UNIT 13

ORGANIC COMPOUNDS CONTAINING NITROGEN

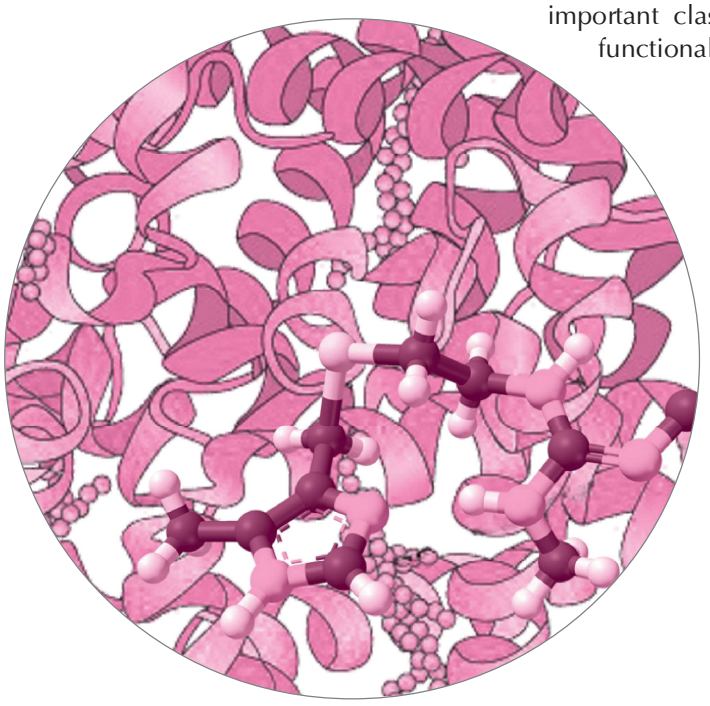
(Amino, Cyano and Diazo Compound

OBJECTIVES

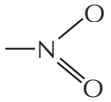
Building on.....

Assessing.....

Preparing for Competition.....



Nitrogen is also an important constituent of many organic compounds. The important classes of organic compounds containing nitrogen as a part of functional group are :

Functional group	Class of compounds	General formula
—NH_2	(i) Primary amines	RNH_2
	(ii) Secondary amines	R_2NH
	(iii) Tertiary amines	R_3N
—C≡N	Cyanides	RCN
—N≡C	Isocyanides	R NC
	Nitro compounds	RNO_2
—O—N=O	Nitrites	RONO
$—N_2^+X^-$	Diazonium salts	$ArN_2^+X^-$

PART A

AMINES

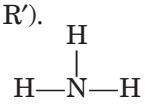
Amines are regarded as derivatives of ammonia in which one, two or all three hydrogen atoms are replaced by alkyl or aryl group.

$$NH_3 \xrightarrow[-H]{+R} RNH_2 \xrightarrow[-H]{+R} R_2NH \xrightarrow[-H]{+R} R_3N$$

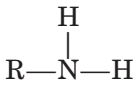
Amines constitute an important class of organic compounds. They occur widely throughout both plants and animals. They are found among proteins, vitamins, alkaloids, hormones etc. Synthetic examples include polymers, drugs, dyestuffs etc. These amines find extensive uses. For example, **quinine** is an important anti-malarial drug, **adrenaline** and **ephedrine** are used for increasing blood pressure, **novacain** is used as anaesthetic in dentistry, **codeine** is used as analgesic (pain killer), **benadryl** is used as antihistaminic drug. Quaternary ammonium salts are used as surfactants.

CLASSIFICATION OF AMINES

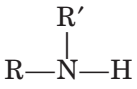
The amines are classified as ***primary (1°)***, ***secondary (2°)*** *or* ***tertiary (3°)*** *according as one, two or three hydrogen atoms of ammonia molecule are replaced by alkyl or aryl groups in ammonia molecule*. If one hydrogen atom of ammonia is replaced by alkyl (R) or aryl group (Ar), we get RNH_2 or $ArNH_2$, a primary (1°) amine. If two H atoms of ammonia or one H atom of RNH_2 is replaced by another alkyl (R′) or Ar group, we get R—NH—R′, which is a 2° amine. The second alkyl or aryl group may be same or different. Replacement of all the three H atoms of ammonia or another H atom of R—NH—R′ by alkyl (R″) or aryl group gives R—N(R′)R″, which is a 3° amine (R″ may be same or different than R or R′).



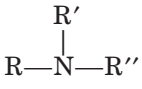
Ammonia



Primary amine (1°)



Secondary amine (2°)



Tertiary amine (3°

(where R, R′ and R″ are alkyl groups).

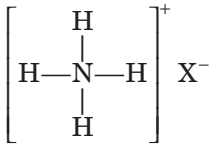
The characteristic groups in primary, secondary and tertiary amines are :

(amino)

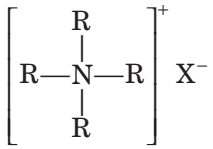
(imino)

(*tert*-nitrogen)

Apart from these three types of amines, there is another class of compounds known as **quaternary ammonium compounds.** These compounds may be regarded as derivatives of ammonium salts in which all the four H-atoms are replaced by alkyl or aryl groups. For example,



Ammonium salt

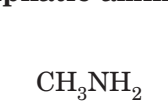


Tetraalkyl ammonium salt

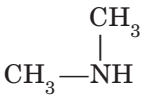
e.g., $[(CH_3)_4N]^+I^-$ Tetramethyl ammonium iodide; $[(C_2H_5)_4N]^+Cl^-$ Tetraethyl ammonium chloride; $[(C_2H_5)_4N]^+OH^-$ Tetraethyl ammonium hydroxide; $[(C_6H_5)_4N]^+Br^-$ Tetraphenyl ammonium bromide

Amines may further be classified into two categories :

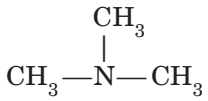
1. Aliphatic amines. *Amines in which the nitrogen atom is directly bonded to one or more alkyl* groups are called **aliphatic amines.** For example,



Methylamine (1°)



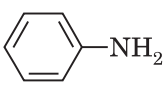
Dimethylamine (2°)



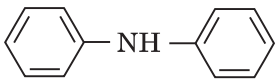
Trimethylamine (3

2. Aromatic amines. These are of two types :

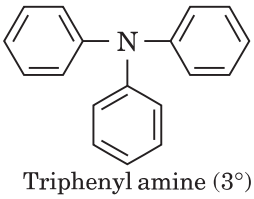
(*a*) Aryl amines. *Amines in which the nitrogen atom is directly bonded to one or more (same or different) aromatic rings or aryl groups are called* **aromatic amines.** For example,



Aniline (1°)

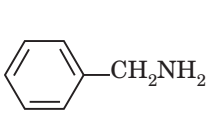


Diphenyl amine (2°)

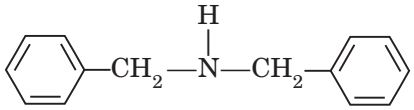


Triphenyl amine (3°)

(*b*) Arylalkyl amines or **side chain substituted amines.** *Amines in which the nitrogen atom is bonded to the side chain of the aromatic ring* are called **arylalkyl amines.** For example,



Benzylamine (1°)



Dibenzylamine (2°)

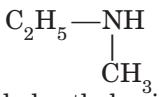
or $(C_6H_5CH_2)_2NH$ $_6H_5CH_2)_3N$

Tribenzylamine (3°)

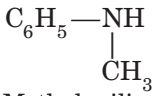
Simple and mixed amines. Secondary and tertiary amines may be classified as **simple** or **mixed amines** according as all the alkyl or aryl groups attached to the nitrogen atom are same or different. For example,

Simple amines : $(CH_3)_2NH$ Dimethylamine; $(CH_3CH_2)_3N$ Triethylamine; $(C_6H_5)_2NH$ Diphenylamine

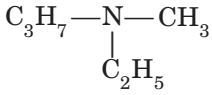
Mixed amines :



Ethylmethylamine



Methylaniline



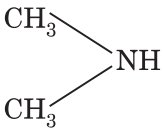
Ethylmethyl-*n*-propylamine

NOMENCLATURE OF AMINES

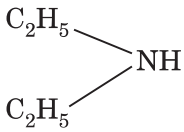
1. Aliphatic amines

Common names. According to **common system,** amines are called **alkylamines** by adding the suffix **amine** to the name of the corresponding **alkyl groups.** In secondary and tertiary amines, when two or more groups are the same, the prefix *di* or *tri* is used before the name of alkyl group. For example,

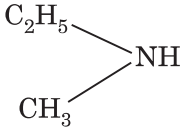
CH_3NH_2 Methylamine; $C_2H_5NH_2$ Ethylamine; $C_3H_7NH_2$ Propylamine



Dimethylamine



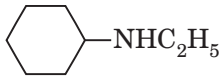
Diethylamine



Methylethylamine

$(C_2H_5)_3N$ Triethylamime

$(C_2H_5)_2NCH_2CH_2CH_2CH_3$ N, N-Diethylbutylamine



N-Ethylcyclohexylamine

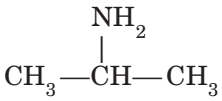
According to **second system,** primary amines are named as the **amino (—NH_2) derivatives** of the corresponding hydrocarbons and are called **aminoalkanes.** In this system, the primary amines are named by adding the **prefix amino** to the name of the parent alkane corresponding to the longest possible straight chain.

