DAY THIRTY THREE

Organic Compounds Containing Nitrogen

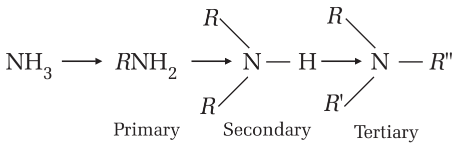
Learning & Revision for the Day

- Amines
- Identification of Primary, Secondary and Tertiary Amines
- Diazonium Salts
- Cyanides
- Isocyanides

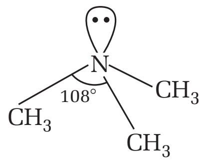
In nature, the nitrogen containing compounds occur among proteins, vitamins, alkaloids and hormones. These include mainly nitrocompounds, amines, diazonium salts, cyanides and isocyanides.

Amines

- These are the derivatives of ammonia in which one, two or all the three hydrogen atoms are replaced by alkyl or aryl groups.
- **Classification** Amines are classified as primary, secondary or tertiary according to the replacement of one, two or three hydrogen atoms from ammonia respectively.



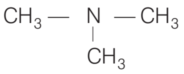
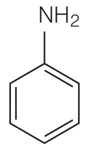
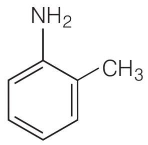
- **Structure** Nitrogen in amines is sp^3- hybridised. The sp^3- hybridised orbitals of nitrogen overlap with orbitals of hydrogen or carbon depending upon the composition of amines. The **fourth hybridised orbital** of nitrogen in all amines has an unshared pair of electrons. Due to the presence of lone pair of electrons, the bond angle C—N—E (where, E is C or H) is less than 109.5° and shape is pyramidal.



Pyramidal shape of trimethylamine

Nomenclature In IUPAC system, amines are named as alkanamines derived by replacement of 'e' of alkane by the word amine.

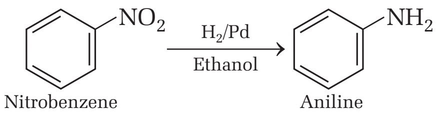
IUPAC names of some alkylamines are given below.

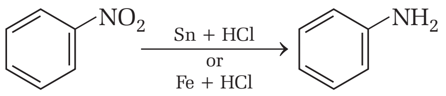
Amine	IUPAC Name
$CH_3CH_2-NH_2$	Ethanamine
$CH_3-NH-CH_2-CH_3$	N-methylethanmine
 $CH_3-\underset{\mid}{\overset{}{N}}-CH_3$ with CH_3 below N	N, N-dimethylmethanamine
	Aniline or benzenamine
	2-methylbenzenamine

Methods of Preparation

Several methods can be used to prepare aliphatic amines, out of which some are specific for 1°, 2°, 3° amines which gives some mixtures of all the three.

(i) **Reduction of nitro compounds** to amines is done by passing hydrogen gas in the presence of finely divided nickel, palladium on platinum and also by reduction with metals in acidic medium.





$$R-NO_2 \xrightarrow{Sn\ +\ HCl} R-NH_2$$

(R = alkyl group) (Primary amine)

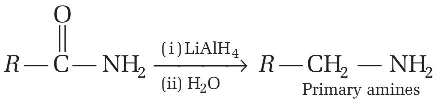
NOTE Under weakly acidic conditions nitrobenzene on electrolytic reduction gives aniline, while under strongly acidic conditions gives *p*-aminophenol.

(ii) **Reduction of cyanides** to primary amines by using Na and alcohol is called **Mendius reaction**.

$$R-C\equiv N \xrightarrow[\text{Na(Hg)} / C_2H_5OH]{H_2/Ni \text{ or}} R-CH_2-NH_2$$

(R may be alkyl or aryl group)

(iii) **Reduction of amides** with $LiAlH_4$ yield amines



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 \xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4} \underset{\text{Primary amines}}{R-CH_2-NH_2}$$

(R may be alkyl or aryl group)

NOTE All the above reactions are used in the preparation of primary amines only.

(iv) When alkyl halide is heated with alcoholic solution of ammonia in a sealed tube at about 373 K, a mixture of amines is obtained. This reaction is called **Hofmann's ammonolysis method**.

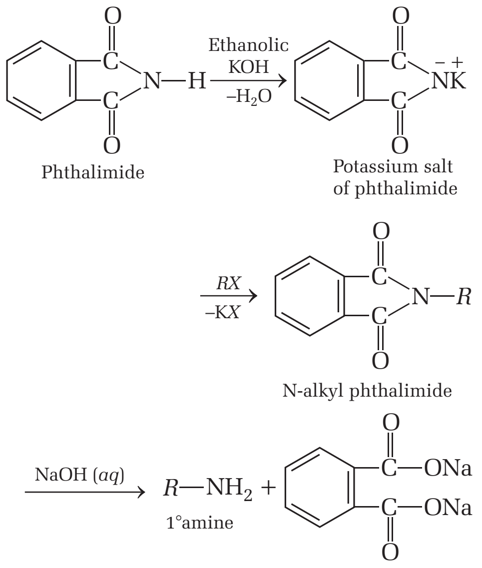
$$NH_3 + RX \longrightarrow \underset{\substack{\text{Substituted}\\\text{ammonium salt}}}{R\overset{+}{N}H_3X^-} \quad (RNH_2 + HX)$$

$$\underset{1°}{RNH_2} \xrightarrow[-HX]{RX} \underset{2°}{R_2NH} \xrightarrow[-HX]{RX} \underset{3°}{R_3N} \xrightarrow{RX} \underset{\substack{\text{Quarternary}\\\text{ammonium salt}}}{R_4\overset{+}{N}X^-}$$

The free amine can be obtained from ammonium salt by treatment with a strong base.

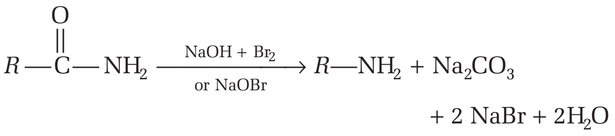
$$R\overset{+}{N}H_3\overset{-}{X} + NaOH \longrightarrow R-NH_2 + H_2O + NaX$$

(v) Phthalimide on treatment with ethanolic potassium hydroxide forms potassium salt of phthalimide, which on heating with alkyl halide followed by alkaline hydrolyis produces the corresponding primary amines. This is called as **Gabriel phthalimide synthesis**.



Aromatic primary amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

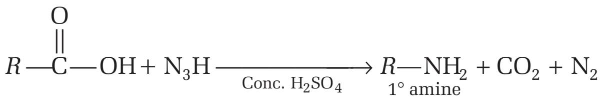
(vi) Amides on reaction with Br_2 in an aqueous or ethanolic solution of NaOH give 1° amine with one C-atom less than that present in the amide. This reaction is called **Hofmann bromamide degradation reaction**.



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 \xrightarrow[\text{or NaOBr}]{NaOH\ +\ Br_2} R-NH_2 + Na_2CO_3 + 2\,NaBr + 2H_2O$$

R = alkyl or C_6H_5

(vii) Carboxylic acid, when warmed with hydrazoic acid (N_3H) in the presence of concentrated sulphuric acid, gives a high yield of primary amines. This reaction is called **Schmidt reaction**.



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + N_3H \xrightarrow[\text{Conc. } H_2SO_4]{} \underset{1^\circ \text{ amine}}{R-NH_2} + CO_2 + N_2$$

Instead of N_3H and conc. H_2SO_4, a mixture of NaN_3 and conc. H_2SO_4 can also be used.

Physical Properties of Amines

Physical properties of amines are as follows :

- The lower aliphatic amines are gases with fishy odour. Aniline and other aryl amines are usually colourless but get coloured on storage due to atmospheric oxidation.
- Boiling points and solubility of isomeric amines decrease with branching, i.e.

$$\underset{\substack{1^\circ \text{ amine} \\ \text{2H-bonding}}}{CH_3-CH_2-CH_2-NH_2}$$

$$> \underset{\substack{2^\circ \text{ amine} \\ \text{1 H-bonding}}}{CH_3-NH-CH_2-CH_3} > \underset{\substack{3^\circ \text{ amine} \\ \text{No H-bonding}}}{(CH_3)_3N}$$

- Amines have lower boiling point than corresponding alcohols.

Chemical Properties of Amines

Amines are reactive and behave as nucleophiles due to the presence of one unshared pair of electron. Some of the reactions of amines are given below:

1. Basic Nature of Amines

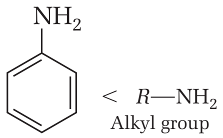
Amines are basic in nature, so react with acids and form salt. Larger the value of K_b or smaller the value of pK_b, stronger is the base.

- The order of basic strength in case of methyl substituted amines and ethyl substituted amines in aqueous solution is as follows :

$$(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$$

$$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$$

- Alkylamines are more basic than arylamines. Because in arylamines, the lone pair of electrons on nitrogen atom is in conjugation with the benzene ring and thus making it less available for protonation.



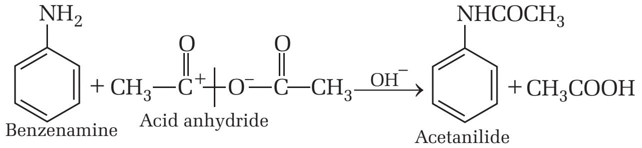
- Electron donating substituent such as $-CH_3$, $-OCH_3$ increases the basicity, while electron withdrawing group decreases the basicity.
- More the *s*-character of the hybrid orbital containing lone pair of electrons, lesser is the basic character.

$$\text{e.g. } \underset{\substack{25\% \\ s\text{-character}}}{R\ddot{N}H_2} > \underset{\substack{33.33\% \\ s\text{-character}}}{R\ddot{N}=CHR'} > \underset{\substack{50\% \\ s\text{-character}}}{RC\equiv N\!:}$$

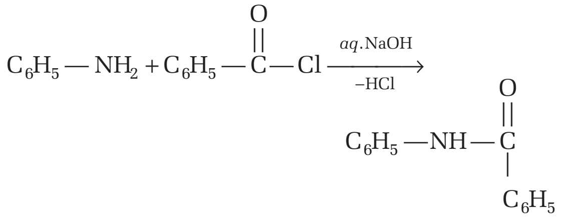
2. Aliphatic or Aromatic

1° amines react with acid chlorides and anhydrides to give N-substituted amide, while 2° amines give N,N-disubstituted amides. This reaction is called **acylation**.

$$\underset{\text{Ethanamine}}{C_2H_5-NH_2} + \underset{\text{Acyl chloride}}{CH_3CO^+Cl^-} \xrightarrow{OH^-} \underset{\text{N-ethylethanamide}}{C_2H_5-NHCOCH_3} + HCl$$



- Reaction of aniline with benzoyl chloride in the presence of *aq*. NaOH solution is called **Schotten Baumann reaction.**



$$C_6H_5-NH_2 + C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-Cl \xrightarrow[-HCl]{aq.NaOH} C_6H_5-NH-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle C_6H_5}{|}}{C}}$$

- Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form carbylamines isocyanides. The reaction is known as **carbylamine reaction**.

$$R-NH_2 + CHCl_3 + 3KOH(\text{alc.}) \xrightarrow{\text{Heat}}$$

$$\text{or } C_6H_5NH_2 \qquad \underset{\substack{\text{Carbylamine} \\ \text{(Foul smelling)}}}{R-NC} + 3KCl + 3H_2O$$

$$\text{or } \underset{\text{Carbylamine}}{R-NC} + 3KCl + 3H_2O$$

$$\text{or } \underset{\text{Phenyl carbylamine}}{C_6H_5NC}$$

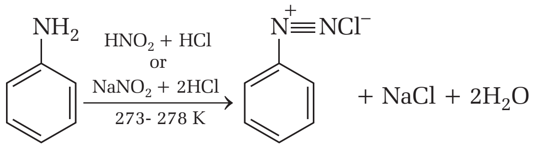
Secondary (R—NH—R) and tertiary amines (R_3N) do not show this reaction, hence it is used as a test for primary amines.

