNO_2 + HCl} Z \xrightarrow[\text{C}_2\text{H}_5\text{OH}]{\text{Boiling}} \text{Tribromobenzene}$$

 (a) Benzoic acid (b) Salicylic acid (c) Phenol (d) Aniline
29. Which of the following reactions will not give primary amine
 (a) $CH_3CONH_2 \xrightarrow{KOH, Br_2}$ (b) $CH_3CN \xrightarrow{LiAlH_4}$
 (c) $CH_3NC \xrightarrow{LiAlH_4}$ (d) $CH_3CONH_2 \xrightarrow{LiAlH_4}$
30. Carbylamine reaction is given by
 (a) 1° amine (b) 3° amine (c) 2° amine (d) Quarternary salts
31. The reaction

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

 is known as
 (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?
 (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
 (a) Aniline (b) Phenol (c) Benzene (d) Nitrobenzene

34. Aromatic primary amine when treated with cold HNO_2 gives
 (a) Benzyl alcohol (b) Nitro benzene (c) Benzene (d) Diazonium salt
35. Which of the following compound is the strongest base
 (a) Ammonia (b) Aniline (c) Methylamine (d) *N*-methyl aniline
36. Nitrobenzene combines with hydrogen in the presence of platinum to produce
 (a) Toluene (b) Benzene (c) Aniline (d) Azobenzene
37. 
 The product is
 (a)  (b)  (c)  (d) 
38. Ethyl amine on heating with CS_2 in presence of HgCl_2 forms
 (a) $\text{C}_2\text{H}_5\text{NCS}$ (b) $(\text{C}_2\text{H}_5)_2\text{S}$ (c) $(\text{C}_2\text{H}_5)_2\text{CS}$ (d) $\text{C}_2\text{H}_5(\text{CS})_2$
39. Which of the following reacts with $\text{NaNO}_2 + \text{HCl}$ to give phenol
 (a) $\text{C}_6\text{H}_5\text{CH}_2\text{NHCH}_3$ (b) $(\text{CH}_3)_2\text{NH}$ (c) CH_3NH_2 (d) $\text{C}_6\text{H}_5\text{NH}_2$
40. Which of the following reactions give RCONH_2
 (a) $\text{R}-\text{C}\equiv\text{N} + \text{H}_2\text{O} \xrightarrow{\text{HCl}}$ (b) $\text{RCOONH}_4 \xrightarrow{\text{heat}}$
 (c) $\text{R}-\text{COCl} + \text{NH}_3 \longrightarrow$ (d) $(\text{RCO})_2\text{O} + \text{NH}_3 \longrightarrow$
41. When chlorobenzene is treated with NH_3 in presence of Cu_2O in xylene at 570 K. The product obtained is
 (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
 (a) Base (b) Acid (c) Catalyst (d) Reducing agent
43. The rate determining step for the preparation of nitrobenzene from benzene is
 (a) Removal of NO_2^+ (b) Removal of NO_3^+
 (c) Formation of NO_2^+ (d) Formation of NO_3^+
44. In this reaction
 $\text{C}_6\text{H}_5\text{NH}_2 + \text{HCl} + \text{NaNO}_2 \rightarrow \text{X}$. Product X is
 (a) Aniline hydrochloride (b) Nitro aniline
 (c) Benzenediazonium chloride (d) None of these

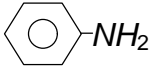
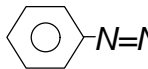

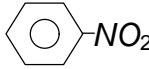
45. The diazonium salts are the reaction products in presence of excess of mineral acid with nitrous acid and
 (a) Primary aliphatic amine (b) Secondary aromatic amine
 (c) Primary aromatic amine (d) Tertiary aliphatic amine
46. In acid medium nitrobenzene is reduced to aniline as shown in the reaction
 $C_6H_5 - NO_2 + 6[H] \rightarrow C_6H_5 - NH_2 + 2H_2O$
 The reducing agent used in this reaction is
 (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 $0^\circ C$, it gives
 (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
 (a) $-NH_2$ (b) $-COOH$ (c) $-CHO$ (d) $(CH_3CO)_2O$
49. In the series of reaction $C_6H_5NH_2 \xrightarrow[0-5^\circ C]{NaNO_2/HCl} X \xrightarrow[CH_2O]{HNO_2} Y + N_2 + HCl$ X and Y are respectively
 (a) $C_6H_5 - N = N - C_6H_5$, $C_6H_5N_2^+Cl^-$ (b) $C_6H_5N_2^+Cl^-$, $C_6H_5 - N = N - C_6H_5$
 (c) $C_6H_5N_2^+Cl^-$, $C_6H_5NO_2$ (d) $C_6H_5NO_2$, C_6H_6
50. Aromatic nitriles ($ArCN$) are not prepared by reaction
 (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 :
 (a) Aniline (b) Salicylic acid (c) Benzaldehyde (d) Chlorobenzene
53. Gabriel's phthalimide synthesis is used for the preparation of
 (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
 (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
 (a) Ethyl alcohol (b) Ethyl bromide (c) Bromobenzene (d) Chlorobenzene

EXERCISE -III

Properties of Nitrogen Containing Compounds:

- Which of the following amine will not react with nitrous acid to give nitrogen
 (a) CH_3NH_2 (b) $\text{CH}_3 - \text{CH}_2 - \text{NH}_2$ (c) $\text{CH}_3 - \underset{\text{CH}_3}{\text{CH}} - \text{NH}_2$ (d) $(\text{CH}_3)_3\text{N}$
- Which of the following compound is expected to be most basic
 (a) Aniline (b) Methylamine (c) Hydroxylamine (d) Ethylamine
- Which of the following compounds is an amino acid
 (a) $\text{CH}_3 - \text{CH}_2 - \overset{\text{O}}{\parallel} \text{C} - \text{O} - \text{NH}_4$ (b) $\text{CH}_3 - \underset{\text{NH}_2}{\text{CH}} - \overset{\text{O}}{\parallel} \text{C} - \text{OH}$
 (c) $\text{CH}_3 - \text{CH}_2 - \overset{\text{O}}{\parallel} \text{C} - \text{NH}_2$ (d) $\text{CH}_3 - \underset{\text{NH}_2}{\text{CH}} - \overset{\text{O}}{\parallel} \text{C} - \text{Cl}$
- Nitro group in nitrobenzene is a
 (a) Ortho director (b) Meta director
 (c) Para director (d) Ortho and para director
- The alkyl cyanides are
 (a) Acidic (b) Basic (c) Neutral (d) Amphoteric
- 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
- Aniline when treated with HNO_2 and HCl at 0°C gives
 (a) Phenol (b) Nitrobenzene (c) A diazo compound (d) None of these
- Nitrosobenzene can be isolated from nitrobenzene under
 (a) Metal and acid (b) Zn dust and NH_4Cl
 (c) Alkaline sodium arsenite (d) Cannot be isolated
- Alkyl cyanides when react with Grignard reagent, the product on hydrolysis found, is
 (a) Aldehyde (b) Ketone (c) Alcohol (d) Acid
- The product formed when benzene is nitrated by fuming nitric acid is
 (a) *m*-dinitrobenzene (b) Nitrobenzene
 (c) *sym*-trinitrobenzene (d) None of these
- Ethyl amine undergoes oxidation in the presence of KMnO_4 to form
 (a) An acid (b) An alcohol (c) An aldehyde (d) A nitrogen oxide

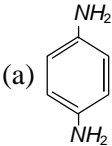
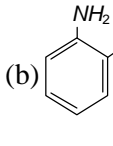
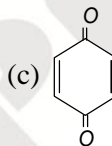
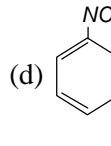
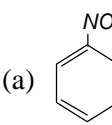
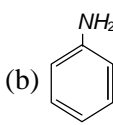
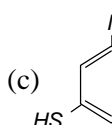
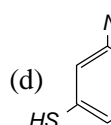
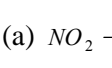
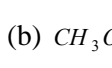
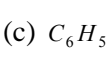
12. Which of the following amines would undergo diazotisation
(a) Primary aliphatic amines (b) Primary aromatic amines
(c) Both (a) and (b) (d) None of these
13. Reaction of primary amines with aldehyde yields
(a) Amides (b) Aldimines (c) Nitriles (d) Nitro compounds
14. When acetamide is treated with HNO_2 , the gas is evolved
(a) H_2 (b) O_2 (c) N_2 (d) CH_4
15. Nitrobenzene on nitration gives
(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
(a) Ammonia (b) Methylamine (c) Dimethylamine (d) Trimethylamine
19. Chloroform when treated with aniline and alcoholic KOH gives
(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
(a) Chloroform and alcoholic KOH (b) Methyl iodide
(c) Chloroform alone (d) Zinc dust
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
(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
 (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
 (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
 (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
 (a) Acetamide (b) Methane (c) $CO_2 + H_2O$ (d) Acetic acid

40. Hofmann's hypobromite reaction affords a method of
 (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
 (a) Diethylamine (b) Ethylamine (c) Aniline (d) Methylamine
42. Identify the product Z in the series
 $CH_3CN \xrightarrow{Na+C_2H_5OH} X \xrightarrow{HNO_2} Y \xrightarrow[H_2SO_4]{K_2Cr_2O_7} Z$
 (a) CH_3CHO (b) CH_3CONH_2 (c) CH_3COOH (d) CH_3CH_2NHOH
43. The end product of the reactions is
 $C_2H_5NH_2 \xrightarrow{HNO_2} A \xrightarrow{PCl_5} B \xrightarrow{H.NH_2} C$
 (a) Ethyl cyanide (b) Ethyl amine (c) Methyl amine (d) Acetamide
44. Primary and secondary amines are distinguished by
 (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
 (a) Nitroparaffin (b) Alkyl cyanide (c) Oxime (d) Alkyl isocyanide
46. Methyl amine reacts with HNO_2 giving
 (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
 (a) Aniline (b) Nitrosobenzene
 (c) Hydrazobenzene (d) Phenylhydroxyl amine
48. The decreasing order of the basic character of the three amines and ammonia is
 (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
 (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
 (a) Phenol (b) Aniline (c) Nitrobenzene (d) Benzene
51. Aniline on treatment with excess of bromine water gives
 (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
(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
(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
(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
(a) *o*- and *p*-nitroanilines (b) *m*-nitroanilines
(c) A black tarry matter (d) No reaction
56. Which statement is not correct
(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
(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
(a) Methyl amine (b) Dimethyl amine (c) Trimethyl amine (d) Aniline
61. Reaction of nitrous acid with aliphatic primary amine in the cold gives
(a) A diazonium salt (b) An alcohol (c) A nitrite (d) A dye
62. In presence of acid, hydrolysis of methyl cyanide gives
(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
(a) CH_3NH_2 (b) $(\text{CH}_3)_2\text{NH}$ (c) $(\text{CH}_3)_3\text{N}$ (d) None of these
64. The fusion of sodium with amine gives mainly
(a) NaCN (b) NaN_3 (c) NaSCN (d) NaNO_2
65. Which of the following is most basic
(a) $\text{C}_6\text{H}_5\text{NH}_2$ (b) $(\text{CH}_3)_2\text{NH}$ (c) $(\text{CH}_3)_3\text{N}$ (d) NH_3