The position of the amino group and of the substituents (if any) are indicated by Arabic numerals. While numbering the chain, the carbon atom containing the amino group should get the lowest possible number.

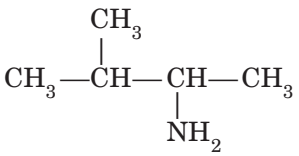
The secondary and tertiary amines are named as *nitrogen substituted primary amine, i.e.,* N-alkylaminoalkanes. While naming these, the word *N-alkyl or N, N-dialkyl* is prefixed to the word amino alkane. The prefixes N and N, N- mean that the alkyl groups are attached to the nitrogen atom rather than to the carbon atom. It may be noted that *if the two or three substituents are different, then the largest alkyl group forms the parent alkane (amino alkane) and the smaller alkyl groups are regarded as substituents.* For example,

$CH_3NHCH_2CH_3$ is named as N-methylaminoethane and not as N-ethylaminomethane

$CH_3CH_2NH_2$ Aminoethane

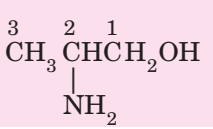


2-Aminopropane

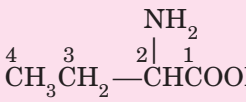


3-Methyl-2-aminobutane

Note : Earlier this method was recommended by IUPAC. However, according to latest IUPAC recommendations, this system is used only for naming amines which have a group of higher priority than —NH_2 group. For example,

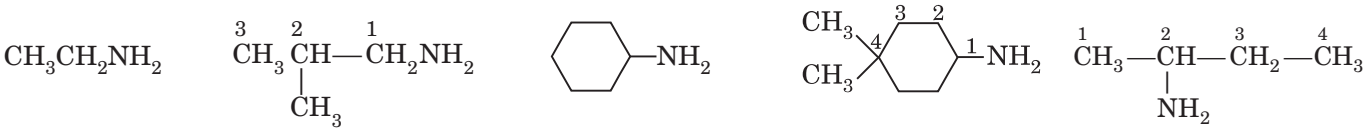


: 2-Aminopropan-1-ol



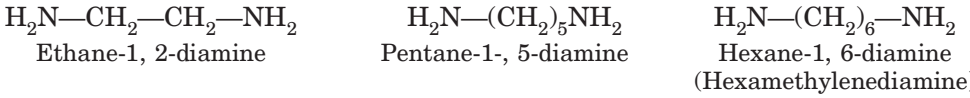
: 2-Aminobutanoic acid

IUPAC names. In the latest **IUPAC system**, the aliphatic amines are also called **alkanamines.** These names are written by replacing **'e'** of the name of parent alkane by suffix **'amine'.** For example, CH_3NH_2 may be named as methanamine. Similarly,



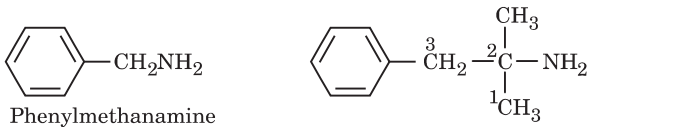
Ethanamine 2-Methylpropan-1-amine Cyclohexanamine 4, 4-Dimethylcyclohexanamine Butan-2-amine

In case more than one amino group is present at different positions in the parent chain, their positions are specified by giving numbers to the carbon atom bearing —NH_2 groups and suitable prefix such as *di*, *tri*, etc is attached to the amine. The letter '***e***' of the suffix of the hydrocarbon part is retained. For example,



Ethane-1, 2-diamine Pentane-1-, 5-diamine Hexane-1, 6-diamine (Hexamethylenediamine)

It may be noted that in case of **aralkylamines,** the position of aryl group on the aliphatic carbon chain is indicated. For example,



Phenylmethanamine 2-Methyl-3-phenylpropan-2-amine

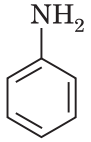
The common and IUPAC names of a few aliphatic amines and aralkylamines are given below :

Amine	Common name	IUPAC name
CH_3NH_2	Methylamine or Aminomethane	Methanamine
$C_2H_5NH_2$	Ethylamine or Aminoethane	Ethanamine
$CH_3CH_2CH_2NH_2$	*n*-Propylamine or 1-Aminopropane	Propan-1-amine
$CH_3CH(NH_2)CH_3$	Isopropylamine or 2-Aminopropane	Propan-2-amine
CH_3NHCH_3	Dimethylamine or N-Methylaminomethane	N-Methylmethanamine
$CH_3CH_2NHCH_3$	Ethylmethylamine or N-Methylaminoethane	N-Methylethanamine
$(CH_3)_3N$	Trimethylamine or N, N-Dimethylaminoethane	N, N-Dimethylmethanamine
$C_2H_5N(CH_3)_2$	Ethyldimethylamine or N, N-Dimethylaminoethane	N, N-Dimethylethanamine
$CH_3CH_2N(CH_2CH_3)CH_3$	Diethylmethylamine or N-Ethyl-N-methylaminoethane	N-Ethyl-N-methylethanamine
$C_2H_5N(C_2H_5)CH_2CH_2CH_2CH_3$	N, N-Diethylbutylamine	N, N-Diethylbutan-1-amine
Aralkylamines		
$C_6H_5CH_2NH_2$	Benzylamine or phenylaminomethane	Phenylmethanamine
$C_6H_5CH_2CH_2NH_2$	β-Phenylethylamine or 2-Phenylaminoethane	2- Phenylethanamine

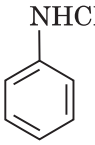
2. Aromatic amines

In common system, aromatic amines are called **aryl amines.** These are written by adding the suffix **amine** to the name of the aryl group. The simplest amine is $C_6H_5NH_2$ and it is known as ***aniline***. It is also accepted IUPAC name. The other simple aromatic amines are named as *derivatives of aniline.*

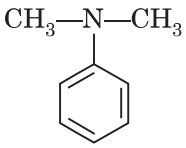
In the **IUPAC system,** the simplest aromatic amine $C_6H_5NH_2$ is called **benzenamine.** Other aromatic amines are named as derivatives of benzenamine and the positions of other groups are indicated by numbers. For example,



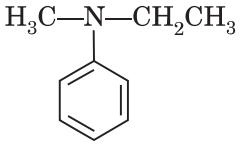
Benzenamine
(Aniline)



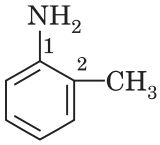
N-Methylbenzenamine
(N-Methylaniline)



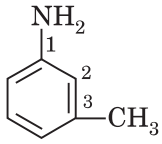
N, N-Dimethylbenzenamine
N, N-Dimethylaniline)



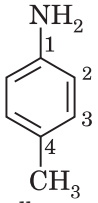
N-Ethyl-N-methylbenzenamine
(N-Ethyl-N-methylaniline)



2 Methylbenzenamine
(2-Methylaniline or *o*-Toluidine)

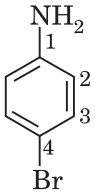


3-Methylbenzenamine
(3-Methylaniline or *m*-Toluidine)

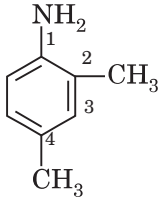


4-Methylbenzenamine
(4-Methylaniline or *p*-Toluidine)

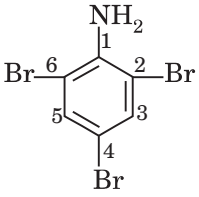
In IUPAC system, benzenamine may also be written as *amino benzene.*



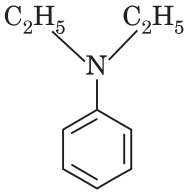
4-Bromobenzenamine
(4-Bromoaniline)



2, 4 imethylbenzenamine
(2, 4-Dimethylaniline)

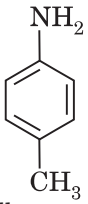


2,4, 6-Tribromobenzenamine
(2, 4, 6-Tribromoaniline)

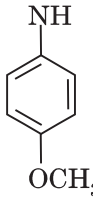


N, N-Diethylbenzenamine
N, N-Diethylaniline)

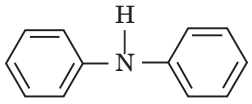
It may be noted that in some cases other names such as *o*/*m*/*p*-toluidine for *o*/*m*/*p*-methylaniline and *o*/*m*/*p*-anisidine for *o*/*m*/*p* methoxy aniline are assigned. Even N-phenyl derivative of aniline is generally called diphenylamine.



4-Methylbenzenamine
or 4-Methylaniline
(*p*-Toluidine)

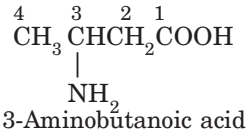


4-Methoxybenzenamine
or 4-Methoxyaniline
(*p*-Anisidine)

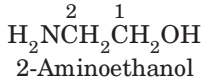


N-Phenylbenzenamine
or N-Phenylaniline
(Diphenylamine)

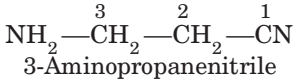
In case of poly functional groups, the amino group is considered as substituent and the other group constitutes the principal functional group and is preferred (in getting lowest position). The compound is named as derivative of the principal functional group.