3. Amines React with Nitrous Acid (HNO_2)

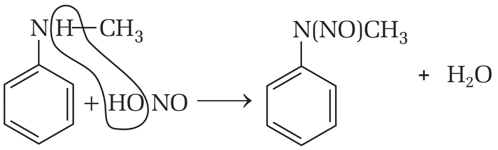
Aliphatic primary amines when react with HNO_2, give alcohol.

$$R-NH_2 \xrightarrow{(HNO_2)/NaNO_2 + HC} R-OH + N_2 + H_2O$$

- Aromatic primary amines when react with HNO_2, give diazonium salts.



- Secondary amines (both aliphatic and aromatic) on reaction with HNO_2 give an oily nitroso compound.



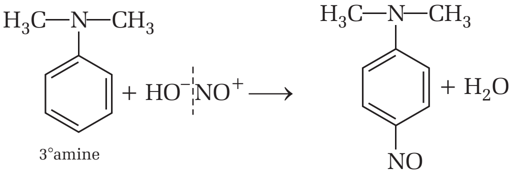
N-methyl-N-nitroso aniline
(yellow oily layer)

- Tertiary aliphatic amines dissolve in a cold solution of nitrous acid to form salts which decompose on warming to give nitrosoamine and alcohol.

e.g. $\underset{3^\circ\text{ amine}}{(C_2H_5)_3N} + HONO \xrightarrow{\text{Cold}} \underset{\text{Salt}}{[(C_2H_5)_3\overset{+}{N}H]\,NO_2^-}$

$$\xrightarrow{\text{Warm}} (C_2H_5)_2N{-}N{=}O + C_2H_5OH$$

- Aromatic tertiary amines react with nitrous acid to give coloured substituted nitroso compound.

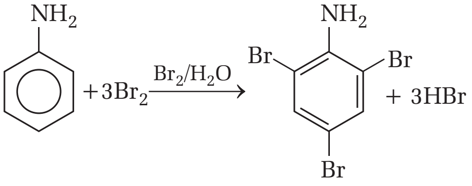


This reaction is used to distinguish 1°, 2° and 3° amines.

4. Aromatic Amines Undergo Electrophilic Substitution Reactions

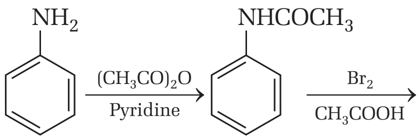
Due to delocalisation of the lone pair of electrons of N-atom over the benzene ring, the electron density increases more at *o*-and *p*-positions. Thus, aniline gives *o*-and *p*-substituted products. Some of the most important electrophile aromatic substitution, i.e. bromination, nitration, sulphonation etc., are given below:

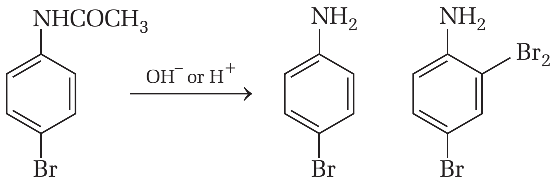
- Aniline react with bromine water at room temperature to give white precipitate of 2, 4, 6-tribromoaniline. This reaction is called **bromination**.



The main problem encountered during electrophilic substitution reactions of aromatic amines is that these have very high reactivity.

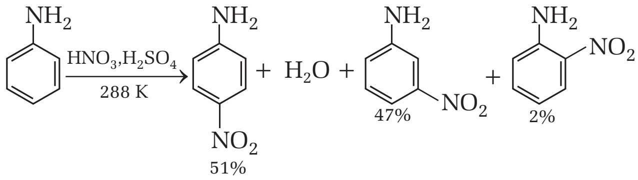
- Monosubstituted aniline derivatives are prepared by protecting the —NH$_2$ group by acetylation with acetic anhydride. This reaction is called **selective bromination**.



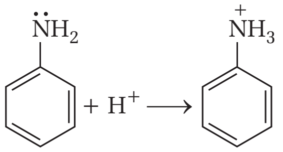


(Major) (Minor)

- Benzene can be treated with a nitric acid to give nitrobenzene. This reaction is called **nitration**. Nitration of aniline gives a mixture of *p*-nitroaniline and *m*-nitroaniline in approx. 1 : 1 ratio.



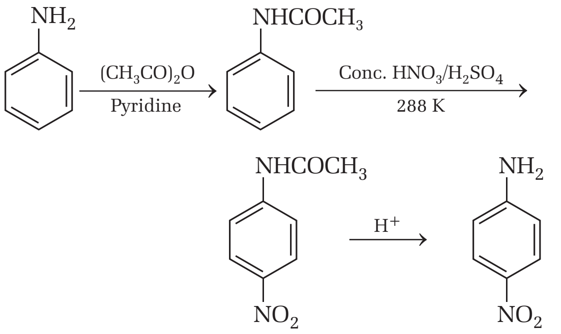
This is due to the fact that aniline gets protonated to form anilinium ion which is *meta*-directing.



Basic

Anilinium ion
(Intermediate)

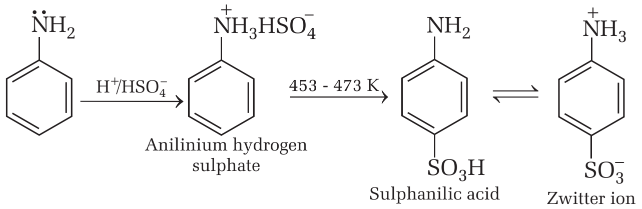
- By protecting the —NH$_2$ group through acetylation with acetic anhydride, the nitration can be controlled and *p*-nitroaniline is obtained as a major product.



p-nitroaniline

NOTE During nitration, if large amount of $KHSO_4$ is added to the mixture of HNO_3 and conc. H_2SO_4, more HSO_4^- ion furnishes and hence, the concentration of NO_2^+ decreases and consequently the rate of electrophilic aromatic reaction also decreases.

- Benzene can be treated with a very concentrated sulphuric acid to give benzene sulphuric acid in a reversible reaction. The reaction is called **sulphonation**.



NOTE Aniline does not undergo Friedel-Crafts reaction (alkylation and acetylation) due to salt formation with $AlCl_3$ (anhy). a Lewis acid, which is used as a catalyst.

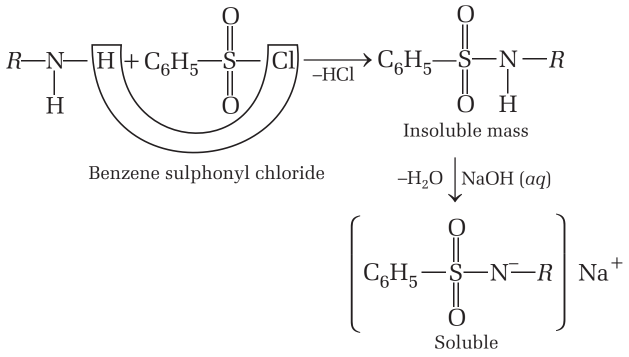
Identification of Primary, Secondary and Tertiary Amines

This can be done by following tests.

Hinsberg's Test

In this method, the amine is treated with benzenesulphonyl chloride (Hinsberg's reagent) in the presence of excess of aqueous NaOH solution.

(i) **Primary amines** give an insoluble mass which is soluble in alkali.



$$R-\underset{\displaystyle H}{\underset{|}{N}}-\boxed{H}+C_6H_5-\overset{\displaystyle O}{\overset{\|}{\underset{\underset{\displaystyle O}{\|}}{S}}}-\boxed{Cl}\xrightarrow[-HCl]{}C_6H_5-\overset{\displaystyle O}{\overset{\|}{\underset{\underset{\displaystyle O}{\|}}{S}}}-\underset{\displaystyle H}{\underset{|}{N}}-R$$

Benzene sulphonyl chloride

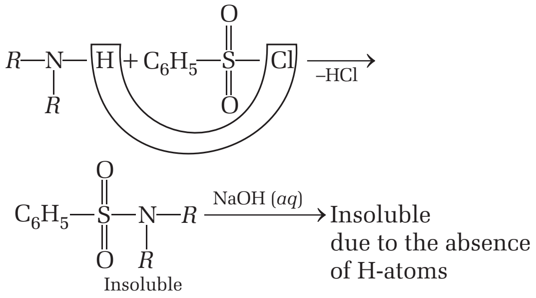
Insoluble mass

$$\downarrow NaOH\,(aq),\ -H_2O$$

$$\left[C_6H_5-\overset{\displaystyle O}{\overset{\|}{\underset{\underset{\displaystyle O}{\|}}{S}}}-\bar{N}-R\right]Na^+$$

Soluble

(ii) **Secondary amines** give an insoluble substance, which remains unaffected by alkali.



$$R-\underset{\displaystyle R}{\underset{|}{N}}-\boxed{H}+C_6H_5-\overset{\displaystyle O}{\overset{\|}{\underset{\underset{\displaystyle O}{\|}}{S}}}-\boxed{Cl}\xrightarrow[-HCl]{}$$

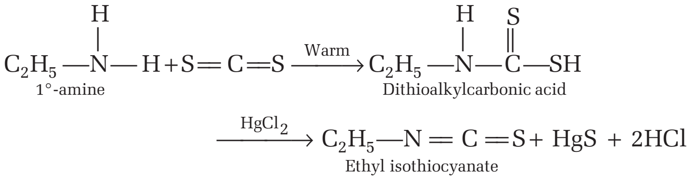
$$C_6H_5-\overset{\displaystyle O}{\overset{\|}{\underset{\underset{\displaystyle O}{\|}}{S}}}-\underset{\displaystyle R}{\underset{|}{N}}-R\xrightarrow{NaOH\,(aq)}\text{Insoluble due to the absence of H-atoms}$$

Insoluble

(iii) **Tertiary amines** do not react with benzene sulphonyl chloride because of the absence of H-atoms.