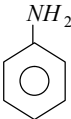
66. In reaction

$$CH_3CN + 2H \xrightarrow[\text{Ether}]{HCl} X \xrightarrow{\text{Boiling } H_2O} Y$$
; the term Y is
 (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
 (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
 (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) $C_6H_5N=\overset{O}{\underset{\uparrow}{N}}-C_6H_5$
70. Aniline when treated with conc. HNO_3 gives
 (a)  (b)  (c)  (d) 
71. Which one of the following is not a base
 (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
 (a) Carbocation (b) Carbanion (c) Benzyne (d) Dianion
73. If methyl is alkyl group, then which order of basicity is correct
 (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
 (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
 (a)  (b)  (c)  (d) 
76. Which one is less alkaline
 (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
 (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
 (a) Alkali (b) Nitrous acid (c) Reducing agent (d) Oxidising agent
79. Arrange the following in increasing order of basicity $CH_3NH_2, (CH_3)_2NH, C_6H_5NH_2, (CH_3)_3N$
 (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

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

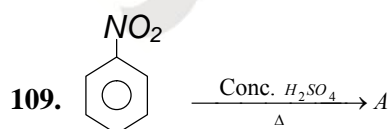
 The compound B is
 (a) Acetic acid (b) Acetone (c) Acetaldehyde (d) Ethyl alcohol
81. CH_3CN is known as acetonitrile because
 (a) It contains an aceto group (b) On hydrolysis it gives acetic acid
 (c) Both (a) and (b) (d) None of these
82. What is formed, when nitrobenzene is reduced using zinc and alkali
 (a) Phenol (b) Aniline (c) Nitrosobenzene (d) Hydrazobenzene
83. $RCOCl + 2Me_2NH \rightarrow A + Me_2NH_2Cl^-$
 Here A is
 (a) $RCON \begin{matrix} \swarrow Me \\ \searrow Me \end{matrix}$ (b) $RCONH_2$ (c) $RCONHMe$ (d) $(RCO)_2NH$
84. Decreasing order of basicity is
 (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
 (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
 (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
 (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
 (a) Hot water (b) dil. HCl (c) dil. $NaOH$ (d) Alcohol
89. Nitrobenzene on further excessive nitration gives
 (a) Trinitrobenzene (b) *m*-dinitrobenzene (c) *p*-dinitrobenzene (d) All of these
90. The compound A with following sequence of reaction gave benzoic acid
 $A \xrightarrow{NaNO_2 / HCl} B \xrightarrow{KCN} C \xrightarrow{H_3O^+} \text{benzoic acid}$. The compound A is
 (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
 (a) (i) and (iii) (b) (iii) and (iv) (c) (i) and (ii) (d) (ii) and (iv)
92. An isocyanide on hydrolysis gives
 (a) An amide (b) A carboxylic acid and ammonia
 (c) A N-substituted amide (d) A 1°-amine and formic acid
93. Methyl isocyanide on hydrolysis gives
 (a) CH_3NH_2 (b) $HCOOH$ (c) CH_3COOH (d) Both (a) and (b)
94. Pure aniline is a
 (a) Colourless solid (b) Brown coloured solid
 (c) Colourless liquid (d) Brown coloured liquid
95. Reduction of methyl isocyanide gives
 (a) Ethylamine (b) Methylamine
 (c) Dimethylamine (d) Trimethylamine
96. Reaction of aniline with benzaldehyde is
 (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 $C_6H_5N = HCC_6H_5$ is known as
 (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
 (a) Isocyanide centre (b) Amido centre
 (c) Cationic centre (d) Nucleophilic centre
99. Electrophilic substitution of  with bromine gives
 (a) 1, 4, 6-tribromo aniline (b) 2, 4, 6-tribromo aniline
 (c) 4-bromo aniline (d) 3-bromo aniline

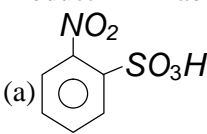
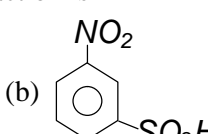
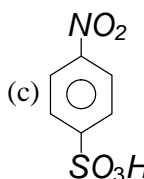
100. Mustard gas is obtained by
 (a) The action of dilute acids on mustard seeds
 (b) Treating ethylene with mustard oil
 (c) Treating sulphur chloride with ethylene
 (d) None of these
101. Which of the following is capable of forming a zwitter ion
 (a) C_6H_5-OH (b) $C_6H_4(NH_2)_2$ (c) $\begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array}$ (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

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

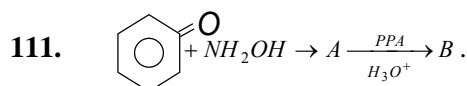
 (a) H_2-Ni (b) $NaBH_4$ (c) $LiAlH_4$ (d) Na -alcohol
103. During acetylation of amines what is replaced by acetyl groups
 (a) Hydrogen atom attached to nitrogen atom
 (b) One or more hydrogen atoms attached to carbon atom
 (c) One or more hydrogen atoms attached to nitrogen atom
 (d) Hydrogen atoms attached to either carbon atom or nitrogen atom
104. Hydrolysis of acetonitrile in acidic medium produces
 (a) CH_3CH_2OH (b) CH_3COOH (c) CH_3NC (d) CH_3COOCH_3
105. Which has a pyramidal structure
 (a) Trimethylamine (b) Methanol (c) Acetylene (d) Water
106. Ethyl amine on acetylation gives
 (a) N-ethyl acetamide (b) Acetamide (c) Methyl acetamide (d) None
107. The refluxing of $(CH_3)_2NCOCH_3$ with acid gives
 (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
 (a) Sandmeyer reaction (b) Carbyl amine reaction
 (c) Hinsberg's reaction (d) $AgNO_3$



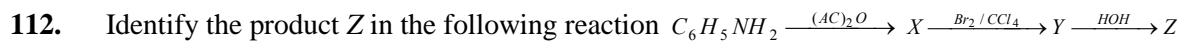
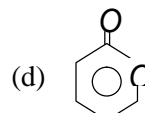
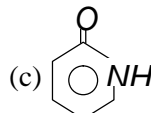
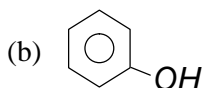
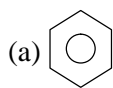
Product 'A' in above reaction is

- (a)  (b)  (c)  (d) None of these

110. Product obtained by electrolytic reduction of nitrobenzene in presence of H_2SO_4 is
 (a) *o*-amino phenol (b) *m*-amino phenol (c) *p*-amino phenol (d) None of these



The product 'B' is



(a) *p*-Bromoaniline

(b) *p*-Bromoacetophenone

(c) *o*-Bromoacetophenone

(d) *o*-Bromoacetanilide

113. Benzaldehyde condenses with *N,N*-dimethylaniline in presence of anhydrous ZnCl_2 to give

(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

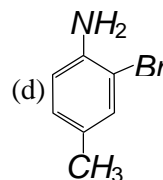
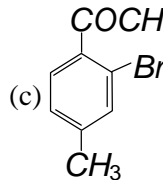
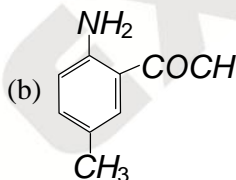
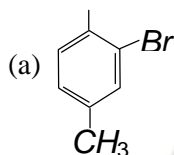
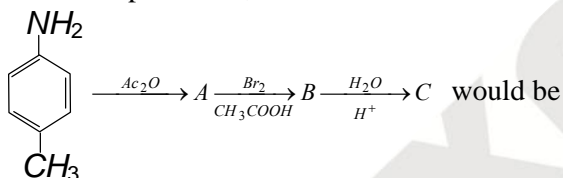
(a) $\text{I} > \text{II} > \text{III}$

(b) $\text{III} > \text{II} > \text{I}$

(c) $\text{II} > \text{III} > \text{I}$

(d) $\text{I} < \text{II} > \text{III}$

115. The final product C, obtained in this reaction



116. The correct order of increasing basic nature for the bases NH_3 , CH_3NH_2 and $(\text{CH}_3)_2\text{NH}$ is

(a) $\text{CH}_3\text{NH}_2 < \text{NH}_3 < (\text{CH}_3)_2\text{NH}$

(b) $(\text{CH}_3)_2\text{NH} < \text{NH}_3 < \text{CH}_3\text{NH}_2$

(c) $\text{NH}_3 < \text{CH}_3\text{NH}_2 < (\text{CH}_3)_2\text{NH}$

(d) $\text{CH}_3\text{NH}_2 < (\text{CH}_3)_2\text{NH} < \text{NH}_3$

117. Nitrobenzene gives *N*-phenylhydroxylamine by

(a) Sn/HCl

(b) $\text{H}_2/\text{Pd}-\text{C}$

(c) Zn/NaOH

(d) $\text{Zn}/\text{NH}_4\text{Cl}$

118. Among the following the weakest base is

(a) $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$

(b) $\text{C}_6\text{H}_5\text{CH}_2\text{NHCH}_3$

(c) $\text{O}_2\text{NCH}_2\text{NH}_2$

(d) CH_3NHCHO

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

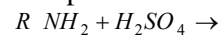
(a) $(\text{CH}_3)_2\text{NH} > (\text{CH}_3)_3\text{N} > \text{CH}_3\text{NH}_2$

(b) $\text{CH}_3\text{NH}_2 > (\text{CH}_3)_2\text{NH} > (\text{CH}_3)_3\text{N}$

(c) $(\text{CH}_3)_3\text{N} > (\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2$

(d) $(\text{CH}_3)_3\text{N} > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_2\text{NH}$

120. Complete the following reaction :

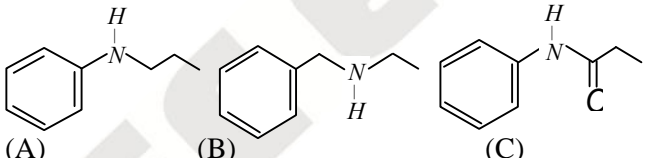
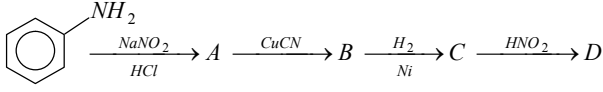


(a) $[\text{R-NH}_3]^+ \text{HSO}_4^-$

(b) $[\text{R-NH}_3]_2^+ \text{SO}_4^{2-}$

(c) $\text{R-NH}_2 \cdot \text{H}_2\text{SO}_4$

(d) No reaction

121. Which of the following compound reacts with chloroform and a base to form phenyl isocyanide ?
 (a) Phenol (b) Aniline (c) Benzene (d) Nitro benzene
122. Which one doesn't liberate NH_3 when undergoes hydrolysis
 (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
 (a) Aniline (b) Benzamide
 (c) Acetamide (d) Nitrobenzene
124. Benzamide on reaction with $POCl_3$ gives
 (a) Aniline (b) Chlorobenzene (c) Benzyl amine (d) Benzonitrile
125. Among the following which one does not act as an intermediate in Hofmann rearrangement
 (a) $RNCO$ (b) $RCO \ddot{N}$ (c) $RCO \ddot{N} HBr$ (d) RNC
126. Aniline reacts with which of these to form Schiff base
 (a) Acetic acid (b) Benzaldehyde (c) Acetone (d) NH_3
127. Which of the following does not reduce Tollen's reagent
 (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 ?