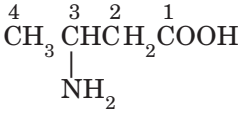
3-Aminobutanoic acid



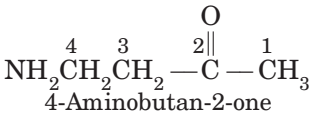
2-Aminoethanol



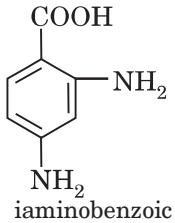
3-Aminopropanenitrile



3-Aminobutanoic acid

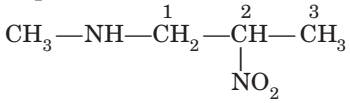


4-Aminobutan-2-one



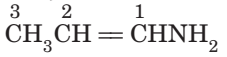
2, 4 iaminobenzoic acid

If, however, all the functional groups are substituent functional groups, the compound is named as a derivative of the compound containing the functional group which comes first in the alphabetical order.

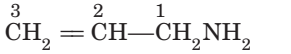


N-Methyl-2-nitropropanamine

In case of unsaturated amines, the amino group is given the preference. For example,



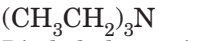
Prop-1-en-1-amine

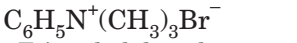


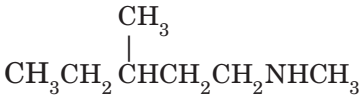
Prop-2-en-1-amine (allylamine)

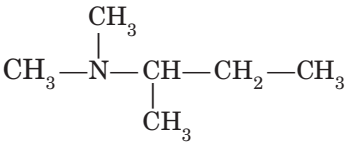
IUPAC Names of Some Complicated Amines

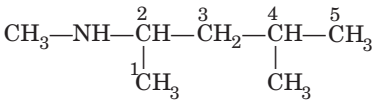

N-Ethyl-N-methylpropan-1-amine

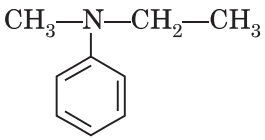

N, N-Diethylethanamine

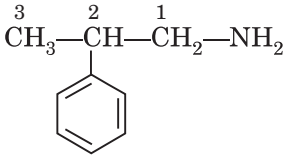

Trimethylphenyl ammonium bromide or Trimethylanilinium bromide

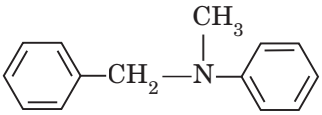

3-Methyl-1-(N-methylamino) pentane or 3-Methyl-1-N-methylpentan-1-amine

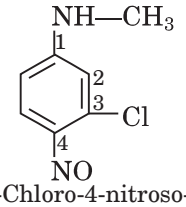

2-(N, N-Dimethylamino) butane or 2-(N, N-Dimethyl) butanamine


4-Methyl-N-methylpentan-2-amine


N-Ethyl-N-methylbenzenamine


2-Phenylpropan-1-amine


N-Benzyl-N-methylbenzenamine

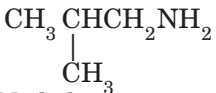

3-Chloro-4-nitroso-1-(N-Methyl) benzenamine

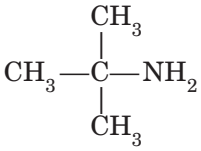
ISOMERISM IN AMINES

Amines exhibit the following types of isomerism:

1. Chain isomerism. Aliphatic amines containing four or more carbon atoms show chain isomerism due to the difference in the nature of carbon chain of alkyl groups attached to the amino group. For example,


Butan-1-amine

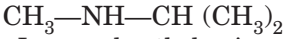

2-Methylpropan-1-amine


Methylpropan-2-amine

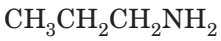
2. Metamerism. This is due to difference in the nature of alkyl groups attached to the same functional group. For example,

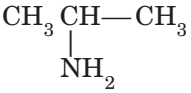

Diethylamine


Methyl-*n*-propylamine


Isopropylmethylamine

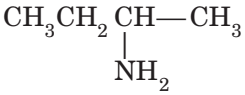
3. Position isomerism. This is due to the difference in position of amino group. For example,


Propan-1-amine

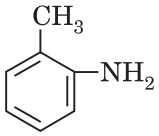

Propan-2-amine

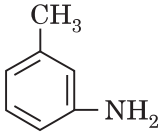
Similarly,

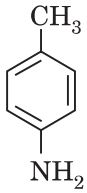

Butan-1-amine


Butan-2-amine

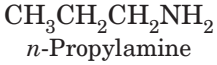
Aromatic amines also show position isomerism.

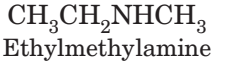

o-Toluidine

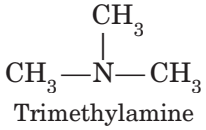

m-Toluidine


p-Toluidine

4. Functional isomerism. Primary, secondary and tertiary amines having the same molecular formula show functional isomerism among themselves because of the nature of amino groups. For example,

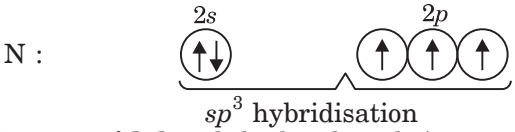

n-Propylamine (1°)


Ethylmethylamine (2°)

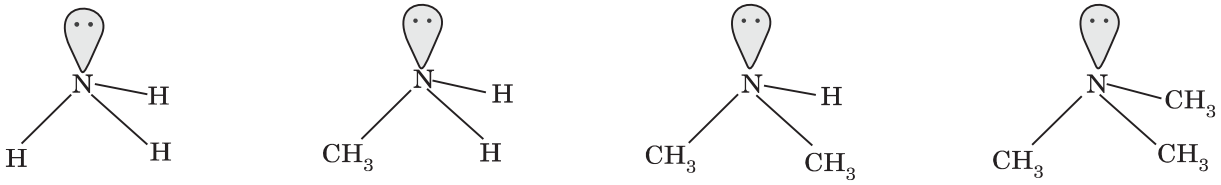

Trimethylamine (3°)

STRUCTURE OF AMINES

Amines are the derivatives of ammonia in which one or more hydrogen atoms have been replaced by alkyl (or aryl) groups. Therefore, the structures of amines are similar to ammonia. As we know, in ammonia, nitrogen atom undergoes sp^3 hybridisation forming four sp^3 hybrid orbitals. Three of these sp^3 hybrid orbitals overlap with *s*-orbital of H forming three N—H bonds. The fourth sp^3 hybrid orbital contains a lone pair of electrons.



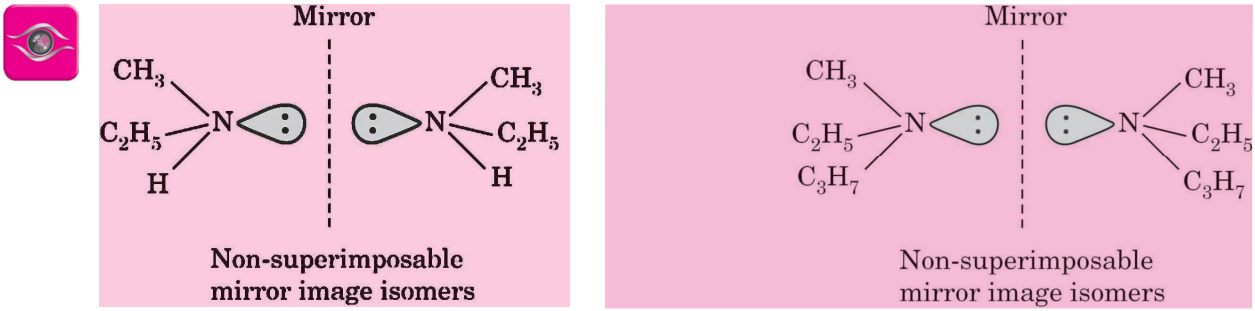
The geometry of the molecule is **pyramidal** and the bond angle in ammonia molecule is 107°. Since amines are derivative of ammonia in which one or more H atoms are replaced by alkyl or aryl groups, therefore, amines are also expected to have pyramidal shape as shown below :



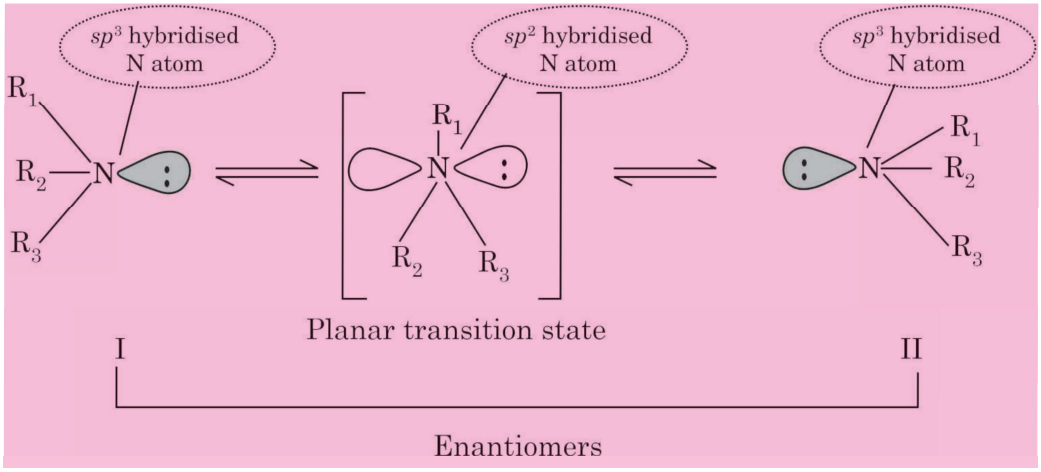
The bond angle in ammonia is 107°. However, due to the presence of methyl groups in amines, the bond angle increases. In case of 3° amine, due to steric hindrance between three bulky alkyl groups, bond angle increases from 107° in ammonia to 108° trimethylamine.