Hofmann Mustard Oil Reaction

It is used as a test for primary amines, In this, 1° amines, when warmed with CS_2, alkyl or aryl thiocyanate with a characteristic smell of mustard oil is formed.



$$\underset{1^\circ\text{-amine}}{C_2H_5-\overset{\displaystyle H}{\overset{|}{N}}-H}+S=C=S\xrightarrow{\text{Warm}}\underset{\text{Dithioalkylcarbonic acid}}{C_2H_5-\overset{\displaystyle H}{\overset{|}{N}}-\overset{\displaystyle S}{\overset{\|}{C}}-SH}$$

$$\xrightarrow{HgCl_2}\underset{\text{Ethyl isothiocyanate}}{C_2H_5-N=C=S}+HgS+2HCl$$

Uses of Amines

The uses of amines are given below:

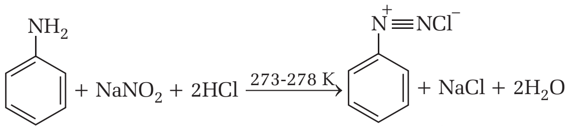
(i) Amines are used as intermediates in drug manufacturing and as reagents in organic synthesis.
(ii) Aromatic amines are used for manufacture of polymers, dyes and as intermediates for additives in rubber industry.
(iii) Quarternary ammonium salts of long chain aliphatic tertiary amines are used as detergents.

Diazonium Salts

Diazonium salts are obtained when primary aromatic amines react with nitrous acid. These salts are used in the preparation of azo dyes and a number of useful halogen substituted arenes.

Preparation

Primary aromatic amines when reacts with HNO_2 form diazonium salts at low temperatures (0-5°C). The reaction is called **diazotisation.**



Benzene diazonium chloride

Physical Properties

- Benzene diazonium chloride is a colourless crystalline solid.
- It is readily soluble in water.
- It is stable in cold but reacts with water.

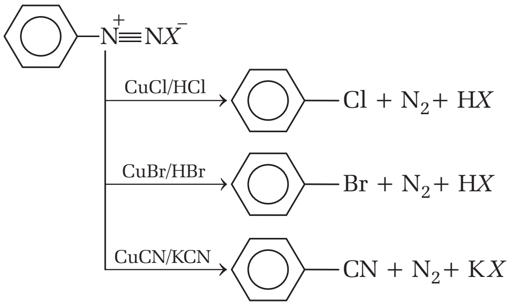
Chemical Properties

Diazonium salts mainly show two types of reactions:

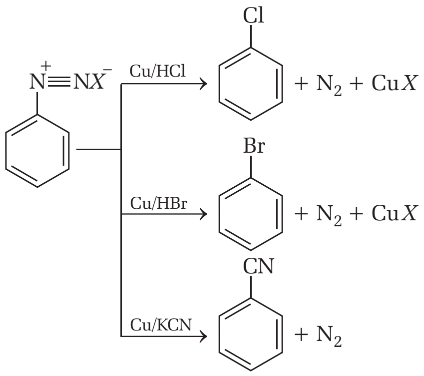
1. Reactions Involving Displacement of Nitrogen

The following are the reactions involved in the displacement of nitrogen in the benzene can be given as:

(i) **Sandmeyer's Reaction** Benzenediazonium Chloride heated with cuprous chloride or cuprous bromide respectively dissolved in HCl or HBr to yield chlorobenzoene or bromobenzene, respectively. Similarly, CN can be introduced by treating benzenediazonium chloride with KCN in aqueous KCN. This procedue using cuprous salts is called Sandmeyer's reaction.

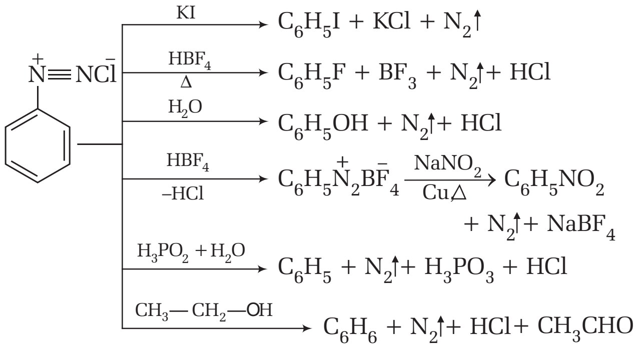


(ii) **Gattermann Reaction** Cl, Br, CN, can be introduced into the benzene ring by treating the diazotisation salts with HCl, HBr and KCN respectively in presence of copper powder. This reaction is called as Gattermann reaction.



NOTE The yield of Sandmeyer's reaction is found to be greater than the Gattermann reaction.

(iii) Diazonium salt also reacts with various reagents as shown in the following flow chart :

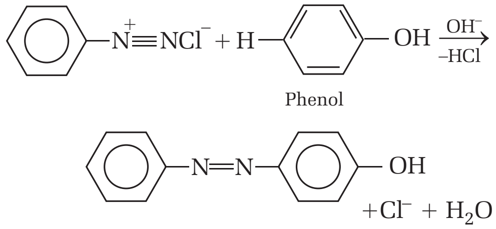


Reactions Involving Retention of Diazo Group

(Coupling Reaction) Benzene diazonium chloride reacts with phenol in which phenol molecule at its *para* position is coupled with diazonium salt to give the product *p*-hydroxy azobenzene.

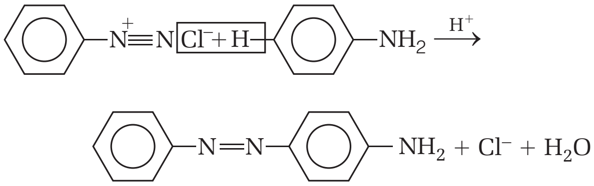
Thus, this reaction is known as **coupling reaction.** Coupling reactions are the **example** of electrophilic substitution reaction.

(i)



p- hydroxyazobenzene
(Orange dye)

(ii)



p-aminoazobenzene
(Yellow dye)

Coupling with phenols is carried out in weakly alkaline medium (pH 9 to 10) because phenate ion produced is coupled with diazonium salt more readily.

Above pH 10, diazonium salt reacts with hydroxide ion to form diazotate ion which does not take part in coupling reaction.

Uses

Diazonium salts are used for the preparation of a large number of aromatic compounds *viz* substitution and coupling compounds.

Cyanides $(R—C\equiv N)$

- **Nomenclature** Its IUPAC name is alkylcyanide.
- **Preparation** These can be prepared by the following ways:

$$RX + KCN(alc.) \longrightarrow \underset{\text{Cyanide}}{RCN} + KX$$

$$\underset{\text{Amide}}{RCONH_2} \xrightarrow{P_2O_5} \underset{\text{Cyanide}}{RCN} + H_2O$$

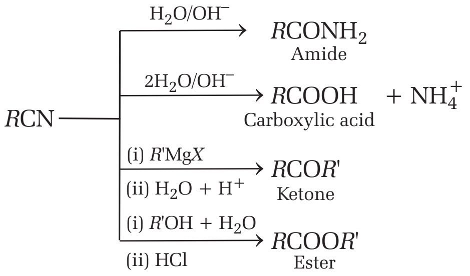
$$RX + Na \xrightarrow{DMF} RCN + NaX$$

Properties

- Alkyl cyanides act as both nucleophile and electrophile. Cyanide provides a synthetic root for stepping up in a particular series. Cyanides undergo reduction reaction by using Na and alcohol to give primary amines. This reaction is called **Mendius reaction**.
- Partial reduction of alkyl or aryl cyanides with $SnCl_2$ + HCl to prepare aldehydes is called **Stephen's reduction**.

$$\underset{\text{Alkyl cyanide}}{R-C\equiv N} \xrightarrow[\Delta]{SnCl_2 + \text{Conc. HCl}} \underset{\text{Aldehyde}}{RCHO}$$

- These undergo various hydrolysis reactions as shown in the following flow chart.



$$RCN \xrightarrow{H_2O/OH^-} \underset{\text{Amide}}{RCONH_2}$$

$$RCN \xrightarrow{2H_2O/OH^-} \underset{\text{Carboxylic acid}}{RCOOH} + NH_4^+$$

$$RCN \xrightarrow[\text{(ii) } H_2O + H^+]{\text{(i) } R'MgX} \underset{\text{Ketone}}{RCOR'}$$

$$RCN \xrightarrow[\text{(ii) HCl}]{\text{(i) } R'OH + H_2O} \underset{\text{Ester}}{RCOOR'}$$

Isocyanides ($R-N \overset{\rightarrow}{=} C$)

They are commonly called as **carbylamines**.

Preparation

These can be prepared by following ways:

(i) These are prepared by reacting alkyl halide with silver cyanide.

$$\underset{\text{Alkyl halide}}{R-X} + \underset{\text{Silver cyanide}}{AgCN} \longrightarrow \underset{\text{Isocyanides}}{RN \overset{\rightarrow}{=} C} + AgX$$

(ii) These are also prepared by **carbylamine reaction**.

Properties

(i) $\underset{\text{Isocyanide}}{RNC} + 2H_2O \xrightarrow{H^+} \underset{1^\circ\text{–amine}}{RNH_2} + \underset{\text{Formic acid}}{HCOOH}$

(ii) $\underset{\text{Isocyanide}}{RNC} \xrightarrow[4[H]]{Na-C_2H_5OH} \underset{2^\circ\text{–amine}}{R-NHCH_3}$

NOTE Methyl isocyanate (MIC) $CH_3N=C=O$ was responsible for Bhopal gas tragedy in December 1984.

Difference between Cyanides and Isocyanides

- Alkyl cyanides have pleasant smell but isocyanides have highly unpleasant odour.
- Alkyl cyanides have lower dipole moment than isocyanides.
- Alkyl cyanide undergoes both acidic and alkaline hydrolysis while alkyl isocyanide undergoes only acidic hydrolysis because negatively charged carbon atom repel OH^- ion of the base.

$$\text{Cyanides} \xrightarrow{H^+/OH^-} \underset{\text{Amide}}{RCONH_2}$$

$$\text{Isocyanides} \xrightarrow{\text{Acids}} 1^\circ \text{ amine} + HCOOH$$

- Cyanides gives 1° amine, while isocyanides gives 2° amine on reduction.

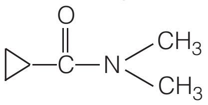
$$\text{Cyanides} \xrightarrow{\text{Reduction}} 1^\circ\text{amine}$$

$$\text{Isocyanides} \xrightarrow{\text{Reduction}} 2^\circ\text{amine}$$

DAY PRACTICE SESSION 1

FOUNDATION QUESTIONS EXERCISE

1 IUPAC name of the following compound is



(a) N,N-dimethyl cyclopropane carboxamide
(b) N-methylcyclo propanamide
(c) cyclopropionamide
(d) None of the above

2 Which of the following reactions is appropriate for converting acetamide to methanamine? → **NEET-2017**

(a) Carbylamine reaction
(b) Hofmann hypobromamide reaction
(c) Stephen's reaction
(d) Gabriel phthalimide synthesis

3 Indicate which nitrogen compound amongst the following would undergo Hofmann reaction?

(a) $RCONHCH_3$	(b) $RCOONH_4$
(c) $RCONH_2$	(d) $RCONHOH$

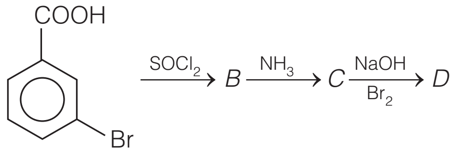
4 Acetamide is treated with the following reagents separately. Which one of these would yield methyl amine?