 (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
 (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
 (a) $C_6H_5CH_2NH_2$ (b) $C_6H_5NHCH_2CH_3$ (c) C_6H_5NHOH (d) $C_6H_5CH_2OH$
131. Electrolytic reduction of nitrobenzene in weakly acidic medium gives
 (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 :
 (a) Diazonium chloride (b) *o*-nitro aniline
 (c) Benzoic acid (d) Chlorobenzene
135. $C_6H_5NH_2 \xrightarrow{NaNO_2/HCl} X \xrightarrow{Cu_2(CN)_2} Y \xrightarrow{H_2O/H^+} Z$
 Z is identified as :
 (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:
 (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
 (a) A Schiff's base (b) An enamine (c) An imine (d) An amine
139. $R - NH - COH \xrightarrow[\text{pyridine}]{POCl_3} \text{product}$
 In the given reaction what will be the product
 (a) $R - N = C = O$ (b) $R - \overset{+}{N} \equiv C^-$ (c) $R - C \equiv N$ (d) None of these.
140. Which of the following is secondary pollutant.
 (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) In spite of substituents nitro group always goes to *m*- position
 (c) In strong acidic medium, nitration of aniline is a nucleophilic 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



- (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) $(CH_3)_3N$
 (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)

EXERCISE - IV

Tests for Nitrogen Containing Compounds:

- When acetamide reacts with Br_2 and caustic soda, then we get
 (a) Acetic acid (b) Bromoacetic acid (c) Methyl amine (d) Ethane
- In organic compounds, nitrogen is tested in Lassaigne's test as
 (a) $NaNH_2$ (b) $NaCN$ (c) $NaNO_2$ (d) $NaNO_3$
- Liebermann's nitroso reaction is used for testing
 (a) Primary amines (b) Secondary amines
 (c) Tertiary amines (d) All the above
- A nauseating smell in the carbylamine test for primary amines is due to the formation of
 (a) Isocyanide (b) Chloroform (c) Cyanide (d) DDT
- A positive carbylamine test is given by
 (a) *N, N*-dimethylaniline (b) 2, 4-dimethylaniline
 (c) *N*-methyl-*o*-methylaniline (d) *p*-methylbenzylamine
- The colour of *p*-amino azobenzene is
 (a) Orange (b) Congo red (c) Bismark brown (d) Indigo
- When primary amine is heated with CS_2 in presence of excess mercuric chloride, it gives isothiocyanate. This reaction is called
 (a) Hofmann bromide reaction (b) Hofmann mustard oil reaction
 (c) Carbylamine reaction (d) Perkin reaction
- Diazo-coupling is useful to prepare some
 (a) Dyes (b) Proteins (c) Pesticides (d) Vitamins

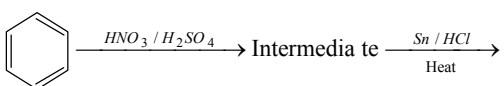
9. Carbylamine test is used in the detection of
 (a) Aliphatic 2° amine (b) Aromatic 1° amine
 (c) Aliphatic 1° amine (d) Both aliphatic and aromatic 1° amines
10. Which of the following substance does not give iodoform test
 (a) C_6H_5CN (b) RNH_2 (c) CH_3OH (d) All
11. Which one of the following compounds when heated with KOH and a primary amine gives carbylamine test
 (a) $CHCl_3$ (b) CH_3Cl (c) CH_3OH (d) CH_3CN

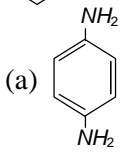
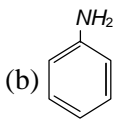
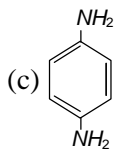
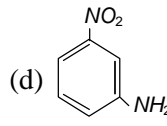
EXERCISE - V

Objective Questions:

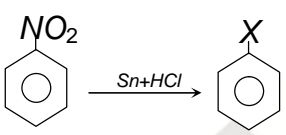
1. The compound

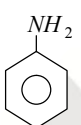
$$\begin{array}{c} R_1 \\ \diagdown \\ N-R_3 \\ \diagup \\ R_2 \end{array}$$
 forms nitroso amines when the substituents are
 (a) $R_1 = CH_3, R_2 = R_3 = H$ (b) $R_1 = R_2 = H, R_3 = C_2H_5$
 (c) $R_1 = H, R_2 = R_3 = CH_3$ (d) $R_1 = CH_3, R_2 = C_2H_5, R_3 = H$
2. The action of nitrous acid on ethyl amine gives
 (a) Ethane (b) Ammonia (c) Ethyl alcohol (d) Nitroethane
3. Aniline when diazotized in cold and then treated with dimethyl aniline gives a coloured product. Its structure would be
 (a) $(CH_3)_2N - \text{C}_6\text{H}_4 - N=N - \text{C}_6\text{H}_5$
 (b) $(CH_3)_2N - \text{C}_6\text{H}_4 - NH - \text{C}_6\text{H}_5$
 (c) $CH_3NH - \text{C}_6\text{H}_4 - N=N - \text{C}_6\text{H}_4NHCH_3$
 (d) $CH_3 - \text{C}_6\text{H}_4 - N=N - \text{C}_6\text{H}_4NH_2$
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 ($R-NH_2$)
 (a) $R - \overset{\overset{O}{\parallel}}{C} - NH \cdot CH_3$ (b) $R - \overset{\overset{O}{\parallel}}{C} - O \cdot NH_4$ (c) $R - \overset{\overset{O}{\parallel}}{C} - NH_2$ (d) $R - \overset{\overset{O}{\parallel}}{C} - NHOH$

5. 

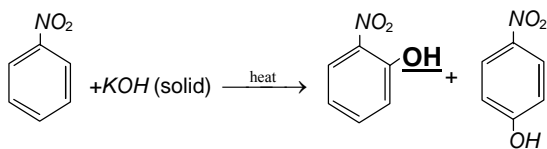
 (a)  (b)  (c)  (d) 
6. The correct order of basicities of the following compounds is

$$\begin{array}{ccc} \text{CH}_3 - \text{C} \begin{array}{l} \nearrow \text{NH} \\ \searrow \text{NH}_2 \end{array} & \text{CH}_3 - \text{CH}_2 - \text{NH}_2 & (\text{CH}_3)_2\text{NH} \\ 1 & 2 & 3 \end{array}$$

$$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3 - \text{C} - \text{NH}_2 \\ 4 \end{array}$$
 (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
 (a) Benzene (b) Nitro benzene (c) Toluene (d) Chloro benzene
8. Aniline reacts with acetaldehyde to form
 (a) Schiff's base (b) Carbylamine (c) Imine (d) None of these
9. *p*-chloroaniline and anilinium hydrochloride can be distinguished by
 (a) Sandmeyer reaction (b) NaHCO_3 (c) AgNO_3 (d) Carbylamine test
10. 

 In the above reaction 'X' stands for
 (a) NH_2 (b) SnCl_2 (c) Cl (d) NH_4^+Cl^-
11.  + $\text{CHCl}_3 + \text{KOH} \rightarrow ?$
 (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
 (a) $\text{CH}_3\text{NH}_2 > (\text{CH}_3)_3\text{N} > (\text{CH}_3)_2\text{NH}$ (b) $(\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_3\text{N}$
 (c) $\text{CH}_3\text{NH}_2 > (\text{CH}_3)_2\text{NH} > (\text{CH}_3)_3\text{N}$ (d) $(\text{CH}_3)_3\text{N} > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_2\text{NH}$
13. The refluxing of $(\text{CH}_3)_2\text{NCOCH}_3$ with acid gives
 (a) $2\text{CH}_3\text{NH}_2 + \text{CH}_3\text{COOH}$ (b) $2\text{CH}_3\text{OH} + \text{CH}_3\text{COOH}$
 (c) $(\text{CH}_3)_2\text{NH} + \text{CH}_3\text{COOH}$ (d) $(\text{CH}_3)_2\text{NCOOH} + \text{CH}_4$
14. Order of basicity of ethyl amines is
 (a) Secondary > Primary > Tertiary (b) Primary > Secondary > Tertiary
 (c) Secondary > Tertiary > Primary (d) Tertiary > Primary > Secondary

15. The following reaction is



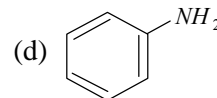
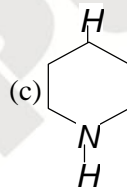
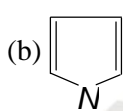
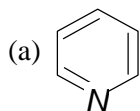
- (a) Nucleophilic substitution
(b) Electrophilic substitution
(c) Free radical substitution
(d) None of these
16. RNH_2 reacts with $C_6H_5SO_2Cl$ in aqueous KOH to give a clear solution. On acidification a precipitate is obtained which is due to the formation of

- (a) $R-\overset{\overset{H}{|}}{N^+}-SO_2C_6H_5OH^-$ (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

- (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



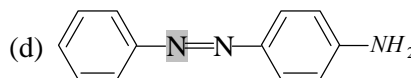
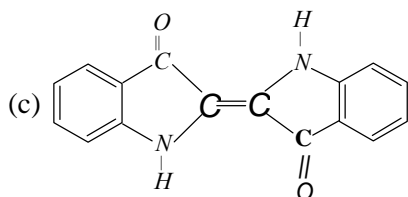
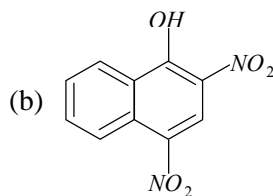
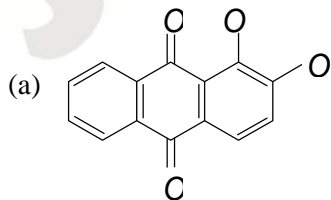
19. Nitroso amines ($R_2N-N=O$) are soluble in water. On heating them with concentrated H_2SO_4 they give secondary amines. The reaction is called

- (a) Perkin's reaction (b) Fittig's reaction
(c) Sandmeyer's reaction (d) Liebermann's nitroso reaction

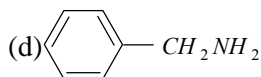
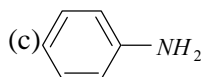
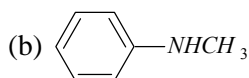
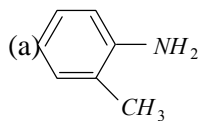
20. A primary amine is formed an amide by the treatment of bromine and alkali. The primary amine has :

- (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

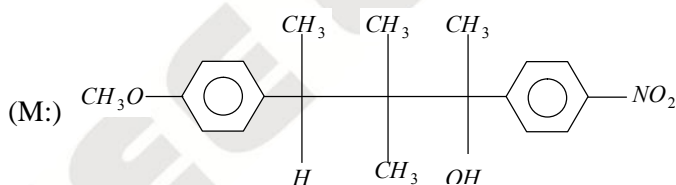
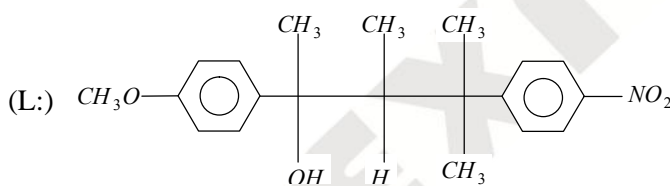
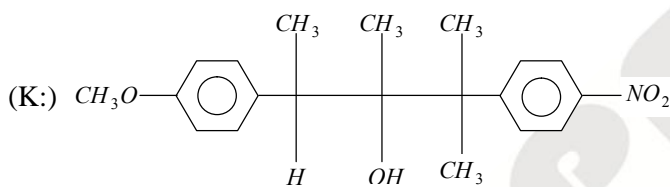
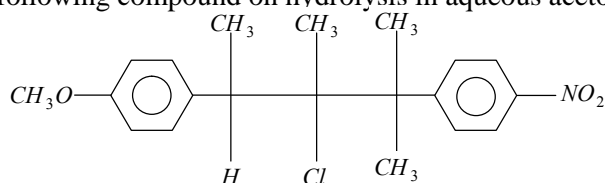
21. The structural formula of Indigo dye is :



22. Which of the following is the strongest base ?



23. The following compound on hydrolysis in aqueous acetone will give



(a) Mixture of (K) and (L)

(b) Mixture of (K) and (M)

(c) Only (M)

(d) Only (K)

EXERCISE - VI

Assertion & Reason:

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 loses takes place during heating
2. Assertion : Amines are basic in nature.
Reason : Presence of lone pair of electron on nitrogen atom.
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 out 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 phthalimide synthesis can be used.
Reason : With proper choice of alkyl halides, phthalimide 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.
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.
20. Assertion : $p-O_2N-C_6H_5COCH_3$ is prepared by Friedel Crafts acylation of nitrobenzene.
Reason : Nitrobenzene easily undergoes electrophilic substitution reaction.
21. Assertion : Alkyl isocyanides in acidified water give alkyl formamides.
Reason : In isocyanides, carbon first acts as a nucleophile and then as an electrophile.