OPTICAL ACTIVITY OF AMINES

The aliphatic amines have pyramidal shape with one lone pair of electrons. Since in amines, N undergoes sp^3 hybridisation, the shape may be regarded as approximately tetrahedral when we assume electron pair on nitrogen as group. Therefore, the amines containing different substituents on nitrogen are **chiral** and we expect secondary and tertiary amines to exhibit optical activity or enantiomerism. For example, methyl ethylamine $CH_3NHC_2H_5$ (a secondary amine) or methyl ethyl propylamine (a tertiary amine) are dissymmetric as shown below:

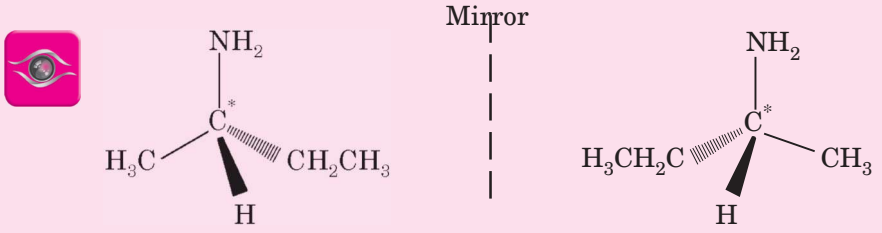


However, unlike chiral carbon compounds, most chiral amines cannot be resolved. This is because the two enantiomeric forms rapidly interconvert into one another by a process called **nitrogen inversion** or **amine inversion**. This is known as ***flipping.*** This inversion which resembles an umbrella turning inside out is very easy and occurs very rapidly (rate = $2.3 \times 10^{10}\ s^{-1}$). As a result of interconversion, it is very difficult to isolate a pure sample of either enantiomer. It has been observed that during nitrogen inversion, the state of hybridisation of N changes from sp^3 to sp^2 to give a planar transition state which can either revert to the starting amine or to its enantiomer (II) as shown below :



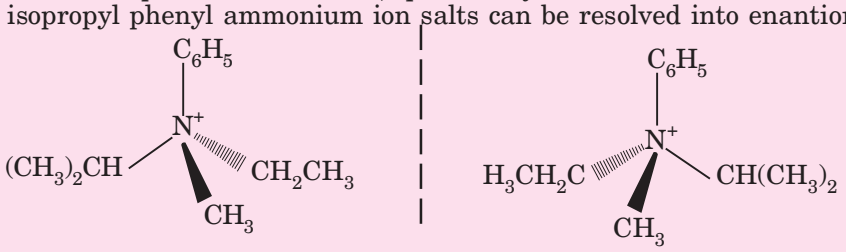
Although most simple amines cannot be resolved into enantiomers, the following types of chiral amines can be resolved :

1. **Amines whose chirality is due to the presence of asymmetric carbon atoms** can be resolved. For example, butan-2-amine can be resolved into enantiomers because the 2-butyl group is chiral.



Enantiomers of butan-2-amine

2. **Quaternary ammonium salts with asymmetric nitrogen atoms** can be resolved. The lone pair of electrons on the nitrogen atom is involved in nitrogen inversion and therefore, it is not possible to resolve the enantiomeric forms. However, if the lone pair of electrons on nitrogen is bonded to a fourth different substituent inversion of configuration is not possible. Therefore, quaternary ammonium salts exhibit optical activity. For example, methyl ethyl isopropyl phenyl ammonium ion salts can be resolved into enantiomers as :



Enantiomers of methylethyl isopropyl phenyl ammonium ion

Similarly, N-oxides of tertiary amines having three different groups *i.e.*, $R_1R_2R_3N^+ — O^-$ also show optical activity because of the absence of a lone pair of electrons on N which causes nitrogen inversion.

SOLVED EXAMPLES

❑ Example 1.

Draw the structures, give names according to IUPAC and indicate primary, secondary and tertiary amines :
(a) eight isomeric amines of formula $C_4H_{11}N$.
(b) five isomeric amines of formula C_7H_9N that contain a benzene ring.

Solution : (*a*) Eight isomeric amines of formula $C_4H_{11}N$

(*i*) $H_3CH_2CH_2CH_2NH_2$
Butanamine (1°)

(*ii*) $CH_3CH_2CH(NH_2)CH_3$
Butan-2-amine (1°)

(*iii*) $CH_3CH(CH_3)CH_2NH_2$
2 ethylpropanamine (1°)

(*iv*) $CH_3C(CH_3)_2NH_2$
2-Methylpropan-2-amine (1°)

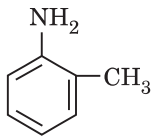
(*v*) $CH_3CH_2CH_2NHCH_3$
N-Methylpropanamine (2°)

(*vi*) $CH_3CH(CH_3)NHCH_3$
N-Methylpropan-2-amine (2°)

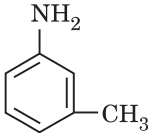
(*vii*) $CH_3CH_2NHC_2H_5$
N-Ethylethanamine (2°)

(*viii*) $CH_3CH_2N(CH_3)_2$
N, N-Dimethylethanamine (3°)

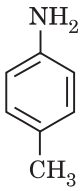
(*b*) Five isomeric amines of formula C_7H_9N containing a benzene ring

(*i*)


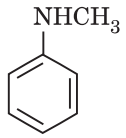
2-Methylbenzenamine
or 2- ethylaminobenzene
(1°)

(*ii*)


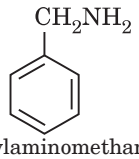
3-Methylbenzenamine
or 3-Methylaminobenzene
(1°)

(*iii*)


4-Methylbenzenamine
or 4-Methylaminobenzene
(1°)

(*iv*) 

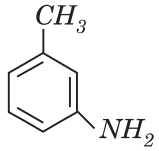
N-Methylbenzenamine
or N-Methylaminobenzene
(2°)

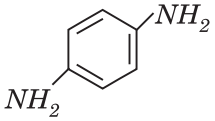
(*v*) 

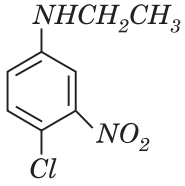
Phenylaminomethane
(1°)

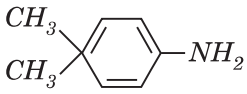
❑ Example 2.

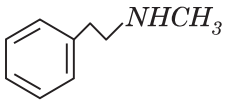
Give the IUPAC names of the following compounds

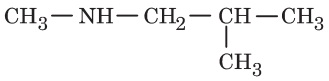
(*a*) 

(*b*) 

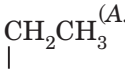
(*c*) 

(*d*) 

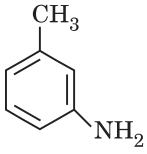
(*e*) 

(*f*) 

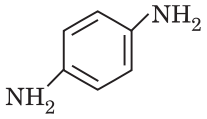
(*A.I.S.B. 2016*)

(*g*) $(CH_3\ CH_2)_2\ N\ CH_3$ (*D.S.B. 2017, Hr.S.B. 2018*) (*h*) $(CH_3)_2\ N\ CH_2CH_3$ (*D.S.B. 2017*) (*i*)  (*Pb.S.B. 2017*)

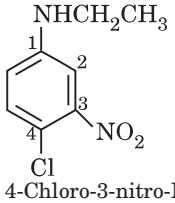
Solution :

(*a*) 

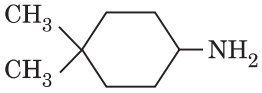
m-Toluidine or 3-Methylbenzenamine

(*b*) 

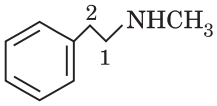
1,4-Benzenediamine

(*c*) 

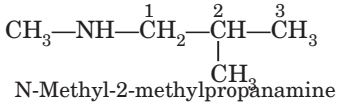
4-Chloro-3-nitro-N-ethylaniline

(*d*) 

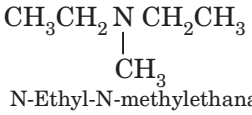
4, 4-Dimethylcyclohexanamine

(*e*) 

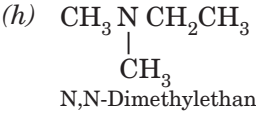
N-Methyl-2-phenylethanamine

(*f*) 

N-Methyl-2-methylpropanamine

(*g*) 

N-Ethyl-N-methylethanamine

(*h*) 

N,N-Dimethylethanamine

(*i*) 

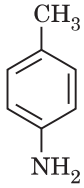
N-Methylethanamine

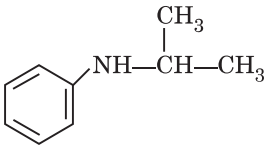
❑ Example 3.