(a) $NaOH/Br_2$	(b) Sodalime
(c) Hot conc. H_2SO_4	(d) PCl_5

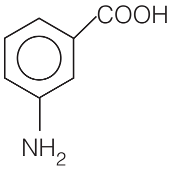
5 In order to prepare a 1° amine from an alkyl halide with simultaneous addition of one CH_2 group in the carbon chain, the reagent used as source of nitrogen is

(a) sodium amide, $NaNH_2$
(b) sodium azide, NaN_3
(c) potassium cyanide, KCN
(d) potassium phthalimide, $C_6H_6(CO)_2N^-K^+$

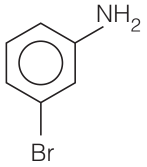
6 In a set of reactions, *m*-bromobenzoic acid gave a product *D*. Identify the product *D*.



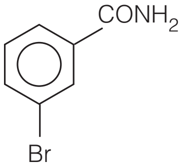
(a)



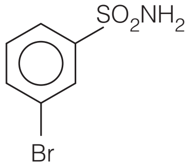
(b)



(c)



(d)

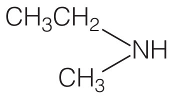


7 Method by which aniline cannot be prepared is ➞ **CBSE-AIPMT 2015**

(a) hydrolysis phenyl isocyanide with acidic solution
(b) degradation of benzamide with bromine in alkaline solution
(c) reduction of nitrobenzene with H_2 /Pd in ethanol
(d) potassium salt of phthalimide treated with chlorobenzene followed by the hydrolysis with aqueous NaOH solution

8 Which of the following should be most volatile?

I. $CH_3CH_2CH_2NH_2$ II. $(CH_3)_3N$
III.



$CH_3CH_2-NH-CH_3$

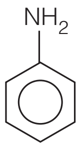
IV. $CH_3CH_2CH_3$

(a) Only II (b) Only IV (c) Only I (d) Only III

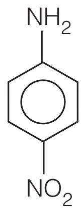
9 The correct statement regarding the basicity of arylamines is ➞ **NEET 2016, Phase I**

(a) arylamines are generally more basic than alkylamines because the nitrogen lone-pair electroos are not deloalized by interaction with the aromatic ring π-electron system
(b) arylamines are generally more basic than alkylamines because of aryl group
(c) arylamines are generally more basic than alkylamines, because the nitrogen atom in arylamines is *sp*-hybridised
(d) arylamines are generally less basic than alkylamines because the nitrogen lone-pair electrons are delocalised by interaction with the aromatic ring π-electron system.

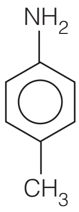
10 The correct increasing order of basic strength for the following compounds is ➞ **NEET 2017**



(I)



(II)

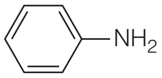


(III)

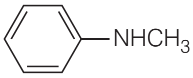
(a) II < III < I (b) III < I < II
(b) III < II < I (d) II < I < III

11 Which of the following is the strongest base?

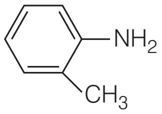
(a)



(b)



(c)



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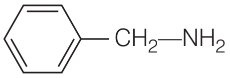


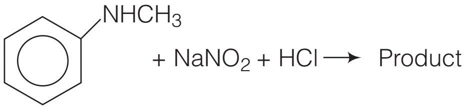
12 Which of the following is more basic than aniline?

(a) Diphenyl amine
(b) Triphenylamine
(c) *p*-nitroaniline
(d) Benzylamine

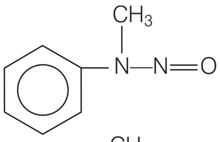
13 The compound obtained by heating a mixture of primary amine and chloroform with ethanolic potassium hydroxide (KOH) is

(a) an alkyl isocyanide (b) an alkyl halide
(c) an amide (d) an amide and nitro compound

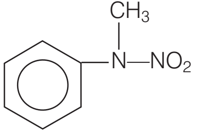
14 Predict the product,



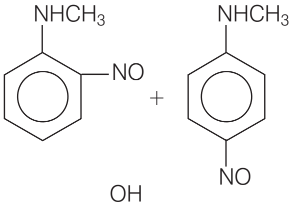
(a)



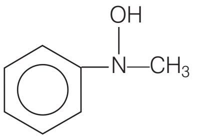
(b)



(c)



(d)



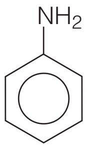
15 The electrolytic reduction of nitrobenzene in strongly acidic medium produces **➞ CBSE - AIPMT 2015**

(a) *p*-aminophenol (b) azoxybenzene
(c) azobenzene (d) aniline

16 Among the following compounds, the one that is most reactive towards electrophilic nitration is **➞ CBSE-AIPMT 2012**

(a) benzoic acid (b) nitrobenzene
(c) toluene (d) benzene

17 Electrophilic substitution reaction of with bromine gives which of the following product ?



(a) 4-bromoaniline (b) 1, 4, 6- tribromoaniline
(c) 2, 4, 6-tribromoaniline (d) 3-bromoaniline

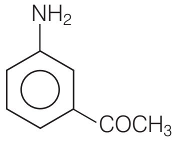
18 Nitration of aniline in strong acidic medium also gives *m*-nitroaniline because **➞ NEET-2018**

(a) in absence of substituents nitro group always goes to *m*-position
(b) in electrophilic substitution reactions amino group is *meta* directive
(c) in spite of substituents nitro group always goes to only *m*-position
(d) in acidic (strong) medium, aniline is present as anilinium ion

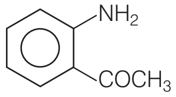
19 Nitrobenzene on reaction with conc. HNO_3 / H_2SO_4 at 80-100°C forms which one of the following products? **➞ NEET-2013**

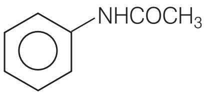
(a) 1, 2-dinitrobenzene (b) 1, 3-dinitrobenzene
(c) 1, 4-dinitrobenzene (d) 1, 2, 4-trinitrobenzene

20 Aniline is an activated system for electrophilic substitution. The compound formed on heating aniline with acetic anhydride is

(a)


(b)


(c)


(d)


21 $C_6H_5NH_2 \xrightarrow[180°C]{H_2SO_4} \underset{para}{H_2NC_6N_4(SO_3H)}$

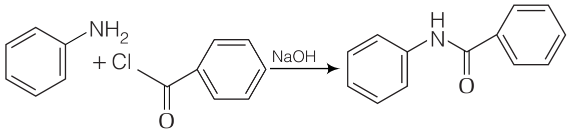
The true statement about the product is

(a) It does not exist as Zwitter ion
(b) —NH_2 displays a powerful basic character
(c) It does not act as inner salt
(d) —SO_3 diminishes the basic character of —NH_2

22 Which of the following compounds will not undergo Friedel-Crafts reaction easily? **➞ NEET 2013**

(a) Xylene (b) Nitrobenzene
(c) Toluene (d) Cumene

23 The following reaction,



is known by the name **➞ CBSE-AIPMT 2015**

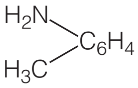
(a) Friedel-Craft reaction (b) Perkin's reaction
(c) Acetylation reaction (d) Schotten-Baumann reaction

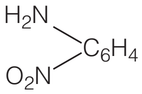
24 An aliphatic amine on treatment with alcoholic carbon disulphide and mercuric chloride forms ethyl isothiocyanate, the reaction is known as

(a) Hofmann reaction
(b) Hofmann rearrangement
(c) Hofmann mustard oil reaction
(d) Hofmann bromamide degradation reaction

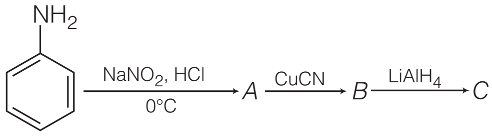
25 Which will not go for diazotisation?

(a) $C_6H_5NH_2$ (b) $C_6H_5CH_2NH_2$

(c)

$(H_2N)(H_3C)C_6H_4$

(d)

$(H_2N)(O_2N)C_6H_4$

26 In the reaction sequence,



The product '*C*' is

(a) benzonitrile (b) benzaldehyde
(c) benzoic acid (d) benzylamine

27 Dye test can be used to distinguish between

(a) ethylamine and acetamide
(b) urea and acetamide
(c) methylamine and ethylamine
(d) ethylamine and aniline

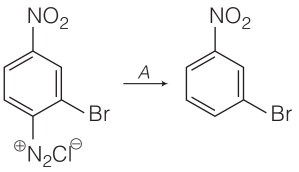
28 Which one of the following is not the correct reaction of aryl diazonium salts?

(a) $C_6H_5N_2^+Cl^- + Cu_2Cl_2 \longrightarrow C_6H_5Cl$
(b) $C_6H_5N_2^+Cl^- + HBF_4 \xrightarrow{Heat} C_6H_5F$
(c) $C_6H_5N_2^+Cl^- + H_3PO_2 \longrightarrow C_6H_5PO_4$
(d) $C_6H_5N_2^+Cl^- + SnCl_2 / HCl \longrightarrow C_6H_5NHNH_2$

29 A compound '*A*' has molecular formula C_7H_7NO. On treatment with Br_2 and KOH, '*A*' gives an amine which gives carbylamine test. '*B*' upon diazotisation and coupling with phenol gives azo dye. '*A*' can be

(a) $C_6H_5CONHCH_3$ (b) C_6H_5NO
(c) $C_6H_5CONH_2$ (d) *p*-$C_6H_4(NH_2)CHO$

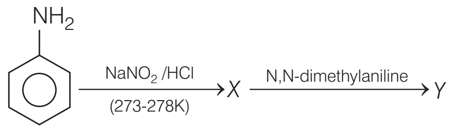
30 In the reaction,



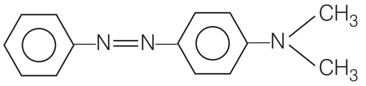
A is

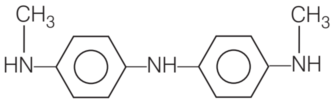
(a) Cu_2Cl_2 (b) H_3PO_3 and H_2O
(c) H^+ /H_2O (d) $HgSO_4$ / H_2SO_4

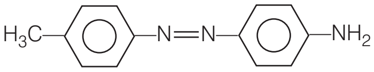
31 Aniline in a set of the following reactions yielded a coloured product '*Y*'.