Self Evaluation Test

- Melting points are normally the highest for
(a) Tertiary amides (b) Secondary amides
(c) Primary amides (d) Amines
- Amines behave as
(a) Lewis acids (b) Lewis bases
(c) Aprotic acids (d) Amphoteric compounds
- Which of the following compound gives dye test
(a) Aniline (b) Methylamine (c) Diphenylamine (d) Ethylamine
- In hydrolysis of aniline, the reagent used is [AFMC 1995]
(a) Dil. HCl (b) Acetyl chloride (c) CH_3OH (d) None of these
- A nitrogen containing organic compound on heating with chloroform and alcoholic KOH , evolved very unpleasant smelling vapour. The compound could be
(a) N, N -dimethyl amine (b) Nitrobenzene
(c) Aniline (d) Benzamide
- The reaction between a primary amine, chloroform and few drops of alcoholic KOH is known as
(a) Cannizzaro reaction (b) Carbylamine reaction
(c) Wurtz's reaction (d) Reimer-Tiemann reaction
- Nitrolim is
(a) $CaC_2 + N_2$ (b) $CaCN_2 + C$
(c) $Ca(CN)_2 + C$ (d) $Ca(CN)_2 + NH_4CN$
- Phenyl isocyanides are prepared from which of the following reactions
(a) Rosenmund's reaction (b) Carbylamine reaction
(c) Reimer-Tiemann reaction (d) Wurtz reaction
- On strong heating, ammonium acetate gives [MNR 1995]
(a) Acetamide (b) Methyl cyanide
(c) Urea (d) Formamide
- Aniline is separated from a mixture by
(a) Fractional crystallization (b) Fractional distillation
(c) Vacuum distillation (d) Steam distillation

11. Molecular formula of chloropicrin is
(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
(a) sp (b) sp^2 (c) sp^3 (d) sp^2d
13. Foul smelling compound formed, during carbyl amine reaction is :
(a) Alcohol (b) Aldehyde
(c) Alkyl isocyanide (d) Carboxylic acid
14. The end product of the reaction
ethyl amine $\xrightarrow{\text{HNO}_2} A \xrightarrow{\text{PCl}_5} B \xrightarrow{\text{KCN}} C$ is
(a) Ethyl amine (b) Diethyl amine
(c) Propane nitrite (d) Triethyl amine

ANSWER KEY

EXERCISE - I

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

EXERCISE - II

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

EXERCISE - III

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				

EXERCISE -IV

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								

EXERCISE -V

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				

EXERCISE - VI

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								

SOLUTION

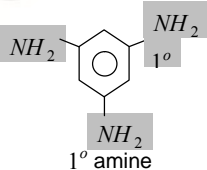
EXERCISE - I

Introduction of Nitrogen Containing Compounds

4. (d) C_3H_9N can form all the 3 amines.
 $CH_3CH_2CH_2-NH_2$, $CH_3-CH_2-NH-CH_3$
 $\quad \quad \quad 1^\circ \text{ amine} \quad \quad \quad 2^\circ \text{ amine}$
 $CH_3-\overset{\overset{CH_3}{|}}{N}-CH_3$
 $\quad \quad \quad 3^\circ \text{ amine}$

5. (c) $(CH_3)_2C=O + H_3C-COCH_3 + NH_3$
 $\quad \quad \quad \downarrow$
 $(CH_3)_2C-NH-CH_2-COCH_3$
 $\quad \quad \quad |$
 $\quad \quad \quad NH_2$
 $\quad \quad \quad \text{diacetone amine}$

8. (d) Allyl isocyanide. $CH_2=CH-CH_2-N \equiv C$

9. (c) 

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....

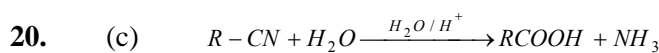
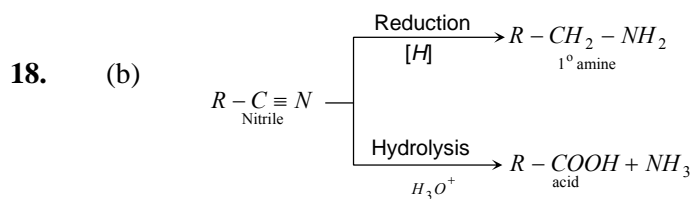
15. (b) Four 1° amines are possible
 $CH_3CH_2CH_2CH_2NH_2$, $(CH_3)_2CHCH_2NH_2$,
 $CH_3CH(NH_2)CH_2CH_3$, $(CH_3)_3CNH_2$

EXERCISE -II

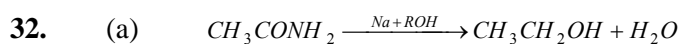
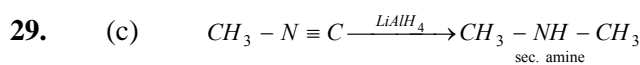
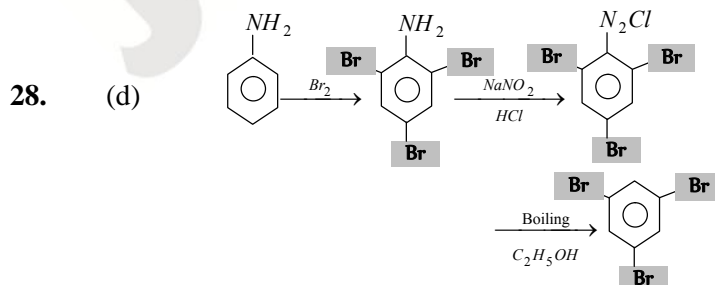
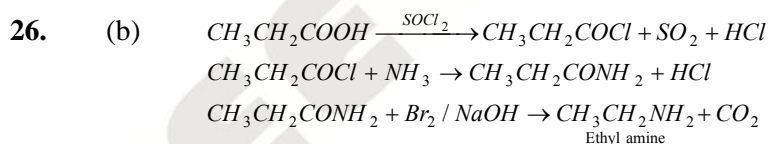
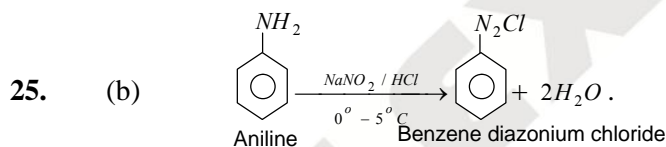
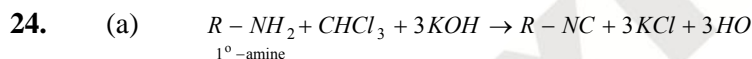
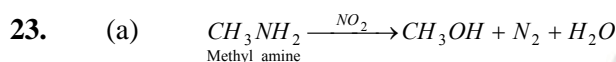
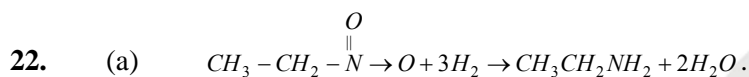
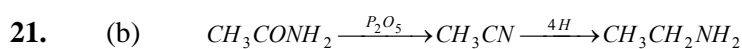
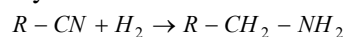
Preparation of Nitrogen Containing Compounds

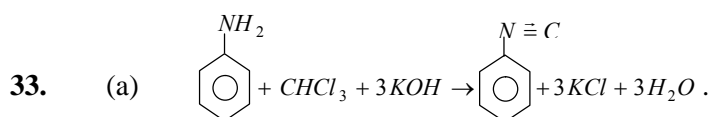
1. (c) Hofmann's bromamide reaction

$$\underset{\text{Acetamide}}{\text{CH}_3 - \text{CO} - \text{NH}_2} + \text{Br}_2 + 4\text{KOH} \xrightarrow{\text{H}_2\text{O}} \underset{\text{Methyl amine}}{\text{CH}_3\text{NH}_2} + \text{K}_2\text{CO}_3 + 2\text{KBr} + 2\text{H}_2\text{O}$$
2. (d) $\text{CH}_3\text{CONH}_2 \xrightarrow{\text{NaOBr}} \text{CH}_3\text{NH}_2$
3. (b) $\underset{\text{Acetamide}}{\text{CH}_3\text{CONH}_2} + \text{Br}_2 + 4\text{NaOH} \rightarrow \underset{\text{Methyl amine}}{\text{CH}_3\text{NH}_2} + \text{Na}_2\text{CO}_3 + 2\text{NaBr} + 2\text{H}_2\text{O}$
4. (b) $\underset{(2c)}{\text{CH}_3 - \text{CO} - \text{NH}_2} \xrightarrow[\text{Hofmann's bromamide}]{\text{NaOH} / \text{Br}_2} \underset{(1c)}{\text{CH}_3 - \text{NH}_2}$
5. (b) $\text{CH}_3\text{C} \equiv \text{N} + 4[\text{H}] \xrightarrow[\text{Reduction}]{\text{Na} + \text{C}_2\text{H}_5\text{OH}} \text{CH}_3\text{CH}_2\text{NH}_2$
6. (b) $\underset{\text{Propionamide}}{\text{CH}_3 - \text{CH}_2 - \text{CO} - \text{NH}_2} + \text{Br}_2 + 4\text{KOH} \rightarrow \text{CH}_3\text{CH}_2\text{NH}_2 + \text{K}_2\text{CO}_3 + 2\text{KBr} + 2\text{H}_2\text{O}$
7. (c) $\text{C}_2\text{H}_5\text{I} + \text{NH}_3 \rightarrow \text{HI} + \text{C}_2\text{H}_5 - \text{NH}_2$
 $\text{C}_2\text{H}_5\text{OH} + \text{NH}_3 \rightarrow \text{H}_2\text{O} + \text{C}_2\text{H}_5 - \text{NH}_2$
9. (c) $\underset{\text{Nitro ethane}}{\text{CH}_3 - \text{CH}_2 - \text{NO}_2} + 6[\text{H}] \xrightarrow{\text{Sn} / \text{HCl}} \underset{\text{Ethyl amine}}{\text{CH}_3 - \text{CH}_2 - \text{NH}_2} + 2\text{H}_2\text{O}$
11. (d) $\text{CH}_3\text{I} \xrightarrow[\Delta]{\text{NH}_3} \underset{\text{Methyl amine}}{\text{CH}_3\text{NH}_2} \xrightarrow{\text{CH}_3\text{I}} \underset{\text{Dimethyl amine}}{(\text{CH}_3)_2\text{NH}} \xrightarrow{\text{CH}_3\text{I}} \underset{\text{Trimethyl amine}}{(\text{CH}_3)_3\text{N}}$
12. (d) $\text{Aniline} + \text{Acetic anhydride} \rightarrow \text{Acetanilide} + \text{CH}_3\text{COOH}$
16. (c) $\text{CH}_3 - \text{N} \equiv \text{C} + 4[\text{H}] \xrightarrow{\text{Reduction}} \underset{2^\circ \text{ amine}}{\text{CH}_3 - \text{NH} - \text{CH}_3}$
17. (a) $\text{CH}_3\text{NO}_2 + 3\text{Cl}_2 + 3\text{NaOH} \rightarrow \underset{\text{Nitromethane}}{\text{CH}_3\text{NO}_2} + 3\text{NaCl} + 3\text{H}_2\text{O}$
 $\underset{\text{(chloropicrin)}}{\text{CCl}_3 - \text{NO}_2} + 3\text{NaOH} \rightarrow 3\text{NaCl} + 3\text{H}_2\text{O}$