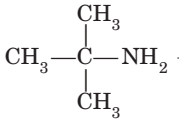
Draw structures for the following compounds :

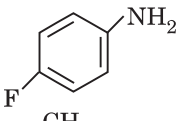
(*a*) *p-toluidine* (*b*) *N-isopropylaniline* (*c*) *t-butylamine*
(*d*) *p-fluoroaniline* (*e*) *N-Ethyl-4-isopropyl-N-methylaniline* (*f*) *p-tert-butylaniline*

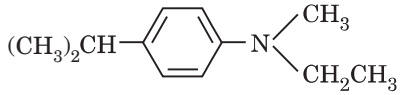
Solution :

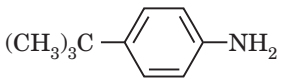
(*a*) *p*-toluidine : 

(*b*) N-isopropylaniline : 

(*c*) *t*-butylamine : 

(*d*) *p*-fluoroaniline : 

(*e*) N-Ethyl-4-isopropyl-N-methylaniline : 

(*f*) *p*-tert-butylaniline : 

Practice Problems

1. Write IUPAC names of the following :

(*i*) $CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HNH_2$ (*ii*) $(CH_3)_3CNH_2$ (*iii*) $C_6H_5(CH_2)_3NH_2$

(*iv*) $NH_2(CH_2)_4\underset{\displaystyle NH_2}{\underset{|}{C}}HCOOH$ (*v*) $C_6H_5-\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2NH_2$ (*vi*) $H_3C-\underset{\displaystyle H}{\underset{|}{N}}-CH_2-CH_3$

(*Karnataka S.B. 2014*)

- **Ans.**

(*i*) Butan-2-amine (*ii*) 2, 2-Dimethylpropanamine (*iii*) 3-Phenylpropanamine

(*iv*) 2, 6-Diaminohexanoic acid (*v*) 2-Phenylpropanamine (*vi*) N-Methylethanamine

2. Write the structural formula of the following and indicate primary, secondary or tertiary amines :

(*i*) (N-Methyl) butan-2-amine (*ii*) 3-(N-Ethylamino) butan-1-ol

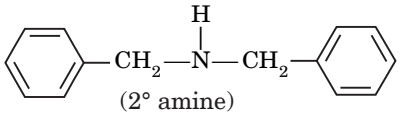
(*iii*) N-Ethyl-N-methylpropanamine (*iv*) Dibenzylamine

- **Ans.**

(*i*) $CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}H-NH-CH_3$ (2° amine)

(*ii*) $CH_3-\underset{\displaystyle NHC_2H_5}{\underset{|}{C}}HCH_2CH_2OH$ (2° amine)

(*iii*) $CH_3CH_2CH_2-\underset{\displaystyle CH_3}{\underset{|}{N}}-C_2H_5$ (3° amine)

(*iv*)  (2° amine)

3. Predict which of the following names are not correct ?

(*i*) N-Butylethanamine (*ii*) 1-Amino-2-ethanol (*iii*) Methylaniline

(*iv*) Propanediamine (*v*) 1-Phenylethanamine

- **Ans.** (*i*) The larger alkyl group should be considered as parent chain. Thus, correct name is N-ethylbutanamine.

(*ii*) —OH group should get preference. Correct name is 2-aminoethanol.

(*iii*) If methyl is bonded to amino N, it should be N-methylaniline. If it is bonded to benzene ring, the correct name should be *o*-, *m*- or *p*-toluidine or 2-, 3- or 4-methyl benzenamine.

(*iv*) The position of amino groups must be mentioned. It should be 1, 2-propanediamine or 1, 3-propanediamine.

(*v*) It is correct.

PREPARATION OF AMINES

The various methods for the preparation of amines are given below :

1. From Alkyl halides

(*a*) By ammonolysis of alkyl halides (Hoffmann's ammonolysis method). When an aqueous or alcoholic solution of ammonia is heated with an alkyl halide at 373 K in a sealed tube, all the three types of amines are obtained. In this reaction, the alkyl halides undergo **nucleophilic substitution reaction** in which the nucleophile ammonia (or amine) displaces the halogen atom. The ammonia molecule first attacks an alkyl halide molecule to form a primary amine salt. This salt then reacts with ammonia to give the corresponding primary amine and ammonium halide.

$$RX + NH_3 \xrightarrow{373\ K} \underset{\text{1° amine salt}}{RNH_3^+X^-}$$

$$RNH_3^+X^- + NH_3 \longrightarrow \underset{\text{1° amine}}{RNH_2} + NH_4^+X^-$$

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

$$RNH_3^+X^- + NaOH \longrightarrow RNH_2 + H_2O + Na^+X^-$$

The primary amine also acts as a nucleophile and reacts further with alkyl halide and this sequence of reactions can lead to the formation of secondary, tertiary and finally quaternary ammonium salts.

$$\underset{\text{1° amine}}{RNH_2} \xrightarrow{RX,\ 373\ K} \underset{\text{2° amine}}{R_2NH} \xrightarrow{RX,\ 373\ K} \underset{\text{3° amine}}{R_3N} \xrightarrow{RX,\ 373\ K} \underset{\text{Quaternary ammonium salt}}{R_4N^+X^-}$$

The process of cleavage of the C—X bond by ammonia or amines is called **Hoffmann's ammonolysis.**

e.g.,

$$CH_3I + NH_3 \xrightarrow{373\ K} \underset{\text{Methylamine (Primary)}}{CH_3NH_2} + HI$$

$$CH_3—NH_2 + CH_3I \xrightarrow{373\ K} \underset{\text{Dimethylamine (Secondary)}}{CH_3—NH—CH_3} + HI$$

$$CH_3—NH—CH_3 + CH_3I \xrightarrow{373\ K} \underset{\text{Trimethylamine (Tertiary)}}{CH_3—\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{N}}}—CH_3} + HI$$

Tertiary amines also combine with methyl iodide to form quaternary ammonium salts.

$$(CH_3)_3N + CH_3I \longrightarrow \underset{\text{Tetramethyl ammonium iodide}}{[(CH_3)_4\,N^+]\,I^-}$$

This reaction is an example of **nucleophilic substitution** *reaction* in which ammonia or amine molecule acts as a nucleophile due to the presence of lone pair on the nitrogen atom. The free amines are obtained from the substituted ammonium salts by treating with ammonia.

Ammonia

$$\underset{\text{Nucleophile}}{H_3\ddot{N}} + \underset{\text{Alkyl halide}}{R—X} \xrightarrow{373\ K} \underset{\text{Substituted ammonium salt}}{RNH_3^+X^-} \xrightleftharpoons{NH_3} \underset{\text{1°amine}}{RNH_2} + NH_4^+X^-$$

1° Amine

$$R\ddot{N}H_2 + R—X \xrightarrow{373\ K} R_2NH_2^+X^- \xrightleftharpoons{NH_3} \underset{\text{2° amine}}{R_2NH} + NH_4^+X^-$$

2° Amine

$$R_2\ddot{N}H + R—X \xrightarrow{373\ K} R_3N^+HX^- \xrightleftharpoons{NH_3} \underset{\text{3° amine}}{R_3N} + NH_4^+X^-$$

3° Amine

$$R_3\ddot{N} + R—X \xrightarrow{373\ K} \underset{\text{Quaternary ammonium salt}}{R_4N^+X^-}$$

The **order of reactivity of halides is : RI > RBr > RCl**

Benzyl haildes also react with aqueous or alcoholic solution of ammonia to from benzyl amines.

Limitations. (***a***) This method gives a mixture of amines and it is very difficult to separate the mixture in the laboratory. However, the composition of the reaction mixture depends upon the amounts of alkyl halide and ammonia taken. There are two ways of getting only one product :

(***i***) **Using large excess of ammonia.** When ammonia is taken in a large excess in the reaction mixture, an alkyl halide is more likely to encounter and react with a molecule of ammonia rather than with a molecule of amine which is present in relatively much smaller amount. Therefore, only primary amine is formed as the main product.

(***ii***) **Using a large excess of alkyl halide.** Under these conditions in the presence of a base which will consume HX formed, quaternary ammonium salt is the main product.

(***b***) The method is not suitable for the preparation of arylamines because *aryl halides are relatively very less reactive than alkyl halides towards nucleophilic substitution reactions.*

2. Reduction of nitro compounds

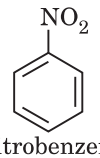
Aliphatic and aromatic amines can be easily prepared by the reduction of corresponding nitro compounds. The reduction can be carried out in a number of ways as discussed below :

(***a***) *Nitro compounds can be* ***catalytically reduced*** *by passing hydrogen gas in the presence of Raney Ni, finely divided platinum or palladium as catalyst at room temperature.*

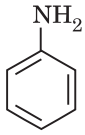
$$R—NO_2 + 6\,[H] \xrightarrow[\text{Pt or Pd, room temp.}]{\text{Raney Ni}} \underset{\text{Aliphatic amine}}{R—NH_2} + 2H_2O$$

or $Ar—NO_2 + 6\,[H] \xrightarrow[\text{Pt or Pd, room temp.}]{\text{Raney Ni}} \underset{\text{Aromatic amine}}{Ar—NH_2} + H_2O$

e.g., $\underset{\text{Nitroethane}}{CH_3CH_2NO_2} + 6\,[H] \xrightarrow[\text{Pt or Pd}]{\text{Raney Ni}} \underset{\text{Ethylamine}}{CH_3CH_2NH_2} + 2H_2O$


Nitrobenzene

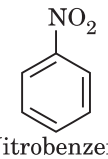
$+ 6\,[H] \xrightarrow{\text{Pt or Pd/C}}$


Aniline

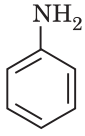
$+ H_2O$

(***b***) *Nitro compounds can be reduced with* ***active metals*** *such as Fe, Sn, Zn etc. and conc. hydrochloric acid.* Reduction with iron scrap and hydrochloric acid is preferred because $FeCl_2$ formed gets hydrolysed to release hydrochloric acid during the reaction. Thus, only a small amount of hydrochloric acid is needed to initiate the reaction.