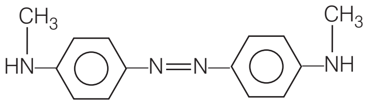


The structure of '*Y*' would be

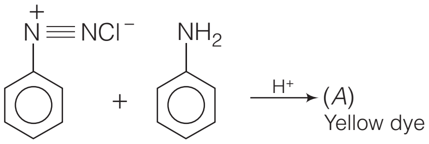
(a)


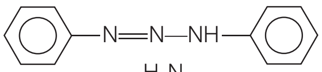
(b)


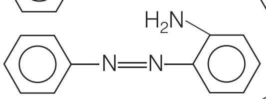
(c)


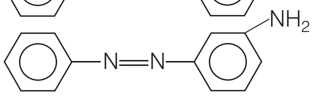
(d)


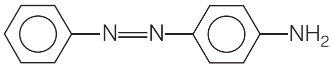
32 In the following reaction, the product (*A*) is



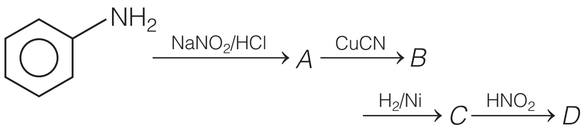
(a)


(b)


(c)


(d)


33 Aniline in a set of reactions yielded a product *D*



The structure of the product *D* would be

(a) $C_6H_5CH_2NH_2$
(b) $C_6H_5NHCH_2CH_3$
(c) C_6H_5NHOH
(d) $C_6H_5CH_2OH$

34 Consider the reaction, $CH_3CH_2CH_2Br + NaCN \longrightarrow CH_3CH_2CH_2CN + NaBr$

This reaction will be the fastest in **→ NEET 2016, Phase II**

(a) ethanol
(b) methanol
(c) N, N′-dimethylformamide (DMF)
(d) water

35 In the reaction,

$$CH_3CN + 2H \xrightarrow[SnCl_2]{HCl} X \xrightarrow{\text{Boiling } H_2O} Y,$$

The term *Y* is

(a) acetone
(b) ethanamine
(c) acetaldehyde
(d) dimethyl amine

36 Which of the following reactions is given by only primary amines?

(a) Reaction with HONO
(b) Reaction with $CHCl_3$ and alcoholic KOH
(c) Reaction with acetyl chloride
(d) Reaction with Grignard's reagent

37 Butane nitrile may be prepared by heating

(a) propyl alcohol with KCN
(b) butyl alcohol with KCN
(c) butyl chloride with KCN
(d) propyl chloride with KCN

38 Which is not the property of ethanenitrile (CH_3CN)?

(a) Undergoes acidic hydrolysis to give carboxylic acid
(b) Undergoes alkaline hydrolysis to give salt of carboxylic acid
(c) It tautomerises to give methyl isocyanide
(d) It gives carbylamine reaction with chloroform

DAY PRACTICE SESSION 2

PROGRESSIVE QUESTIONS EXERCISE

1 The best method to synthesise *m*-dibromobenzene using the reaction.

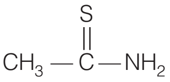
(a) Benzene $\xrightarrow{Br_2/Fe/Br_3/heat}$

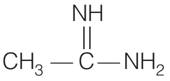
(b) Aniline $\xrightarrow{Br_2,\ H_2O} [\quad] \xrightarrow[2.\ CuBr]{1.\ HONO}$

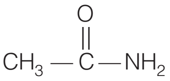
(c) Nitrobenzene $\xrightarrow[H_2SO_4,\Delta]{Fuming\ HNO_3} [\quad] \xrightarrow[C_2H_5OH,heat]{Fe/HCl} [\quad] \xrightarrow[2.\ CuBr]{1.\ HONO}$

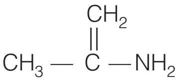
(d) Bromobenzene $\xrightarrow[H_2SO_4]{HNO_3} [\quad] \xrightarrow[C_2H_5OH,heat]{Fe/HCl} [\quad] \xrightarrow[2.\ CuBr]{1.\ HONO}$

2 The compound which is most basic in aqueous medium is

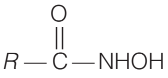
(a) 
$CH_3-\overset{\overset{S}{\|}}{C}-NH_2$

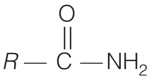
(b) 
$CH_3-\overset{\overset{NH}{\|}}{C}-NH_2$

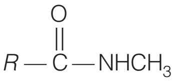
(c) 
$CH_3-\overset{\overset{O}{\|}}{C}-NH_2$

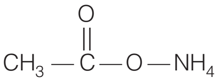
(d) 
$CH_3-\overset{\overset{CH_2}{\|}}{C}-NH_2$

3 Indicate which of the following nitrogen compound would undergo Hofmann's reaction (i.e. reaction with Br_2 and strong KOH) to furnish the primary amine ($R-NH_2$).

(a) 
$R-\overset{\overset{O}{\|}}{C}-NHOH$

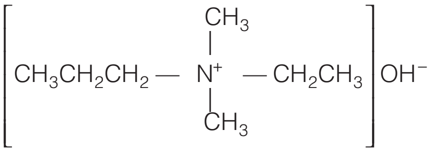
(b) 
$R-\overset{\overset{O}{\|}}{C}-NH_2$

(c) 
$R-\overset{\overset{O}{\|}}{C}-NHCH_3$

(d) 
$CH_3-\overset{\overset{O}{\|}}{C}-O-NH_4$

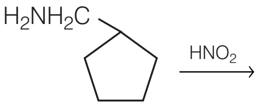
4 An aliphatic nitro compound turns red with the addition of a concentracted NaOH solution, followed by the addition of an excess of an $NaNO_2$ solution and then dilute H_2SO_4. The colour disappear with the addition of the excess of an acid but reappears if the solution is made alkaline. The aliphatic nitro compound is

(a) $CH_3CH_2NO_2$
(b) $(CH_3)_2\ CHNO_2$
(c) $(CH_3)_3\ CNO_2$
(d) All of these

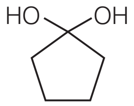
5 When 
$\left[CH_3CH_2CH_2-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{N^+}}}}-CH_2CH_3\right]OH^-$

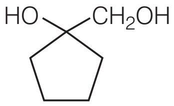
is heated, then

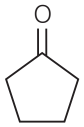
(a) propene is the major product
(b) ethene and $C_3H_7N\ (CH_3)_2$ are the only products.
(c) ethene and propene are obtained, while ethene as the major product
(d) equimolar amounts of ethene and propene are obtained

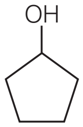
6 

? Product is

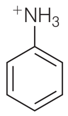
(a) 

(b) 

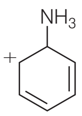
(c) 

(d) 

7. Examine the following two structures for the anilinium ion and choose the correct statement from the ones given below



(I)



(II)

(a) II is not acceptable as canonical structure because carbonium ions are less stable than ammonium ions
(b) II is not an acceptable canonical structure because it is non-aromatic
(c) II is not an acceptable canonical structure because in it N has 10 valence electrons
(d) II is an acceptable canonical structure

8 Choose the incorrect statement.

(a) In the case of primary, secondary and tertiary amines, the basic strength depends on the extent of hydrogen bonding in the protonated amines
(b) The presence of groups like $-OCH_3$ and $-CH_3$ increases the basic strength of amines
(c) The presence of groups like $-NO_2$ $-CN$ and halogens reduces the basic strength of amines
(d) The basic strength of amines depends on their concentration

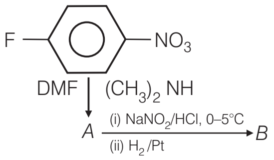
9 What is the decreasing order of basicity of 1°, 2° and 3° ethyl amines and ammonia?

(a) $NH_3 > C_2H_5NH_2 > (C_2H_5)_2NH > (C_2H_5)_3N$
(b) $(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$
(c) $(C_2H_5)_2NH > C_2H_5NH_2 > (C_2H_5)_3N > NH_3$
(d) $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$

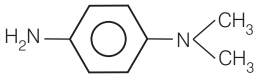
10 In the reaction of (S) 2-phenylpropamide with NaOBr/H_2O to give 1-phenylethylamine

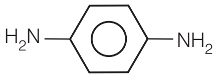
(a) there is retention of configuration
(b) there is inversion of configuration
(c) a mixuture of two products is obtained
(d) there is no reaction

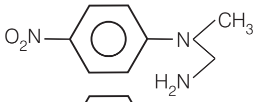
11



In the above sequence *B* is

(a) 

(b) 

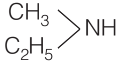
(c) 

(d) 

12 A compound of molecular formula C_3H_9N when reacts with benzene sulphonyl chloride gives a product soluble in dilute NaOH solution. The compound should be

(a) $(CH_3)_3N$

(b) $(CH_3)_2CH—NH_2$

(c) 

(d) All of the above

13 In the following reactions, reactants *A*, *B* and *C* are:

$C_2H_5NH_2 + A \longrightarrow C_2H_5N=CH—C_6H_5 + H_2O$

$\text{Urea} + B \longrightarrow H_2N—NHCONH_2 + NH_3$

$C_2H_5NH_2 + C \longrightarrow C_2H_5Cl + H_2O + N_2$

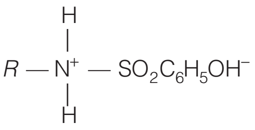
(a) $CH_3CHO, NH_2—NH_2$ and PCl_5

(b) $C_6H_5CHO, NH_2—NH_2$ and $SOCl_2$

(c) $C_6H_5CHO, NH_2—NH_2$ and NOCl

(d) CH_3CHO, $NH_2—NH_2$ and PCl_3

14 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

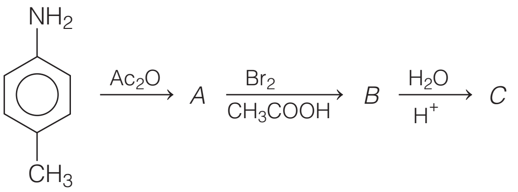
(a) 
$R—\overset{H}{\underset{H}{N^+}}—SO_2C_6H_5OH^-$

(b) $R—N^-SO_2C_6H_5K^+$

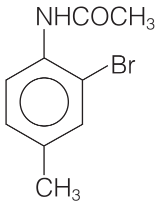
(c) $C_6H_5SO_2NH_2$

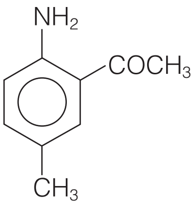
(d) $R—NH—SO_2—C_6H_5$

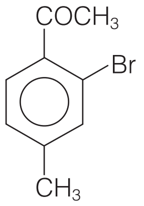
15

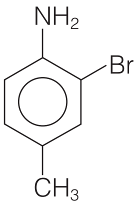


The final product '*C*' in the above reaction is

(a) 

(b) 

(c) 

(d) 

16 $Y \underset{Z}{\overset{\text{Reduction}}{\rightleftharpoons}} [R_2C=NH] \xrightarrow{H_3O^+} X$

In the above sequence of reactions *X, Y, Z* are respectively

(a) aldehyde, ketone, NH_3 (b) ketone, 1° amine, $KMnO_4$

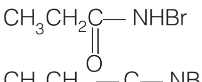
(c) ketone, 2° amine, $KMnO_4$ (d) ketimine, 1° amine, H_2SO_5

17 Given the following sequence of reactions,

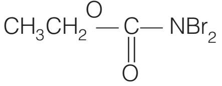
$$CH_3CH_2I \xrightarrow{NaCN} A \xrightarrow[\text{Partial hydrolysis}]{OH^-} B \xrightarrow{Br_2/NaOH} C$$

The major product '*C*' is

(a) $CH_3CH_2NH_2$

(b) 
$CH_3CH_2\underset{\underset{O}{\|}}{C}—NHBr$

(c) $CH_3CH_2—COONH_4$

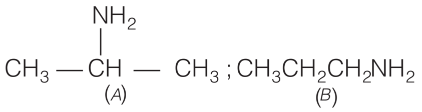
(d) 
$CH_3CH_2—\underset{\underset{O}{\|}}{C}—NBr_2$

18 An organic amino compound reacts with aqueous nitrous acid at low temperature to produce an oily nitrosoamine. The compound is