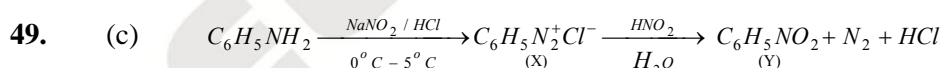
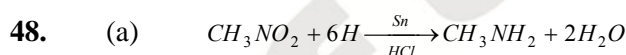
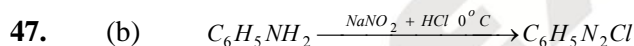
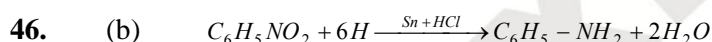
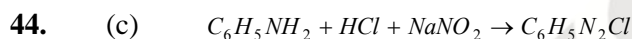
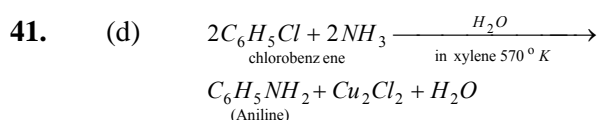
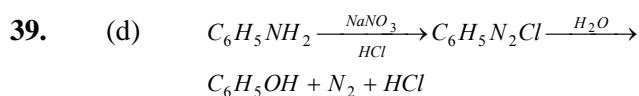
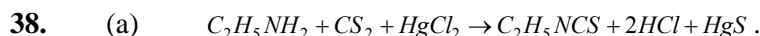
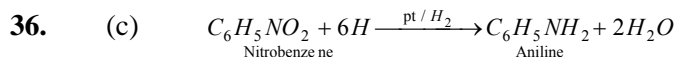


It yields amine when reduced as –





35. (c) Methyl amine is the strongest base.



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

$$ArN_2^+ + CuCN \rightarrow ArCN + N_2 + Cu^+$$

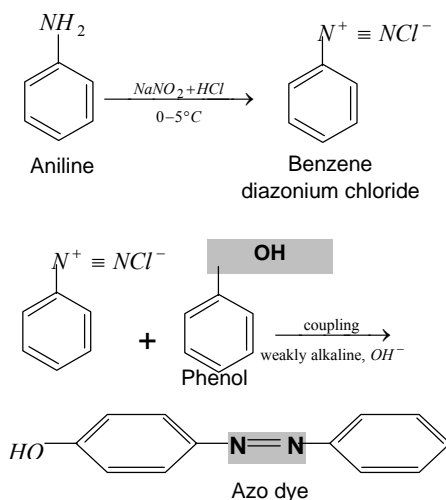
$$ArCONH_2 \xrightarrow[-H_2O]{P_2O_5} ArCN$$

$$ArCONH_2 + SOCl_2 \rightarrow ArCN + SO_2 + 2HCl$$

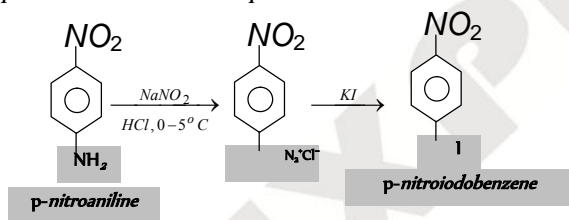
51. (c) Secondary amines gives oily nitrosamine with nitrous acid.

$$(CH_3CH_2)_2NH + HONO \rightarrow \underset{\text{oily}}{(CH_3CH_2)_2N.NO} + H_2O$$

52. (a) When aniline is treated with HNO_2 at $0-5^\circ C$ then diazonium salt is formed and by the coupling of diazonium salt and phenol azo dyes are prepared.



54. (a) *p*-nitrobenzene from *p*-nitroaniline.



55. (b) $C_2H_5Br + KCN \xrightarrow{\text{alcohol}} C_2H_5CN + KBr$

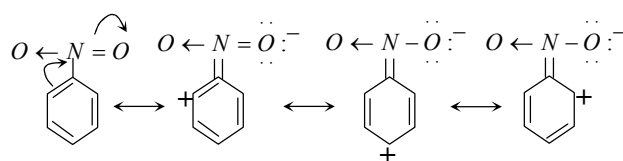
EXERCISE -III

Properties of Nitrogen Containing Compounds

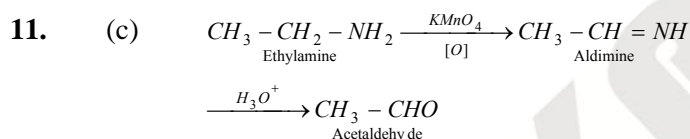
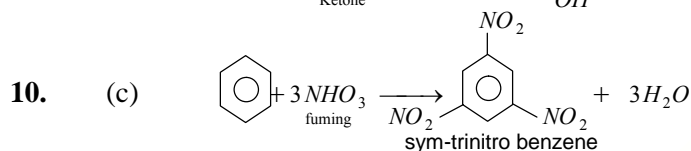
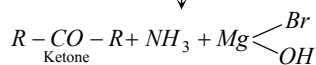
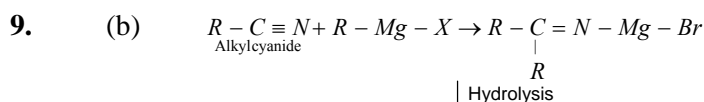
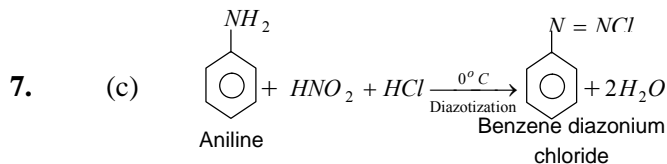
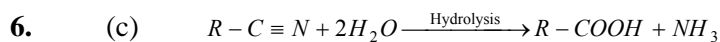
- (d) Tertiary amine does not react with nitrous acid because in it α -H atom is absent.
- (d) Due to +ve I.E. of alkyl group, *N*-atom of amines acquires partial -ve charge and thus electron pair is easily donated.
- (b) $CH_3 - \underset{\substack{| \\ NH_2}}{CH} - COOH$

The compounds in which both amino ($-NH_2$) as well as acidic ($-COOH$) group is present is called amino acid.

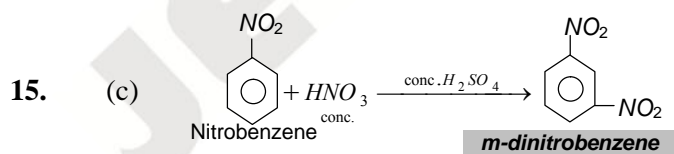
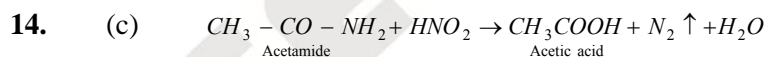
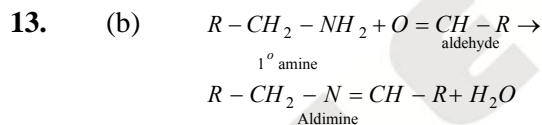
4. (b)



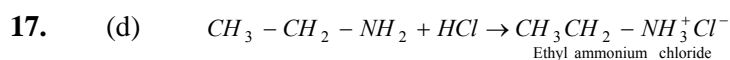
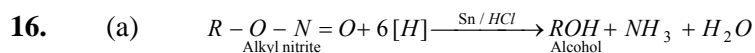
Presence of $-NO_2$ group decreases electron density at o - and p - positions. Hence, incoming electrophile goes to m position. Therefore it is m -directing group.



12. (b) Only primary aromatic amines can undergo diazotisation.

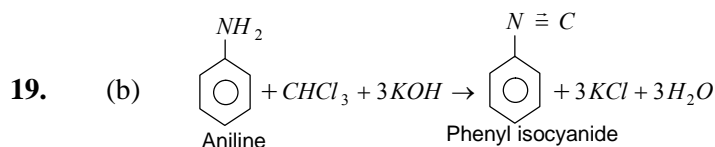


$-NO_2$ group is meta directing group.



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

18. (a) $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > \overset{\cdot\cdot}{N}H_3$
 2° amine is most basic 1° amine 3° amine Ammonia is least basic



20. (c) Because in tertiary nitroalkanes α -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.

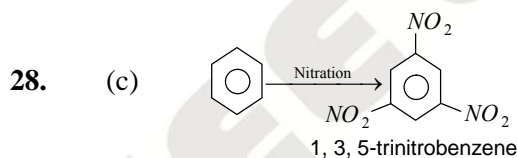
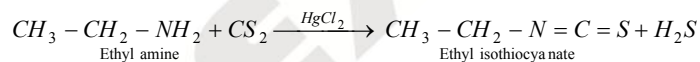
22. (d) Friedel-Craft's reaction is used for the preparation of alkyl benzene or acetophenone. It is not a method to prepare amine.



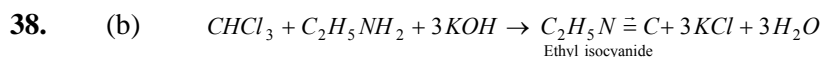
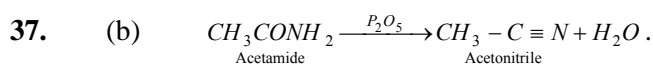
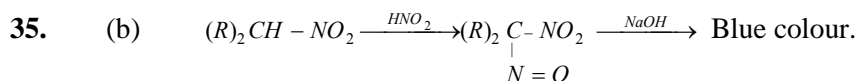
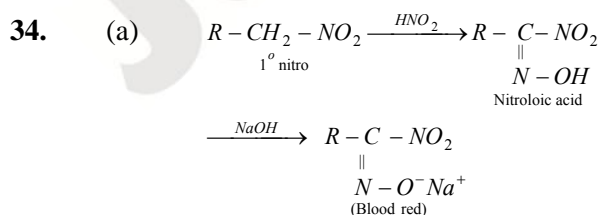
This litmus paper test shows basic nature of amine.