$\underset{\text{Nitroethane}}{CH_3CH_2NO_2} + 6\,[H] \xrightarrow[\text{or Fe/HCl}]{\text{Sn/HCl}} \underset{\text{Ethylamine}}{C_2H_5NH_2} + 2H_2O$


Nitrobenzene

$+ 6\,[H] \xrightarrow[\text{or Fe/HCl}]{\text{Sn/HCl}}$


Aniline

$+ 2H_2O$

A mixture of $SnCl_2$ and conc. HCl has also been used for the reduction of aromatic nitro compounds.

This is a good method for the preparation of aromatic amines because these cannot be prepared from the corresponding aryl halides on treatment with ammonia. The required nitro compounds can be easily prepared by the nitration of arenes.

(***c***) *Nitro compounds can also be reduced to amines with lithium aluminium hydride, $LiAlH_4$*

$\underset{\text{Nitroethane}}{CH_3CH_2NO_2} \xrightarrow{LiAlH_4, \text{dry ether}} \underset{\text{Ethylamine}}{CH_3CH_2NH_2}$

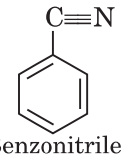
However, reduction of aromatic nitro compounds with $LiAlH_4$ gives azo compounds and not primary amines.

$\underset{\text{Nitrobenzene}}{2C_6H_5NO_2} \xrightarrow{LiAlH_4, \text{dry ether}} \underset{\text{zobenzene}}{C_6H_5—N=N—C_6H_5}$

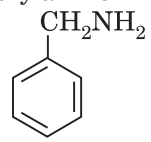
3. Reduction of nitriles (cyanides) and isonitriles (isocyanides)

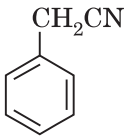
Nitriles can be reduced to corresponding amines using H_2 / Raney Ni or Pt, $LiAlH_4$ or Na(Hg), C_2H_5OH.

$CH_3CN + 4[H] \xrightarrow[Na(Hg)/C_2H_5OH]{H_2/Ni \text{ or } LiAlH_4} \underset{\text{Ethylamine}}{CH_3CH_2NH_2}$

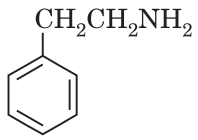

Benzonitrile

$\xrightarrow[\text{or } H_2/\text{Raney Ni}]{LiAlH_4}$


Benzylamine



$\xrightarrow[\text{or } H_2, \text{catalyst}]{LiAlH_4}$


2-Phenylethan-1-amine

The method of reduction of cyanide with sodium and alcohol is called **Mendius reaction.**

HELP

Synthetic Importance: This reaction is very important for **ascent of amines series**. This is because alkyl nitriles can be readily prepared by the action of alcoholic NaCN or KCN on alkyl halides. The method can be used to prepare primary amines having one carbon more than the parent alkyl halide.

$R—X \xrightarrow[-KX]{\text{alc. KCN}} \underset{\text{Alkyl nitrile}}{R—CN} \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4, \text{ether}} \underset{\text{(one more carbon atom)}}{R—CH_2—NH_2}$

The reduction of isocyanides under similar conditions gives **secondary amines** *i.e.*, N-alkyl amines.

$$\underset{\text{Alkyl isocyanide}}{R{-}N{\equiv}C} + 4\,[H] \xrightarrow[\text{Raney Ni}]{LiAlH_4,\ \text{ether}} \underset{\text{N-Methyl alkylamine (2°)}}{R{-}NH{-}CH_3}$$

$$\underset{\text{Methyl isocyanide}}{H_3NC} + 4[H] \xrightarrow[\text{Raney Ni}]{LiAlH_4,\ \text{ether}} \underset{\text{Dimethyl amine}}{CH_3{-}NH{-}CH_3}$$

$$\underset{\text{Phenyl isocyanide}}{{}_6H_5N{\equiv}C} + 4[H] \xrightarrow[\text{or } LiAlH_4]{\text{Raney Ni}} \underset{\text{N-Methyl aniline (2°)}}{C_6H_5{-}NH{-}CH_3}$$

NOTE

This method can be used only for the preparation of 2° amines in which one of the alkyl groups is always methyl.

4. Reduction of amides

Amides are reduced to the corresponding amines by $LiAlH_4$ or Na/C_2H_5OH. Primary, secondary or tertiary amines can be prepared by this method by the reduction of corresponding amides.

$$\underset{\text{Amide}}{R{-}\overset{\overset{O}{\|}}{C}{-}NH_2} \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4,\ \text{ether}} \underset{\text{Amine}}{R{-}CH_2NH_2}$$

It may be noted that the product contains same number of carbon atoms as the original amide.

e.g.,

$$\underset{\text{Acetamide}}{CH_3{-}\overset{\overset{O}{\|}}{C}{-}NH_2} + 4[H] \xrightarrow[\text{Ether}]{LiAlH_4} \underset{\text{Ethylamine}}{CH_3CH_2NH_2} + H_2O$$

$$\underset{\text{Benzamide}}{C_6H_5CONH_2} \xrightarrow[\text{Ether}]{LiAlH_4} \underset{\text{Benzylamine}}{C_6H_5CH_2NH_2}$$

Secondary and tertiary amines can be prepared by the reduction of secondary and tertiary amides respectively.

$$\underset{\substack{\text{N-Methylacetamide}\\(2°)}}{CH_3CONHCH_3} \xrightarrow[\text{Ether}]{LiAlH_4} \underset{\substack{\text{Ethylmethyl amine}\\(2°)}}{CH_3CH_2NHCH_3}$$

$$\underset{\substack{\text{N, N-Dimethylacetamide}\\(3°)}}{CH_3CON\begin{matrix}\diagup CH_3\\ \diagdown CH_3\end{matrix}} \xrightarrow[\text{Ether}]{LiAlH_4} \underset{\substack{\text{Ethyldimethylamine}\\(3°)}}{CH_3CH_2{-}N\begin{matrix}\diagup CH_3\\ \diagdown CH_3\end{matrix}}$$

5. Hoffmann bromamide degradation method

Primary amines can be prepared from amides by treatment with Br_2 and KOH or NaOH. The *amine formed contains one carbon atom less than the parent amide.* Therefore, *this method is used for stepping down the series in organic conversions.*

$$\underset{\text{Amide}}{RCONH_2} + Br_2 + 4KOH \longrightarrow \underset{\text{1°-Amine}}{RNH_2} + K_2CO_3 + 2KBr + 2H_2O$$

e.g.,

$$\underset{\text{Acetamide}}{CH_3CONH_2} + Br_2 + KOH \longrightarrow \underset{\text{Methyl amine}}{CH_3NH_2} + KBr + K_2CO_3 + H_2O$$

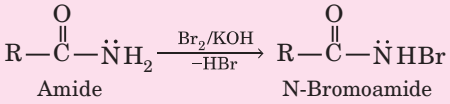
$$\underset{\text{Benzamide}}{\text{C}_6\text{H}_5\text{CONH}_2} + Br_2 + 4KOH \longrightarrow \underset{\text{Aniline}}{\text{C}_6\text{H}_5\text{NH}_2} + 2KBr \quad K_2CO_3 + 2H_2O$$

This reaction involves the migration of alkyl group from carbonyl in the precursor to nitrogen with the elimination of CO_2. Therefore, the reaction provides the product containing one carbon atom less than the starting material.

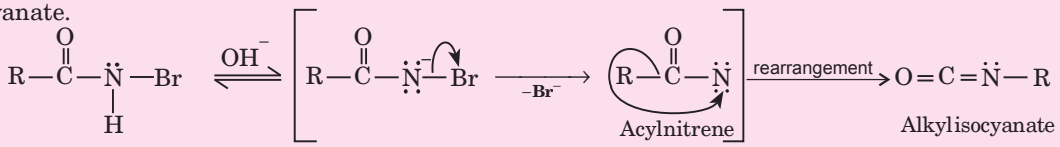
Mechanism : Hoffmann Bromamide reaction

The reaction is believed to proceed by the following sequence of steps :

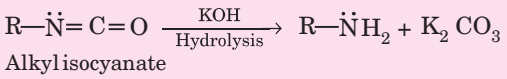
Step 1. The amide undergoes base promoted bromination to form N-bromoamide.



Step 2. The N-bromoamide reacts with OH^- ion to form an anion which rearranges spontaneously with the loss of a Br^- ion to form an isocyanate.

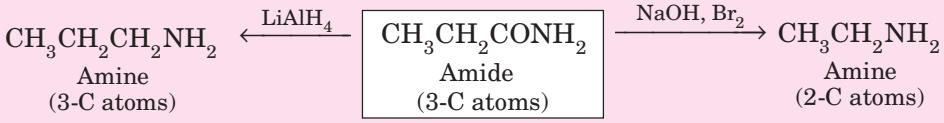


Step 3. The alkyl isocyanate gets hydrolysed by aqueous base to form an amine and carbonate ion.