(a) CH_3NH_2 (b) $CH_3CH_2NH_2$

(c) $(CH_3CH_2)_3N$ (d) $CH_3CH_2—NHCH_2CH_3$

19 Two compounds (*A*) and (*B*) are treated with nitrous acid,


$\underset{(A)}{CH_3—\overset{NH_2}{\overset{|}{CH}}—CH_3}$; $\underset{(B)}{CH_3CH_2CH_2NH_2}$

The corresponding stable carbocation intermediates are

(From *A*) (From *B*)

(a) $CH_3—CH_2—\overset{+}{C}H_2$ $CH_3—CH_2—\overset{+}{C}H_2$

(b) $CH_3—\overset{+}{C}H—CH_3$ $CH_3—\overset{+}{C}H—CH_3$

(c) $CH_3—\overset{+}{C}H—CH_3$ $CH_3—CH_2—\overset{+}{C}H_2$

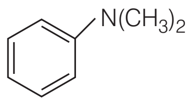
(d) None of the above

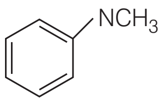
20 Toluene is nitrated and the resulting product is reduced with tin and hydrochloric acid. The product so obtained is diazotised and then heated with cuprous bromide. The reaction mixture so obtained contains

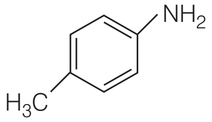
(a) mixture of *o*-and *p*-bromotoluenes

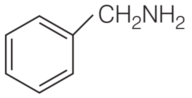
(b) mixture of *o*-and *p*-dibromobenzenes
(c) mixture of *o*-and *p*-bromoanilines
(d) mixture of *o*-and *m*-bromotoluenes

21 Amongst the compounds given, the one that would form a brilliant coloured dye on treatment with $NaNO_2$ in dil. HCl followed by addition to an alkaline solution of β-naphthol is

(a) 

(b) 

(c) 

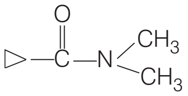
(d) 

ANSWERS

SESSION 1	**1** (a)	**2** (b)	**3** (c)	**4** (a)	**5** (c)	**6** (b)	**7** (d)	**8** (b)	**9** (d)	**10** (d)
	11 (d)	**12** (d)	**13** (a)	**14** (a)	**15.** (d)	**16** (c)	**17** (c)	**18** (d)	**19** (b)	**20** (d)
	21 (b)	**22** (b)	**23** (d)	**24** (c)	**25** (b)	**26** (d)	**27** (d)	**28** (c)	**29** (c)	**30** (b)
	31 (a)	**32** (d)	**33** (d)	**34** (c)	**35** (c)	**36** (b)	**37** (b)	**38** (d)		
SESSION 2	**1** (c)	**2** (c)	**3** (b)	**4** (a)	**5** (c)	**6** (d)	**7** (c)	**8** (d)	**9** (d)	**10** (a)
	11 (a)	**12** (b)	**13** (c)	**14** (b)	**15** (d)	**16** (b)	**17** (a)	**18** (d)	**19** (b)	**20** (a)
	21 (c)									

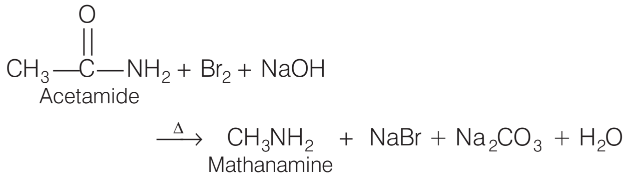
Hints and Explanations

SESSION 1

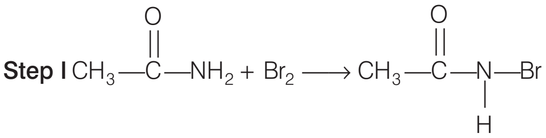
1 

N, N-dimethyl cyclopropane carboxamide

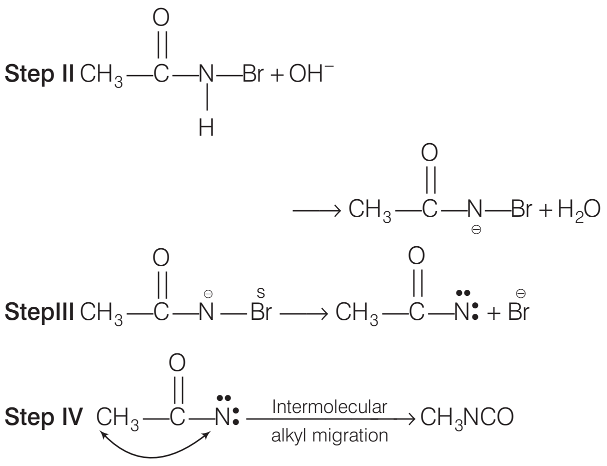
2 The conversion of amide with no substituent on nitrogen to an amine containing one carbon less by the action of alkaline hypobromide or bromine in presence of NaOH. This reaction is Hofmann's bromamide reaction. It involves the migration of alkyl or aryl group with its electron pair to electron deficient N from adjacent carbon. The reaction involves the intermediates of isocyanate.



$$\underset{\text{Acetamide}}{CH_3-\overset{O}{\overset{\|}{C}}-NH_2} + Br_2 + NaOH \xrightarrow{\Delta} \underset{\text{Mathanamine}}{CH_3NH_2} + NaBr + Na_2CO_3 + H_2O$$



$$\textbf{Step I}\ CH_3-\overset{O}{\overset{\|}{C}}-NH_2 + Br_2 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-Br$$



$$\textbf{Step II}\ CH_3-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-Br + OH^- \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-\underset{\ominus}{N}-Br + H_2O$$

$$\textbf{StepIII}\ CH_3-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{N}-\overset{s}{Br} \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-\ddot{N}\!: + \overset{\ominus}{Br}$$

$$\textbf{Step IV}\ CH_3-\overset{O}{\overset{\|}{C}}-\ddot{N}\!: \xrightarrow[\text{alkyl migration}]{\text{Intermolecular}} CH_3NCO$$

$$\textbf{Step V}\ CH_3NCO + 2OH^- \xrightarrow{\Delta} CH_3NH_2 + CO_3^{2-}$$

3 When amides react with bromine in the presence of caustic alkali to form a primary amine carrying one carbon atom less than the parent amide, then the reaction is known as Hofmann bromamide reaction.

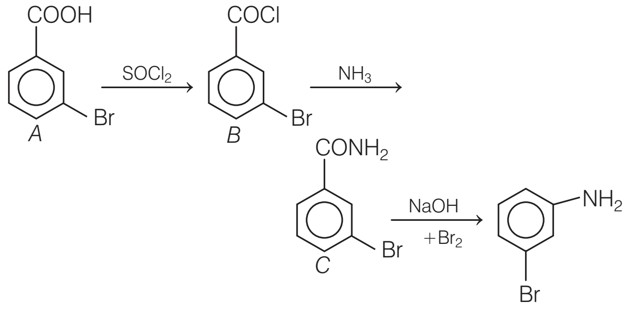
$$RCONH_2 + Br_2 + 4KOH \xrightarrow{\text{Heat}} RNH_2 + K_2CO_3 + 2KBr + 2H_2O$$

4 Among the given reagents, only NaOH/Br_2 converts —$CONH_2$ group to —NH_2 group, thus it is used for converting acetamide to methyl amine. This reaction is called **Hofmann bromamide reaction**, in which primary amides on treatment with Br_2 / NaOH form primary amines.

$$\underset{\text{Acetamide}}{CH_3CONH_2} + NaOH + Br_2 \longrightarrow \underset{\text{Methyl amine}}{CH_3NH_2} + NaBr + Na_2CO_3 + H_2O$$

5 $RX + \underset{\substack{\text{Potassium}\\\text{cyanide}}}{KCN} \longrightarrow RCN + KX \xrightarrow{\text{Reduction}} R—CH_2—NH_2$

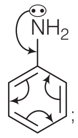
6



7 Due to resonance in chlorobenzene C—Cl bond acquires double bond character hence, C—Cl bond is inert towards nucleophile (phthalimide ion). Therefore, aniline cannot be prepared.

8 1° and 2° amines due to intermolecular H-bonding have higher boiling points and hence, less volatile than 3° amine and hydrocarbon which are almost non-polar. Therefore, due to weak dipole-dipole interactions, 3° amine have higher boiling point (i.e. less volatile) than hydrocarbons. In other words, $CH_3CH_2CH_3$ has the least boiling point and hence, is most volatile.

9



;

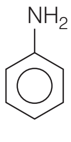
$R—\ddot{N}H_2$

Aryl amine (less basic)

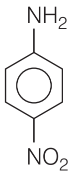
Alkyl amine (more basic)

Due to delocalisation of lone pair of electrons of N-atom to the benzene ring, it losses its basicity and becomes less basic than alkyl amine. On the other hand, alkyl amine has free lone pair of electron as well as +*I*-effect of alkyl group increases electron density on N-atom enhancing its basic nature.

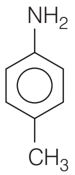
10 This type of problem can be solved by application of electron-withdrawing and electron-donating group.



(I)



(II)



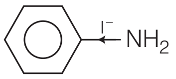
(III)

In III, —CH_3 group is an electron donating and *o* / *p* directing group which increase the electron density on benzene ring at *ortho or para* position while in II, —NO_2 group is an electron withdrawing group which decrease the electron density on benzene ring. Hence, the III is more basic than II. In I, there is no substituent attached, due to which I is more basic than II and less basic than III.

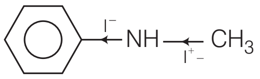
Therefore, the correct order of basic strength of above compounds is II < I < III.

11 CH_3— (an electron releasing (+*I* effect) group increases electron density at N-atom, due to which basic nature is increased.

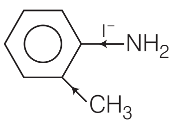
(a)



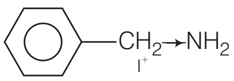
(b)



(c)



(d)



C_6H_5 decreases electron density at N-atom thus basic nature is decreased. (Lone-pair on N in aniline compounds is delocalised along with π-electrons in benzene).

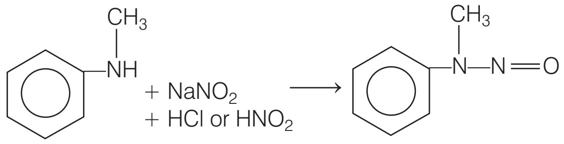
Thus, (d) is the strongest base.

12 Benzylamine is more basic than aniline because benzyl group is electron donating group due to +*I*-effect. Phenyl and nitro group are electron attractive groups so, they are able to decrease the electron density of N of —NH_2 group. Hence, they are less basic with aniline.

13 $RNH_2 + CHCl_3 + 3KOH(\text{alc.}) \longrightarrow \underset{\text{Alkyl isocyanide}}{RNC} + 3KCl + 3H_2O$

This reaction is known as carbylamine test.
(only 1° amine gives this reaction)

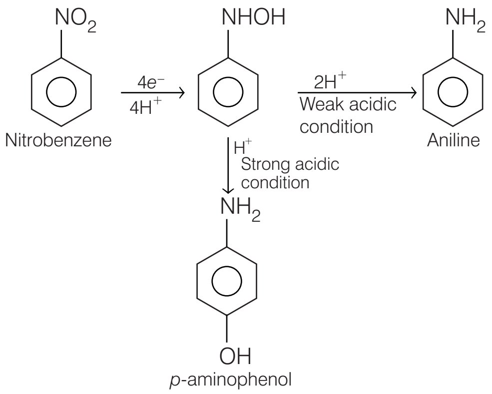
14 Both aliphatic and aromatic secondary amines reacts with $NaNO_2$ + HCl or (HNO_2) to form N-nitrosamines which are insoluble in dilute mineral acids and separate out as neutral yellow oily compounds.