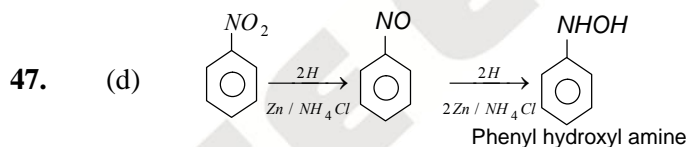
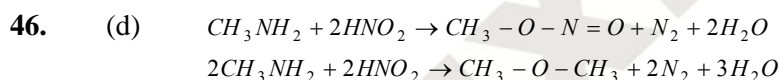
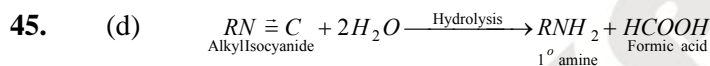
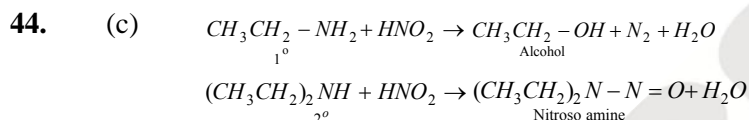
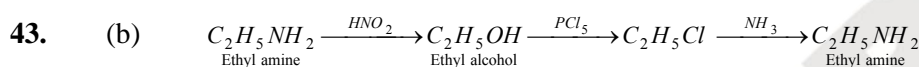
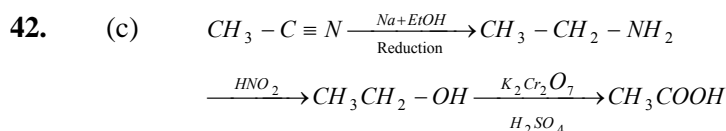
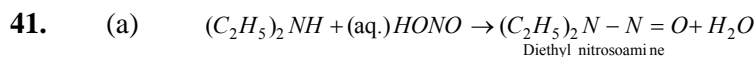
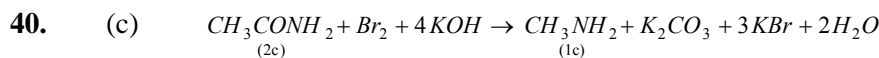
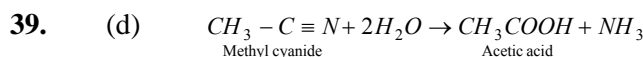
24. (c) Presence of alkyl group increases electron density on nitrogen atom due to +I effect. Thus basic nature increases.

25. (a) Mustard oil reaction

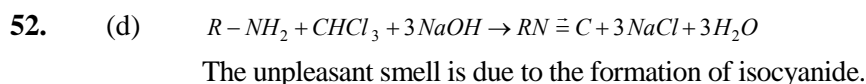
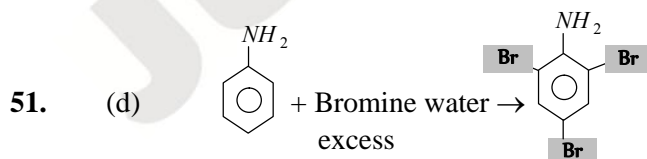


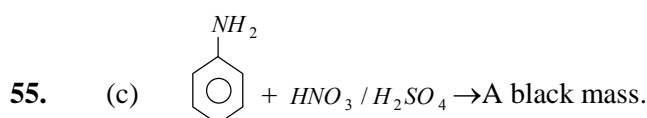
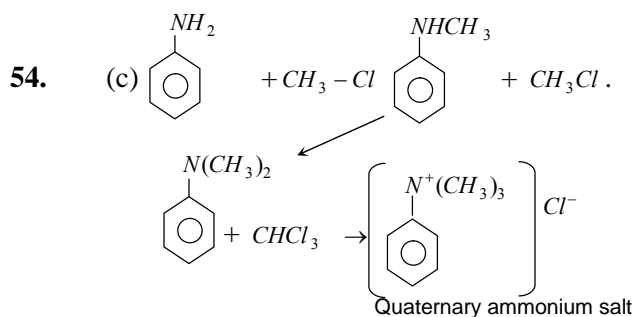
3- nitro group can be introduced.



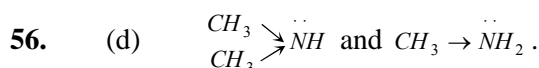


50. (b) Because the N atom in aniline has a lone pair to donate and also due to +I effect of $-NH_2$ group.



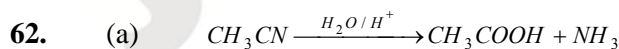
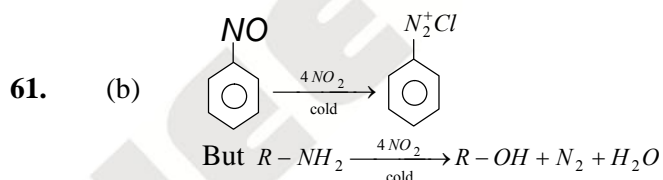
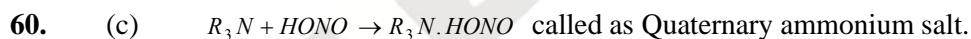
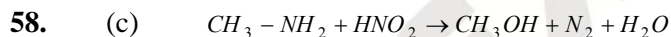


Nitration of aniline without protecting the amino group is not possible because HNO_3 is a strong oxidising agent which oxidises aniline.



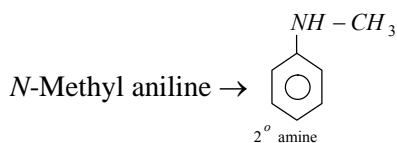
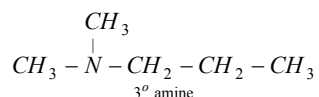
In methyl amine only one electron releasing group is present but in dimethyl amine two electron releasing groups are present which increase the basicity higher in diethyl amine.

57. (d) Nitro compounds are not explosive but stable compound.



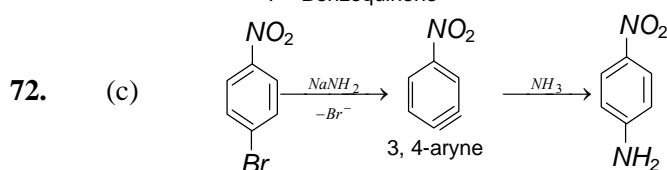
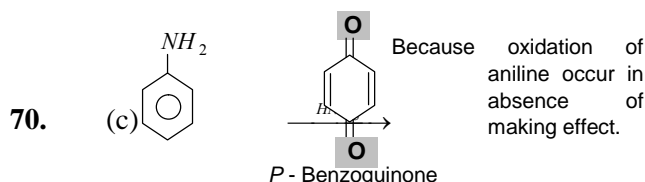
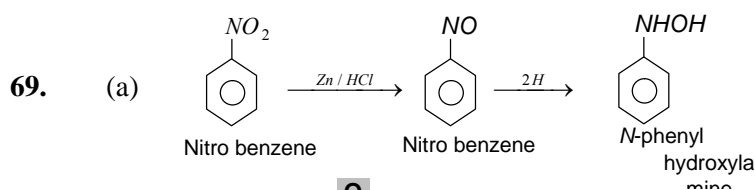
63. (c) 3° amine cannot be Acetylated because replacable H -atom is absent.

67. (e) Because
 N,N dimethyl propanimine

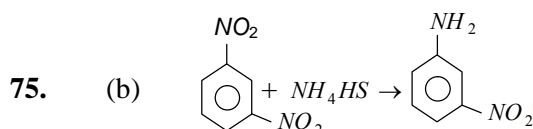


aniline $\rightarrow 1^\circ$ amine.

68. (c) Replacable H^- is absent.



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

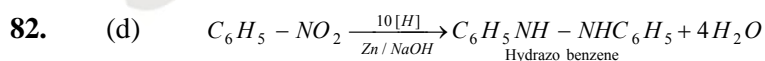
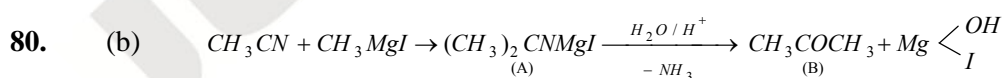


76. (a) Because of presence of electron withdrawing group - NO_2 .

77. (a) To suppress the concentration of the aniline available for coupling other rise coupling occurs.



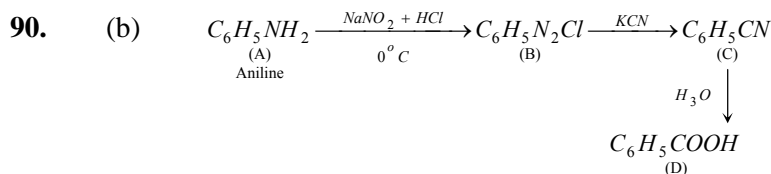
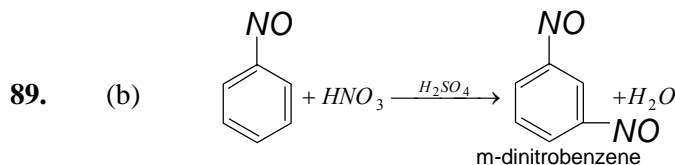
79. (c) $C_6H_5NH_2 < (CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$



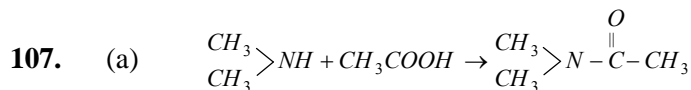
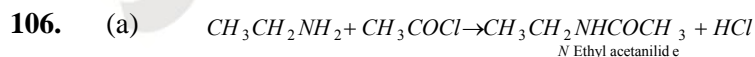
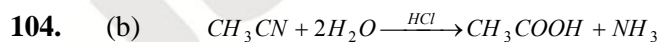
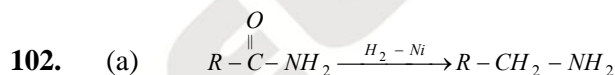
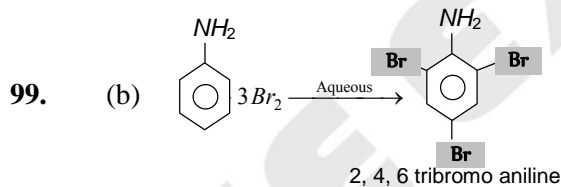
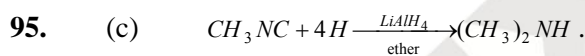
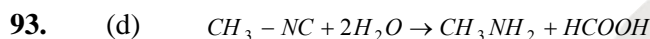
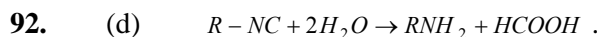
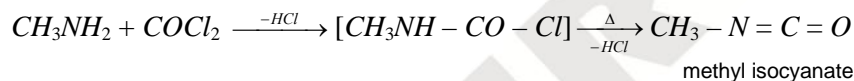
86. (b) Phenol react with aniline to give diazonium salt by coupling but Methyl amine not react with phenol.

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° , 2° and 3° amine from their mixture.