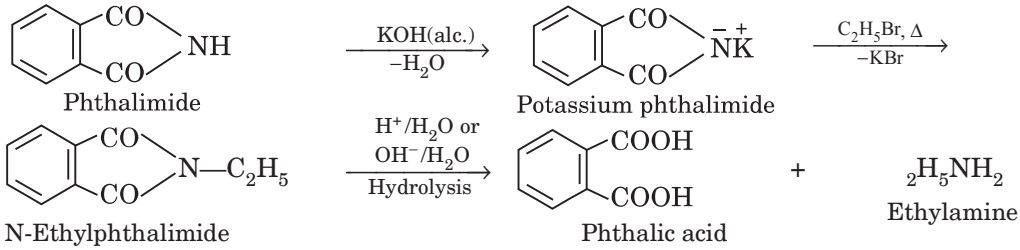
NOTE

It may be noted that primary amines can be obtained from amides either by reduction with $LiAlH_4$ or by treating with Br_2 and NaOH. The *reduction with $LiAlH_4$ gives amine having same number of C-atoms as the original amide while reduction with NaOH and Br_2 gives amine having one carbon atom less than the original amide.*



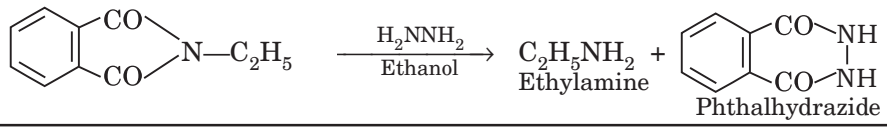
6. Gabriel phthalimide synthesi

This method is used for preparing only *primary amines*. In this method, phthalimide is treated with alcoholic KOH to give potassium phthalimide, which is treated with alkyl halide or benzyl halide to form N-alkyl or aryl phthalimide. The hydrolysis of N-alkyl phthalimide with 20% HCl under pressure or refluxing with NaOH gives primary amine.



Phthalic acid can again be converted into phthalimide and is used again and again. This method is very useful because it gives pure amines.

It may be noted that the hydrolysis of N–alkylphthalimide with aqueous acid or base is generally slow. The more convenient method is by the treatment of alkyl phthalimide with hydrazine (NH_2NH_2).



REMEMBER

Aryl halides cannot be converted to aryl amines by **Gabriel synthesis** because they do not undergo nucleophilic substitution with potassium phthalimide. Therefore, **aromatic primary amines such as aniline, toluidines etc. cannot be prepared by this method.**

7. Reduction of azides

Primary amines can be prepared from alkyl halides by first converting the alkyl halide to alkyl azide. Alkyl azides are prepared by nucleophilic substitution of alkyl halides by sodium azide. Then alkyl azides are reduced to alkyl amines with sodium and alcohol or lithium aluminium hydride or by catalytic hydrogenation with H_2 / Pd—C.

$$RX + \underset{\text{Sodium azide}}{NaN_3} \longrightarrow \underset{\text{Alkyl azide}}{RN_3} + NaX$$

$$RN_3 \xrightarrow[Na/C_2H_5OH]{LiAlH_4 \text{ or}} RNH_2 + N_2$$

$$RN_3 \xrightarrow{Pd/C,\ H_2} RNH_2 + N_2$$

The reaction may also be written as :

$$\underset{\text{Sodium azide}}{Na^+ \overset{\delta+}{N_3^-} + R\overset{\delta-}{-}X} \longrightarrow \underset{\text{Alkyl azide}}{R-\ddot{N}=N^+=\ddot{N}:^-} \xrightarrow[\text{or } LiAlH_4]{H_2,Pd/C} \underset{1°\text{–Amine}}{R-\ddot{N}H_2} + N_2$$

e.g., $C_6H_5CH_2CH_2X + \underset{\text{Azide ion}}{N_3^-} \xrightarrow[-X^-]{} \underset{\text{2-Phenyl ethyl azide}}{C_6H_5CH_2CH_2N_3} \xrightarrow{LiAlH_4} \underset{\text{2-Phenyl ethyl amine}}{C_6H_5CH_2CH_2NH_2} + N_2$

8. By reduction of oximes

Primary amines can be prepared by the reduction of oximes of aldehydes and ketones with either Na/C_2H_5OH or $LiAlH_4$. The oximes can be obtained from aldehydes and ketones by reaction with hydroxylamine.

$$\underset{\text{Aldoxime}}{RCH=NOH} + [H] \xrightarrow[Na/C_2H_5OH]{LiAlH_4 \text{ or}} \underset{1° \text{ Amine}}{RCH_2NH_2} + H_2O$$

e.g., $\underset{\text{Acetaldoxime}}{CH_3CH=NOH} + 4[H] \xrightarrow[Na/C_2H_5OH]{LiAlH_4 \text{ or}} \underset{\text{Ethanamine}}{CH_3CH_2NH_2} + H_2O$

$$\underset{\text{Ketoxime}}{\begin{matrix}R\\R\end{matrix}\!\!>\!C=NOH} + [H] \xrightarrow[Na/C_2H_5OH]{LiAlH_4 \text{ or}} \underset{1° \text{ Amine}}{\begin{matrix}R\\R\end{matrix}\!\!>\!CHNH_2} + H_2O$$

$$\underset{\text{Acetoxime}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C=NOH} + 4[H] \xrightarrow[Na/C_2H_5OH]{LiAlH_4 \text{ or}} \underset{\substack{\text{Propan-2-amine}\\\text{(Isopropylamine)}}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CHNH_2} + H_2O$$

9. Reductive amination of aldehydes and ketones

Primary amines may be prepared by reacting aldehyde or ketone with ammonia to form intermediate imines which can be reduced with H_2, Ni.

$$\underset{\text{Aldehyde}}{R-\overset{H}{\overset{|}{C}}=O} + NH_3 \xrightarrow[-H_2O]{\text{Heat}} \underset{\text{Imine}}{R-\overset{H}{\overset{|}{C}}=NH} \xrightarrow{H_2,\ Ni} \underset{1° \text{ Amine}}{R-CH_2NH_2}$$

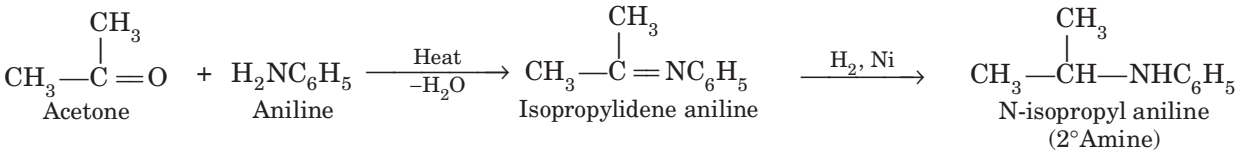
e.g., $\underset{\text{Acetaldehyde}}{CH_3-\overset{H}{\overset{|}{C}}=O} + NH_3 \xrightarrow[-H_2O]{\text{Heat}} \underset{\text{Acetaldimine}}{CH_3-\overset{H}{\overset{|}{C}}=NH} \xrightarrow{H_2,\ Ni} \underset{\text{Ethylamine}}{CH_3CH_2NH_2}$

$$\underset{\text{Ketone}}{R-\overset{R'}{\overset{|}{C}}=O} + NH_3 \xrightarrow[-H_2O]{\text{Heat}} \underset{\text{Dialkyl ketimine}}{R-\overset{R'}{\overset{|}{C}}=NH} \xrightarrow{H_2,\ Ni} \underset{1° \text{ Amine}}{R-\overset{R'}{\overset{|}{C}}H-NH_2}$$

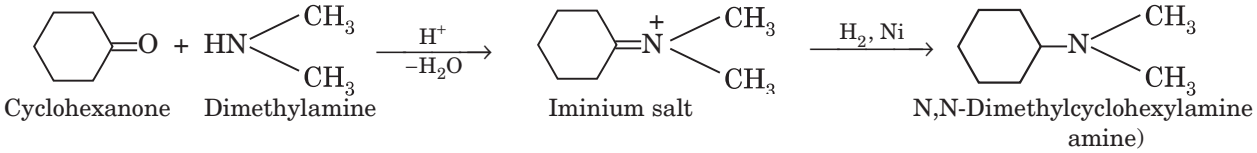
$$\underset{\text{Acetone}}{CH_3-\overset{CH_3}{\overset{|}{C}}=O} + NH_3 \xrightarrow[-H_2O]{\text{Heat}} \underset{\text{Dimethyl ketimine}}{CH_3-\overset{CH_3}{\overset{|}{C}}=NH} \xrightarrow{H_2,\ Ni} \underset{\text{Isopropylamine}}{CH_3-\overset{CH_3}{\overset{|}{C}}H-NH_2}$$

This reaction leading to the conversion of an aldehyde or a ketone to the corresponding amine on treatment with ammonia in the presence of a reducing agent (H_2, Ni) is called **reductive amination.**

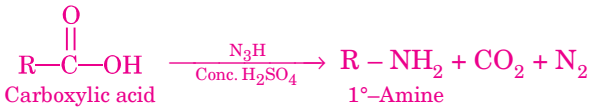
It may be noted that if instead of NH_3, a primary amine is used in the above reaction, secondary amine is obtained. For example,



Similarly, with secondary amines, tertiary amines are formed. For example,



10. Schmidt reaction : Carboxylic acids react with hydrazoic acid (N_3H) in the presence of conc. H_2SO_4 to form primary amines with the evolution of CO_2 and N_2.



e.g., $C_6H_5COOH \xrightarrow[\text{Conc. } H_2SO_4]{N_3H} C_6H_5NH_2 + CO_2 + N_2$

Benzoic acid — Aniline

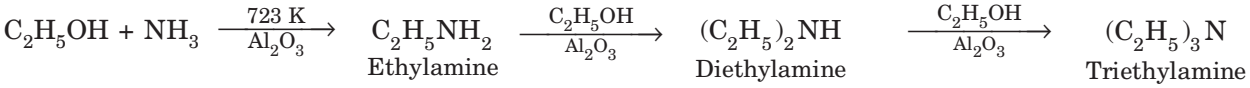
REMEMBER

N_3H is hydrazoic acid and N_3^- is azide ion *e.g.*, NaN_3 : sodium azide.