N-methylaniline (2°amine)

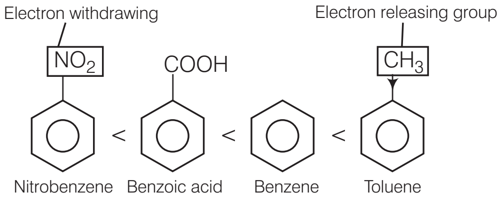
N-nitroso-N-methylaniline (nitroso compound) (yellow oily liquid)

15 Under weakly acidic conditions nitrobenzene on electrolytic reduction gives aniline but under strongly acidic conditions gives *p*-aminophenol.



16 Presence of electron releasing group like $-R$, —OH etc., increases the electron density at *o*/*p*-position and thus, makes the benzene ring more reactive (at *o*/*p*-positions) towards electrophile. On the other hand, electron withdrawing group like —COOH, $-NO_2$ etc., if present, reduces electron density and thus, reduces the activity of benzene nucleus towards electrophile.

Thus, the order of the given compounds towards electrophilic nitration is



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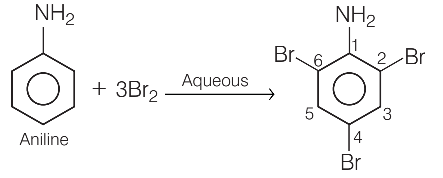
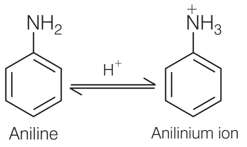
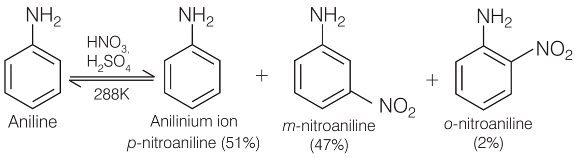


2, 4, 6-tribromoaniline

18 In strongly acidic medium, aniline is protonated to form the anilinium ion.



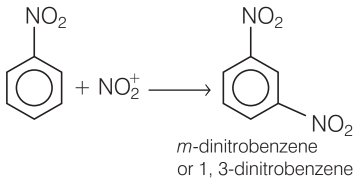
Since, anilinium ion so formed is *meta* directing, thus besides *ortho* and *para* derivatives, significant amount of *meta* derivative is also formed.



19 NO_2 group being electron withdrawing that's why it reduces the electron density at *ortho* and *para*-positions. Hence, as compare to *ortho* and *para* the *meta*-position is electron rich on which the electrophile (nitronium ion) can easily attacks during nitration.

$$HNO_3 + H_2SO_4 \longrightarrow H_2NO_3^+ + HSO_4^-$$
$$\downarrow$$
$$H_2O + NO_2^+$$

Electrophile
(nitronium ion)



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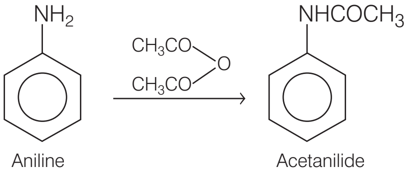
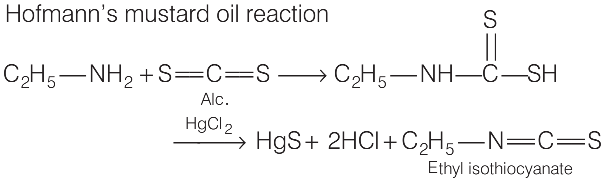


21 Sulphanilic acid exists as a dipolar ion (Zwitter ion) it diminishes the basic character of $-NH_2$.

22 Nitrobenzene is strongly deactivated, hence will not undergo Friedel-Crafts reaction.

23 Schotten-Baumann reaction is a method to synthesise amides from amines and acid chlorides.

24 Hofmann's mustard oil reaction



$$C_2H_5-NH_2 + S=C=S \longrightarrow C_2H_5-NH-\overset{\overset{S}{\|}}{C}-SH$$
$$\xrightarrow[\text{HgCl}_2]{\text{Alc.}} HgS + 2HCl + C_2H_5-N=C=S$$

Ethyl isothiocyanate

25 A reaction in which $-NH_2$ group is converted into diazo group $(-\overset{+}{N}\equiv N)$ at low temperature (0–5°C) is called diazotisation.Only 1° aromatic amine (primary aromatic amine) form diazonium salts. Diazotised salts are stable in cold aqueous solution.

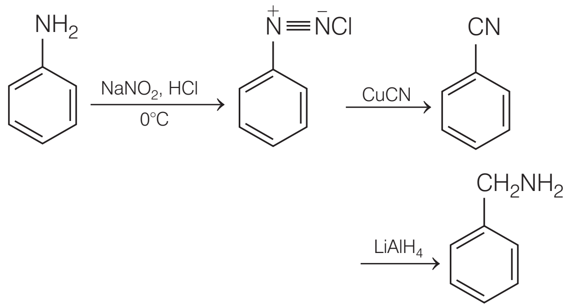
$$C_6H_5NH_2 + HCl \xrightarrow{0-5^\circ C} C_6H_5\overset{+}{N}H_3Cl^-$$

$$NaNO_2 + HCl \xrightarrow{0-5^\circ C} HNO_2 + NaCl$$

$$C_6H_5\overset{+}{N}H_3Cl^- + HNO_2 \xrightarrow{0-5^\circ C} C_6H_5\overset{+}{N}_2Cl^- + 2H_2O$$

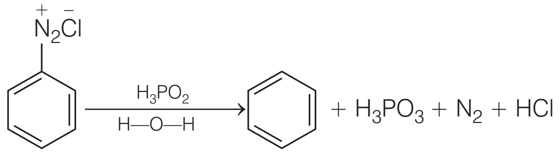
Hence, in the option a, c, d, the NH_2 group is directly bonded to benzene ring and easy to form diazo compound. In option (b), the CH_2 group prevents the diazotisation.

26



27 $C_6H_5NH_2$ (aromatic amine) gives dye test where as ethylamine (aliphatic amine) does not.

28

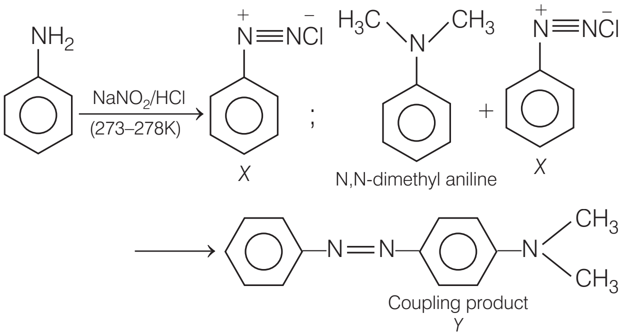


29 $$\underset{A}{C_6H_5CONH_2} \xrightarrow{Br_2 + KOH} \underset{B}{C_6H_5NH_2}$$

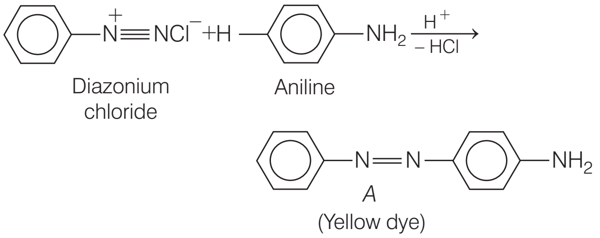
Aniline (*B*) upon diazotisation and coupling with phenol gives azo dye.

30 H_3PO_3 and H_2O reduced the $—\overset{+}{N}_2Cl^-$ to —H

31 $NaNO_2/HCl$ causes diazotisation of $—NH_2$ group and the diazonium chloride gives a coupling product with active aryl nucleus.



32 The complete reaction is

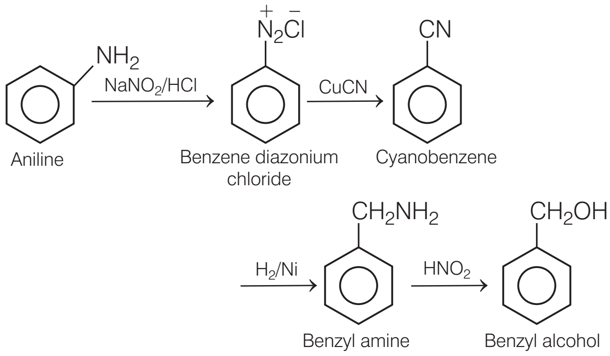


(Yellow dye)

(*p* -azo benzene compound)

The above reaction is a **coupling reaction** of aniline with diazonium salt to give azo benzene compound. This coupling reaction takes place at the *para*-position to $—NH_2$ group of benzene. This reaction act as electrophilic substitution reaction of aniline.

33



34 The given reaction follows S_N2 mechanism and S_N2 reactions are favoured in polar aprotic medium like DMSO, DMF... etc.

$$CH_3CH_2CH_2Br + NaCN \xrightarrow{DMF} CH_3CH_2CH_2CN + NaBr$$

So, the correct option is (c).

35 $$SnCl_2 + 2HCl(g) \longrightarrow SnCl_4 + 2[H]$$

$$CH_3CN + 2[H] + HCl \longrightarrow \underset{X}{CH_3CH{=}NH\cdot HCl}$$

$$\xrightarrow[\text{boil}]{H_2O} \underset{Y}{CH_3CHO} + NH_4Cl$$

36 $$\underset{1^\circ\text{-}amine}{RNH_2} + CHCl_3 + 3KOH \xrightarrow{\Delta} RNC + 3KCl + 3H_2O$$

37 $$\underset{\text{Propyl chloride}}{CH_3CH_2CH_2Cl} + KCN \longrightarrow \underset{\text{Butane nitrile}}{CH_3CH_2CH_2CN} + KCl$$

38 (a) CH_3CN undergoes acidic hydrolysis to give carboxylic acid.

$$CH_3CN \xrightarrow{H_2O/H^+} CH_3CONH_2 \xrightarrow{H_2O/H^+} \underset{\text{Acetic acid}}{CH_3COOH} + NH_3$$

(b) CH_3CN undergoes alkaline hydrolysis to give salt of carboxylic acid.

$$CH_3CN \xrightarrow[H_2O]{NaOH} CH_3CONH_2 \xrightarrow[H_2O]{NaOH} \underset{\text{Sodium acetate}}{CH_3COONa} + NH_3$$

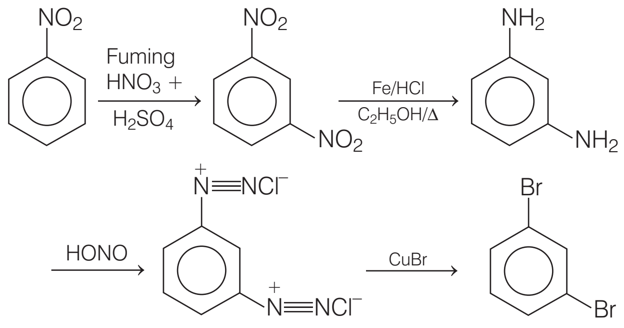
(c) CH_3CN tautomerises to give methyl isocyanide.

$$CH_3—C\equiv N \rightleftharpoons C \overset{\leftarrow}{=} N—CH_3$$

(d) Carbylamine reaction is given by aliphatic and aromatic primary amines both. CH_3CN does not give carbylamine reaction with chloroform because it is not an amine both.