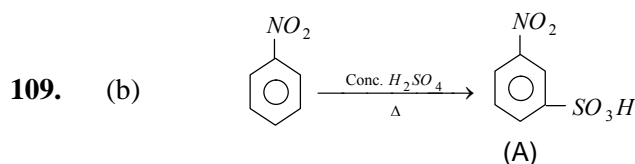
88. (b) A mixture of benzene and aniline can be separated by dil. HCl .

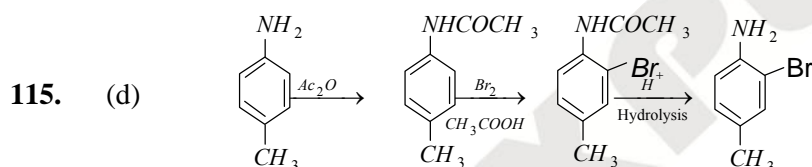
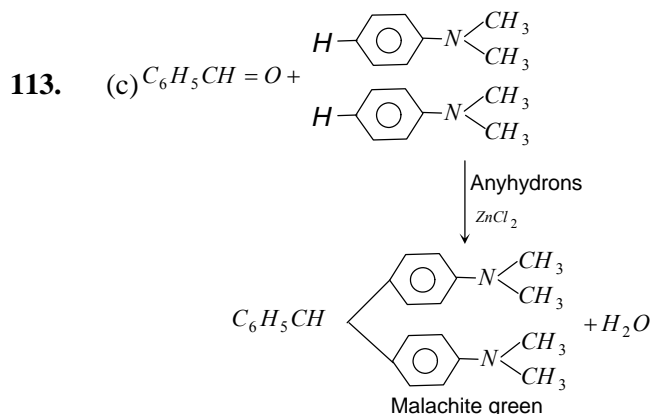
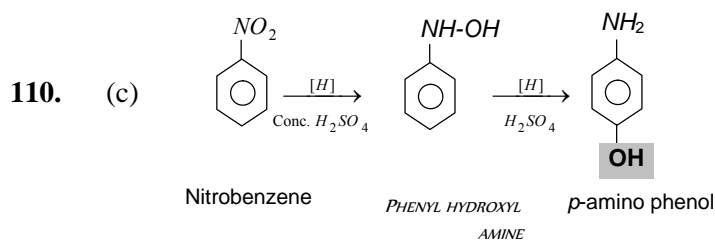


91. (c) Methyl isocyanate is industrially prepared by the action of methyl amine with phosgene.



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

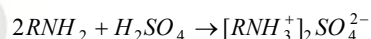




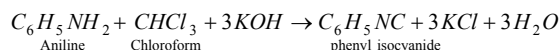
119. (a) Basicity of amines increase with increase in number of $-CH_3$ groups (or any group which cause $+I$ effect), due to increase in electron density on N atom. As a rule, the basicity of t -amine should be more than that of s -amine, but actually it is found to be lesser than s -amines. This is due to steric hindrance 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 :



120. (b) Amines are basic in nature, hence form salts with acid.



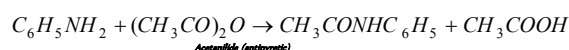
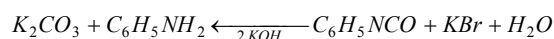
121. (b) We know that

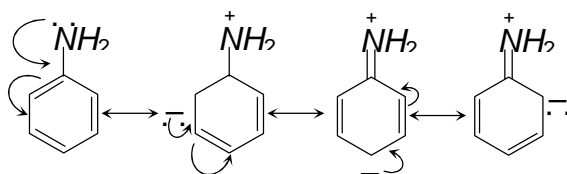
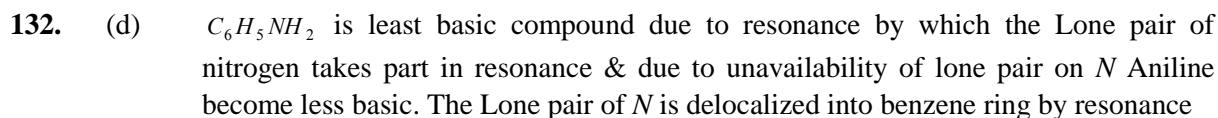
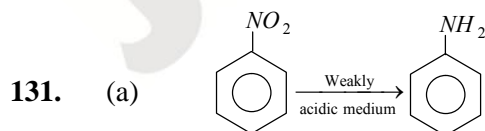
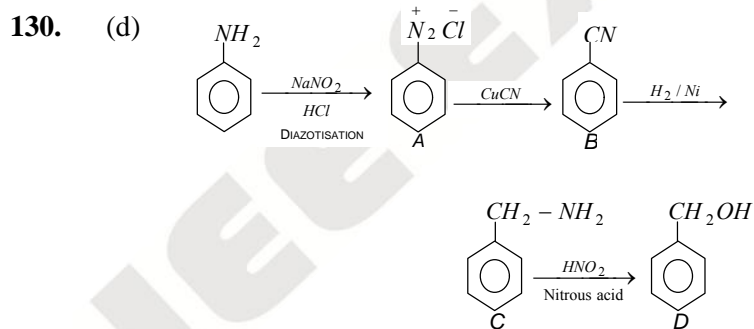
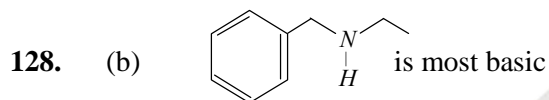
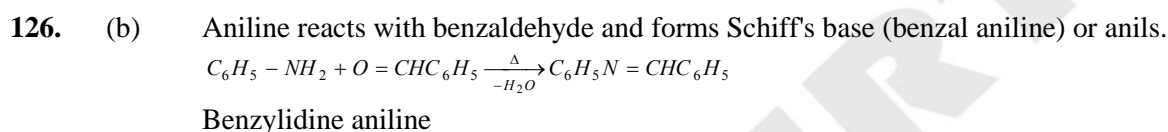
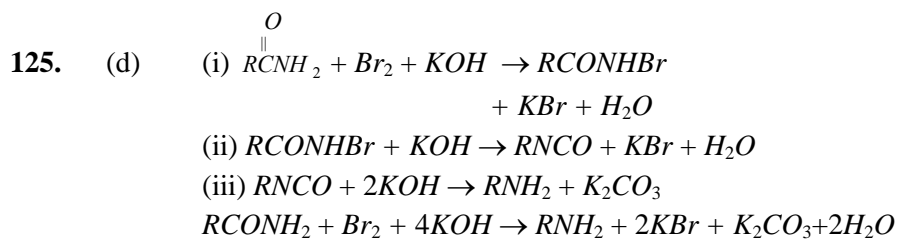
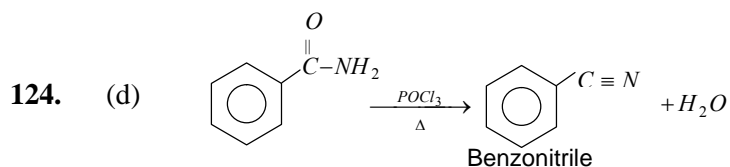


Thus in this reaction phenyl isocyanide is produced. this is called carbylamine reaction.

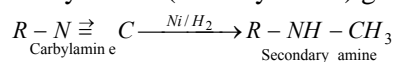
122. (d) Isocyanides on hydrolysis forms primary amines not ammonia

123. (b) $C_6H_5CONH_2 + Br_2 + KOH \rightarrow C_6H_5CONHBr + KBr + H_2O$

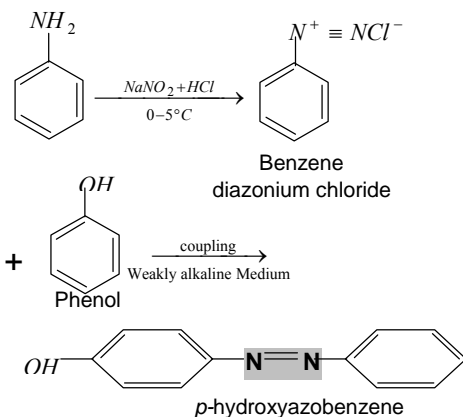




133. (b) Carbylamine (or isocyanides) give secondary amine on reduction.

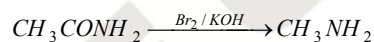


134. (a) Azo dye is prepared by the coupling of phenol and diazonium chloride.



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.



137. (c)
- $$CH_3CN + 2H \xrightarrow[\text{Ether}]{HCl} HC \equiv CH \xrightarrow[\text{Acetaldehyde}]{\text{Boiling } H_2O} CH_3CHO$$

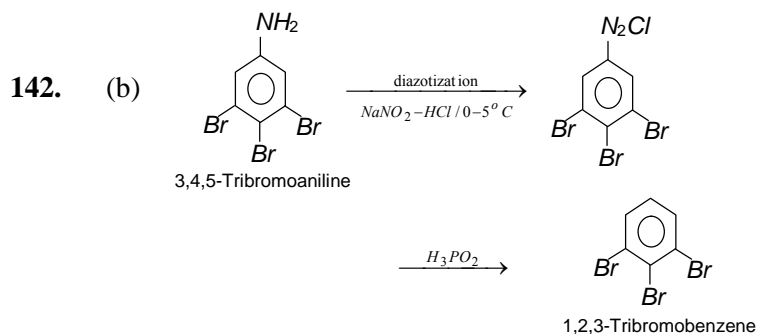
138. (b)
-

139. (b) *N*-alkyl formamides when dehydrated with $POCl_3$ 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)
-
- Aniline
- p*-nitro aniline (51%) *m*-nitro aniline (47%) *o*-nitro aniline (2%)

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.



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.

EXERCISE -IV

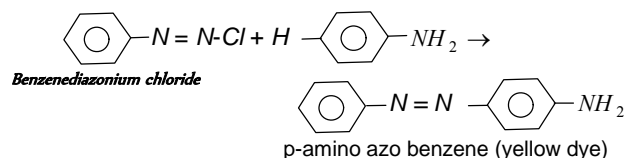
Tests for Nitrogen Containing Compounds

1. (c) $CH_3CONH_2 + Br_2 + 4NaOH \rightarrow$
 Acetamide
 $CH_3NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$
 Methyl amine

5. (b)
-
- is a type of 1° amine and hence gives +ve carbyl test

6. (a)
-
- Orange Colour

8. (a) Diazo-coupling is useful to prepare some dyes.

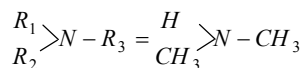


11. (a) $CHCl_3$ gives carbylamine test.
 $RNH_2 + CHCl_3 + 3KOH(alc.) \xrightarrow{\Delta}$
 $RN \equiv C + 3KCl + 3H_2O$
 alkyl isocyanide

EXERCISE - V

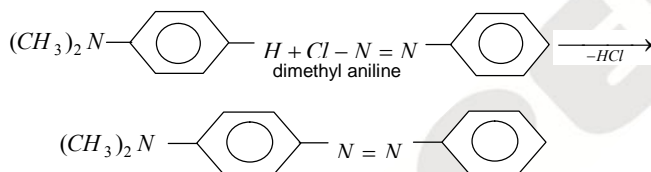
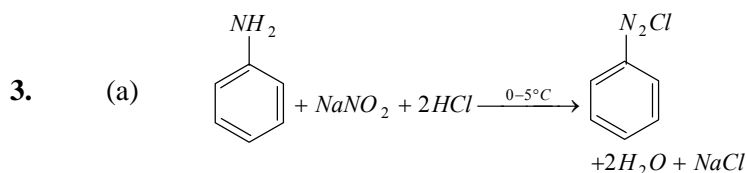
Critical Thinking Questions

1. (c) $R_1 = H$ and $R_2 = R_3 = CH_3$

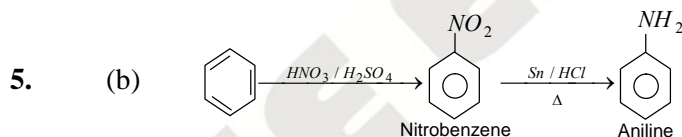
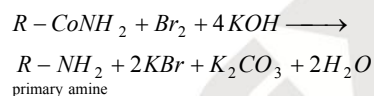


Sec. amine reacts with Nitrous acid to form nitroso amine yellow liquid.

2. (c) $CH_3CH_2NH_2 + HNO_2 \rightarrow CH_3CH_2OH + N_2 + H_2O$
Ethyl amine Ethyl alcohol



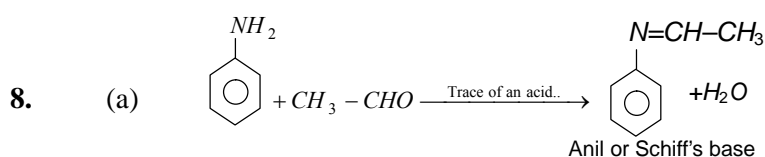
4. (c) Hofmann degradation of amide



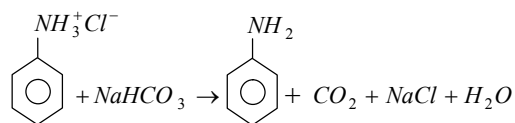
6. (b) The relative basic character of 1° , 2° and 3° amines also depends upon the nature of the alkyl group.

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.

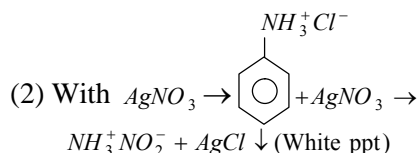


9. (bc) (1) With
- $\text{NaHCO}_3 \rightarrow$

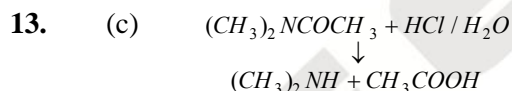
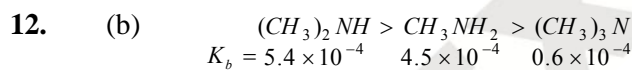
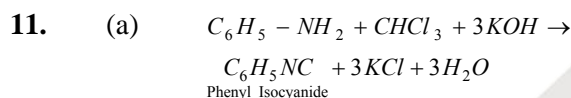
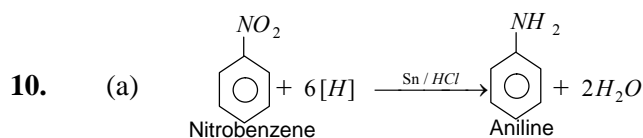


Anilinium hydrochloride is an acid salt and liberates CO_2 from NaHCO_3 .

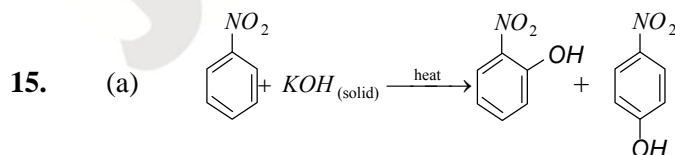
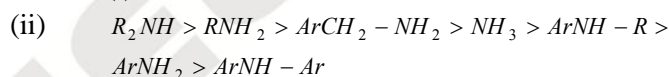
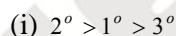
But p-chloro aniline is basic not acidic it does not liberate CO_2 .



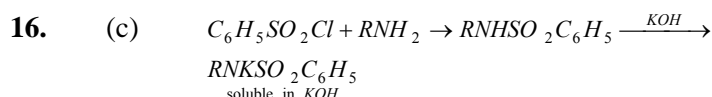
p-chloro aniline does not contain ionic chlorine so it does not give white ppt with AgNO_3



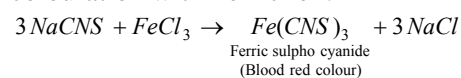
14. (a) Order of basicity of amines

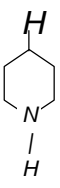


Because OH^- is nucleophile.

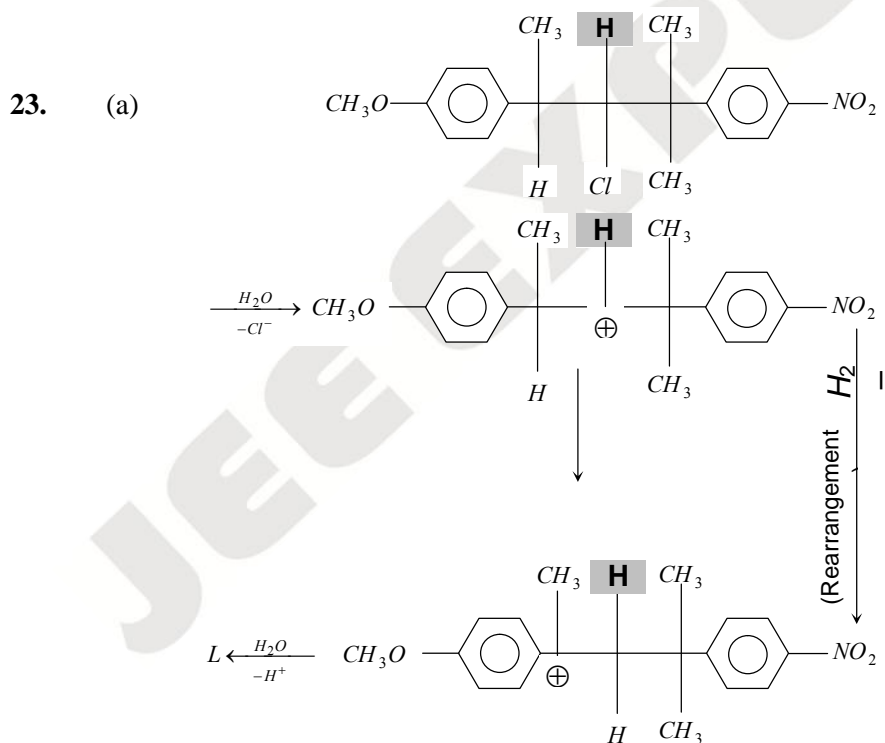
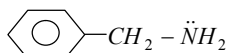


17. (b) When sulphur and nitrogen both are present in organic compound during Lassaigne's Test, both changes into "sodium thiocyanate". (NaSCN) which gives a blood red colouration with Ferric ion.



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 & resulting they become less basic.
19. (d) Liebermann's Nitroso reaction.
20. (a)
$$\underset{\text{(Acetamide)}}{\text{CH}_3\text{CONH}_2} + \text{Br}_2 + 4\text{KOH} \xrightarrow{-2\text{H}_2\text{O}}$$

$$\underset{\text{(Methyl amine)}}{\text{CH}_3\text{NH}_2} + 2\text{KBr} + 2\text{K}_2\text{CO}_3$$
21. (c) The class of Indigo dye is Indigoid or vat dye. Indigo dyes are insoluble in water.
22. (d) Lone pair of $\ddot{\text{N}}$ are not taking part in conjugation whereas in other parts lone pairs are taking part in conjugation



EXERCISE - VI

Assertion and Reason

- (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.
- (a) Amines are basic due to the presence of a lone pair of electrons on nitrogen atom. The lone pair can be easily donated.
- (b) The reason being that the terminal carbon atom in isocyanide has electron-deficient carbon having a sextet of electrons and hence undergoes addition reactions with ozone.
- (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 .

$$\underset{\text{Ethyl amine}}{C_2H_5 - NH_2} + \underset{\text{Chloroform}}{CHCl_3} + 3KOH(alc) \xrightarrow{\Delta} C_2H_5 - N \equiv C + 3KCl + 3H_2O$$
- (b) Nucleophilic species which have more than one site of reaction are called ambident nucleophiles.

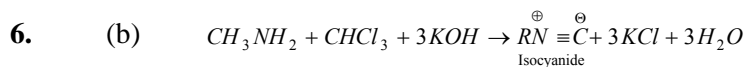
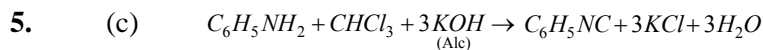
$$:\bar{C} = N: \leftrightarrow C = \bar{N}:$$
- (c) $-SO_3H$ group being more acidic than $-CO_2H$ group can easily transfer a proton to the amino group.
- (a) $HNO_3 + 2H_2SO_4 \rightleftharpoons 2HSO_4^- + NO_2^+ + H_3O^+$
- (c) Only primary aliphatic amines can be prepared by Gabriel phthalimide reaction.
- (c) Reaction can be used to prepare 1° , 2° , 3° amines and finally quaternary ammonium salts.
- (b) Nitroarene cannot be distilled under normal atmospheric pressure. This is because either they decompose or they explode on strong heating.
- (c) Only 1° amines undergo Hofmann bromamide reaction. Since $CH_3CONHCH_3$ is a 2° amine therefore, it does not undergo Hofmann bromamide reaction.
- (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.
- (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) $RNH_2 + CHCl_3 + 3KOH (alc) \rightarrow R-N \equiv C + 3KCl + 3H_2O$
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.
- $$R \overset{+}{N} \equiv \overset{-}{C} + E^+ \longrightarrow R \overset{+}{N} \equiv C E \xrightarrow{Nu} RN \equiv C(Nu)E$$
- $$R \overset{+}{N} \equiv \overset{-}{C} + H_2O \longrightarrow RN = CHO H \longrightarrow \underset{\text{alkylformamide}}{RNHCHO}$$

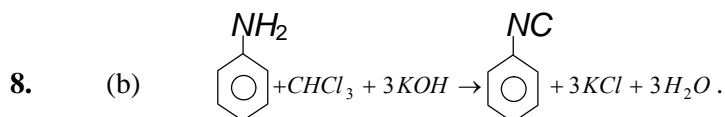
SELF EVALUATION TEST

ANSWER KEY & SOLUTION

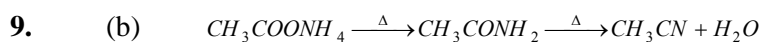
1. (c) The higher boiling points of amide is because of Intermolecular hydrogen bonding
- $$\begin{array}{c} -H-N-C=O- \\ | \quad | \\ H \quad R \end{array} \quad \begin{array}{c} -H-N-C=O- \\ | \quad | \\ H \quad R \end{array} \quad \begin{array}{c} -H-N-C=O- \\ | \quad | \\ H \quad R \end{array}$$
- 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 lone pair of e^- . It can donate a lone 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.



7. (b) Nitrolim is a mixture of calcium cyanamide and carbon.



Carbyl amine reaction.



10. (d) Steam distillation 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.

$$\therefore \ddot{N}H_3 \rightarrow \frac{5+3}{2} \Rightarrow 4 \Rightarrow sp^3.$$

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.