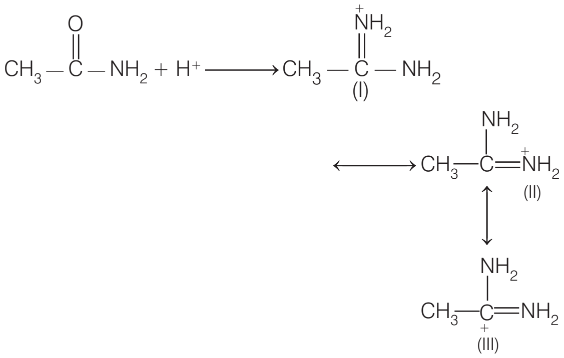
SESSION 2

1



m-dibromobenzene

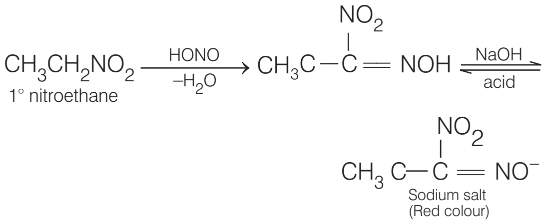
2 After gain of H^+, it shows three resonating structures and hence, becomes more stable.



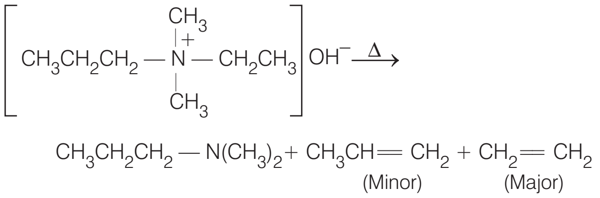
3 Hofmann's degradation of amide

$$RCONH_2 + Br_2 + 4KOH \longrightarrow \underset{\text{Primary amine}}{R-NH_2} + 2KBr + K_2CO_3 + 2H_2O$$

4 Primary nitroalkanes when treated with nitrous acid form nitrolic acid which when dissolve in alkali gives, salt of nitrolic acid, which is red in colour. In excess of acid, the salt dissociates, thus colour disappears while in excess of alkali the red colour reappears.



5 In Hofmann elimination reaction, less substituted alkene is the main product.



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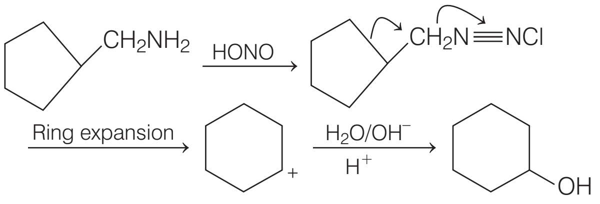


7 In canonical structure, N can not have 10 valence electrons so, structure II is not acceptable.

8 Concentration does not affect the basic strength of amines. Thus, option (d) is incorrect.

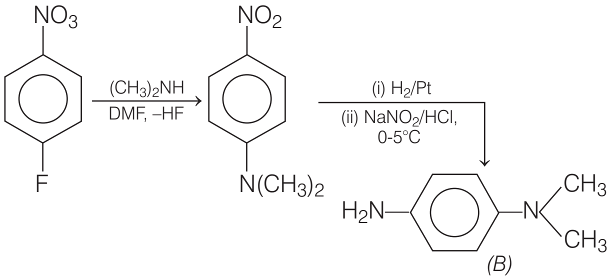
9 (d) As the number of alkyl groups increases, the electron density on nitrogen atom also increases, so the basic character increases but 3° amines are less basic than 2° amines due to steric hindrance of 3° amines, so the correct order of basicity is :

Ammonia < 1° < 3° < 2°

$$NH_3 < C_2H_5NH_2 < (C_2H_5)_3N < (C_2H_5)_2NH$$

10 Hofmann bromamide degradation takes place with complete retention of stereochemical configuration in the migrating alkyl group.

11



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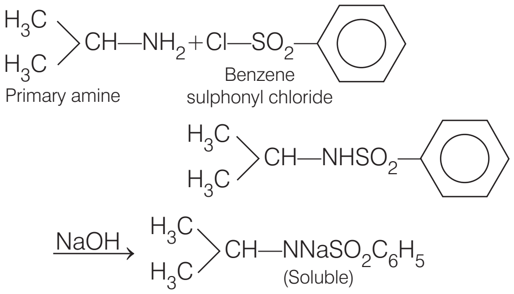

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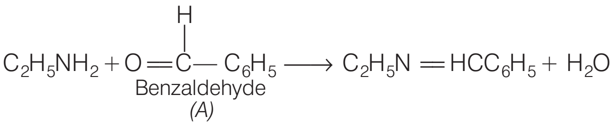


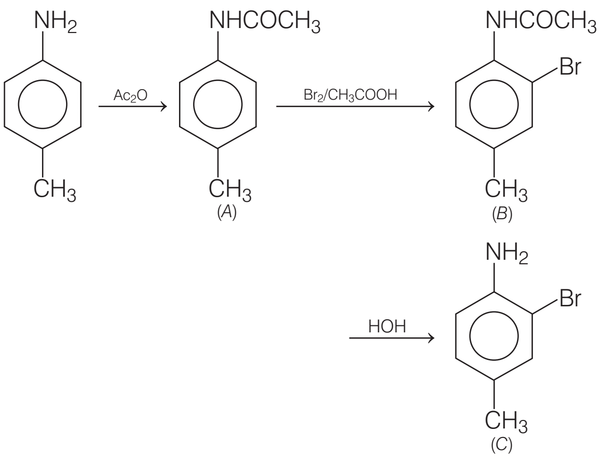
$$C_2H_5NH_2 + \underset{\underset{(A)}{\text{Benzaldehyde}}}{O = \overset{\overset{\displaystyle H}{|}}{C} - C_6H_5} \longrightarrow C_2H_5N = HCC_6H_5 + H_2O$$

$$\underset{\text{Urea}}{NH_2CO\boxed{NH_2 \; + H}} \underset{\underset{(B)}{\text{Hydrazine}}}{NH \cdot NH_2} \longrightarrow NH_2CONHNH_2 + NH_3$$

$$\underset{(C)}{C_2H_5NH_2} + NOCl \longrightarrow C_2H_5Cl + H_2O + N_2$$

14 $$\underset{\substack{\text{Benzene sulphonyl}\\ \text{chloride}}}{C_6H_5SO_2Cl} + RNH_2 \longrightarrow \underset{\substack{\text{N-alkyl benzene}\\ \text{sulphonamide}}}{RNHSO_2C_6H_5} \xrightarrow{KOH} \underset{\text{(Soluble in KOH)}}{R—NKSO_2C_6H_5K^+}$$

15



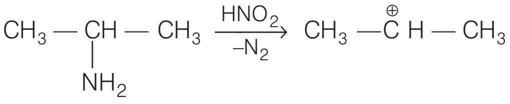
16 $$\underset{\substack{1° \text{ amine}\\(Y)}}{R_2CH—NH_2} \underset{\substack{KMnO_4\\(Z)}}{\overset{[O]}{\rightleftharpoons}} [R_2C{=}NH] \xrightarrow{H_3O^+} \underset{\substack{\text{Ketone}\\(X)}}{R_2C{=}O}$$

17 $$CH_3CH_2\,I \xrightarrow{NaCN} CH_3CH_2CN \xrightarrow{OH^-} CH_3CH_2CONH_2 \xrightarrow{Br_2/NaOH} CH_3CH_2NH_2$$

18 Secondary amines give oily nitrosoamine with nitrous acid.

$$\underset{\text{Secondary amine}}{(CH_3CH_2)_2NH} + \underset{\substack{\text{Nitrous}\\ \text{acid}}}{HNO_2} \longrightarrow \underset{\text{Oily nitrosoamine}}{(CH_3CH_2)_2N—NO} + H_2O$$

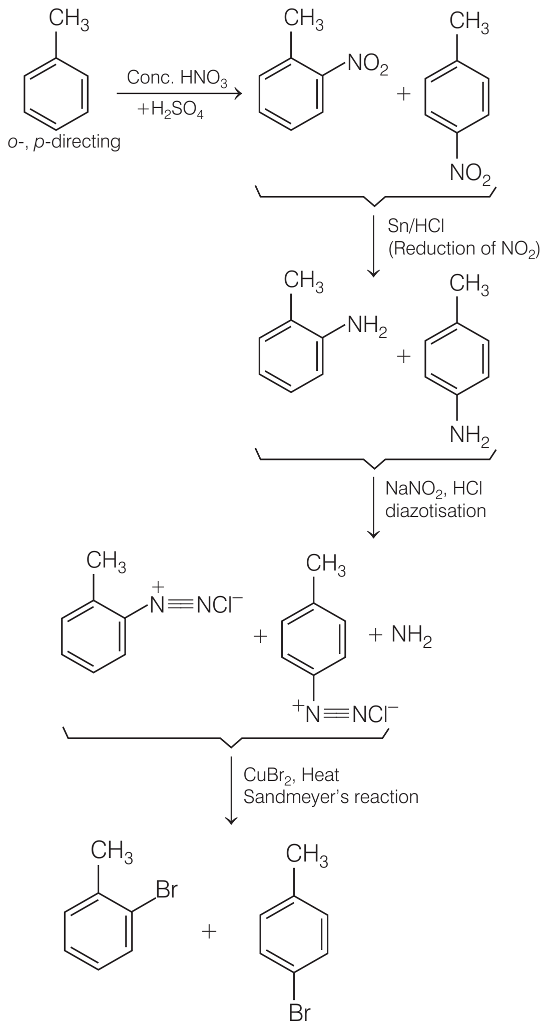
19



$$\underset{(A)}{CH_3—\underset{\substack{|\\NH_2}}{CH}—CH_3} \xrightarrow[-N_2]{HNO_2} CH_3—\overset{\oplus}{C}H—CH_3$$

$$\underset{(B)}{CH_3—CH_2—CH_2NH_2} \xrightarrow{HNO_3} \underset{1° \text{ carbocation}}{CH_3CH_2\overset{\oplus}{C}H_2} \xrightarrow{1,2\text{-hydride shift}} \underset{\substack{2° \text{ carbocation}\\ \text{(More stable)}}}{CH_3\overset{\oplus}{C}HCH_3}$$

20



o-and *p*-bromotoluenes

21 As we know, benzenediazonium salt forms brilliant coloured dye with β-naphthol, the compound under consideration must be *p* -toluidine (c) as it is a primary aromatic amine. Primary aromatic amine on treatment with $NaNO_2$ in dil. HCl forms the corresponding diazonium chloride salt.