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

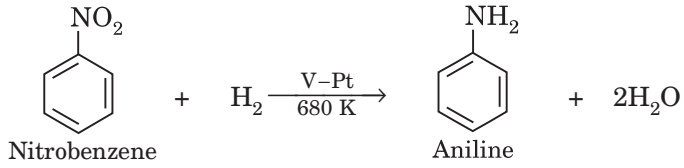
INDUSTRIAL PREPARATION OF AMINES

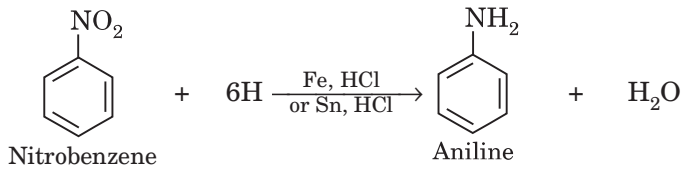
1. From alcohols. On an industrial scale, aliphatic amines are prepared by passing vapours of an alcohol and ammonia over alumina at 723 K. This reaction is called **Sabatier and Mailhe method.**



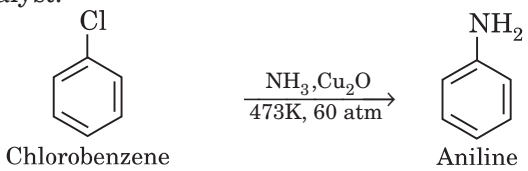
The mixture of three amines is separated by fractional distillation.

2. Aniline. On an industrial scale, aniline is prepared by the reduction of nitrobenzene by catalytic hydrogenation (H_2/Pt or V or CuO) or by chemical means using Fe/HCl or Sn/HCl.





Aniline is also prepared on a large scale by treating chlorobenzene with ammonia at 473 K and 60 atm pressure using copper oxide as catalyst.



SOLVED EXAMPLES

❑ Example 4.

Write chemical equations for the following reactions :

(a) Reaction of ethanolic NH_3 with C_2H_5Cl.

(b) Ammonolysis of benzyl chloride and reaction of amine so formed with two moles of CH_3Cl. **N.C.E.R.T.**

Solution :

(*a*) $C_2H_5Cl \xrightarrow[\text{Ethanolic}]{NH_3}$ Chloroethane $\rightarrow C_2H_5NH_2$ Ethanamine $\xrightarrow{C_2H_5Cl}$ $C_2H_5-\underset{H}{\overset{|}{N}}-C_2H_5$ N-Ethylethanamine $\xrightarrow{C_2H_5Cl}$ $C_2H_5-\underset{C_2H_5}{\overset{|}{N}}-C_2H_5$ N, N-Diethylethanamine

(*b*) $C_6H_5CH_2Cl \xrightarrow{NH_3}$ Benzyl chloride $\rightarrow C_6H_5CH_2NH_2$ Benzylamine $\xrightarrow{2\ CH_3Cl}$ $C_6H_5-CH_2-\underset{CH_3}{\overset{|}{N}}-CH_3$ N, N-Dimethylphenylmethanamine

❑ Example 5.

Write chemical equations for the following conversions :

(i) $C_6H_5CH_2NH_2$ into $C_6H_5CH_2OH$ *(ii) C_2H_5Cl into $(C_2H_5)_3N$*

(iii) Propene into butylamine *(iv) n propyl bromide into ethylamine*

(v) enzene into benzylamine

Solution :

(*i*) $C_6H_5CH_2NH_2 \xrightarrow[NaNO_2,\ HCl]{HONO} [C_6H_5CH_2NH_3^+Cl^-] \xrightarrow{Water} C_6H_5CH_2OH$

Benzylamine Benzyl alcohol

(*ii*) $C_2H_5Cl \xrightarrow{NH_3} C_2H_5NH_2 \xrightarrow{C_2H_5Cl} C_2H_5-\underset{H}{\overset{|}{N}}-C_2H_5 \xrightarrow{C_2H_5Cl} C_2H_5-\underset{C_2H_5}{\overset{|}{\underset{C_2H_5}{\overset{|}{N}}}}$

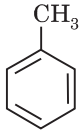
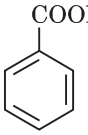
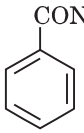
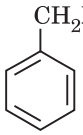
N, N-Diethylethanamine

(*iii*) $CH_3CH{=}CH_2 \xrightarrow[Peroxide]{HBr} CH_3CH_2CH_2Br \xrightarrow{KCN} CH_3CH_2CH_2CN \xrightarrow{LiAlH_4} CH_3CH_2CH_2CH_2NH_2$

Propene Butylamine

(*iv*) $CH_3CH_2CH_2Br \xrightarrow[Heat]{aq.\ KOH} CH_3CH_2CH_2OH \xrightarrow[H^+]{K_2Cr_2O_7} CH_3CH_2COOH \xrightarrow{SOCl_2} CH_3CH_2COCl \xrightarrow{NH_3} CH_3CH_2CONH_2 \xrightarrow[NaOH]{Br_2} CH_3CH_2NH_2$

n-Propyl bromide Ethylamine

(*v*) Benzene $\xrightarrow[AlCl_3]{CH_3Cl}$  $\xrightarrow{O}$  $\xrightarrow{NH_3}$  $\xrightarrow{LiAlH_4}$ 

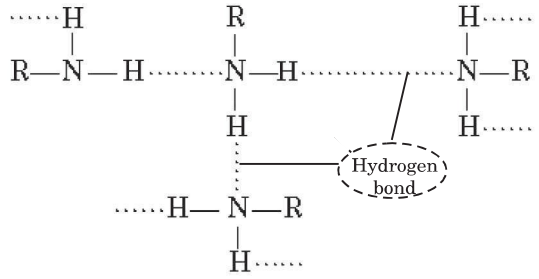
Benzylamine

PHYSICAL PROPERTIES OF AMINES

The important physical properties of amines are given below :

1. Physical state and smell. Lower members of the aliphatic amines family such as methylamine, dimethyl amine, ethylamine are gases at ordinary temperatures and have smell like ammonia. The higher members with three or more C atoms are mostly liquids having fishy smell and still higher ones are solids. Most of the amines have unpleasant odour. Aromatic amines, in general are toxic. Most of the amines in pure form are colourless but as they are easily oxidised, they become coloured due to impurities and atmospheric oxidation.

2. Boiling points. Amines have higher boiling points than hydrocarbons of comparable molecular masses. This is due to the reason that amines are polar compounds and with the *exception of tertiary amines* form associated molecules due to intermolecular hydrogen bonding between nitrogen of one and hydrogen of another molecule as shown alongside:



However, amines have lower boiling points than those of alcohols or carboxylic acids. This is due to the reason that electronegativity of nitrogen (3.0) is lower than that of oxygen (3.5) and therefore, O—H bonds present in alcohols and carboxylic acids are more polar than the N—H bond in amines. As a result, the hydrogen bonds in alcohols and carboxylic acids are

stronger and consequently they have higher boiling points. This is given below :

Compound	Molar mass	b.p. (K)
$CH_3CH_2CH_3$	44	231
$CH_3CH_2NH_2$	45	290
CH_3CHO	44	293
CH_3CH_2OH	46	3
HCOOH	46	374

Compound	Molar mass	b.p. (K)
n-C_5H_{12}	72	30
n-$C_4H_9NH_2$	73	350.8
n-C_4H_9OH	74	390.
n-C_2H_5COOH	74	474.4

Among isomeric amines, the intermolecular association is more in primary amines than in secondary amines. This is because in primary amines there are two hydrogen atoms available for hydrogen bond formation, while secondary amines have only one hydrogen atom for hydrogen bond formation. Tertiary amines do not have intermolecular association due to absence of hydrogen atom available for hydrogen bond formation. Therefore, the primary and secondary amines have highest boiling point whereas tertiary amines have lowest boiling points. Thus, the order of boiling points of isomeric amines is as follows :

Primary > Secondary > Tertiary

e.g., $CH_3CH_2CH_2NH_2$ Propylamine (1°) b.p. : 323 K

$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{N}}H$ Ethylmethylamine (2°) b.p. : 307 K

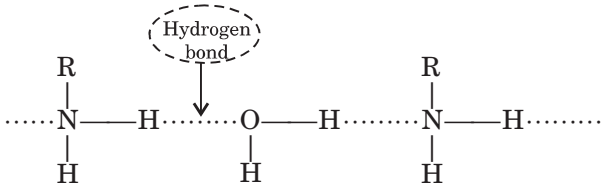
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{N}}-CH_3$ Trimethylamine (3°) b.p. : 276 K

n-$C_4H_9NH_2$ Butyl amine(1°) b.p. : 350.8 K

$(C_2H_5)_2NH$ Diethyl amine(2°) b.p. : 329.3 K

$C_2H_5N(CH_3)_2$ Ethyldimethylamine b.p. : 310.5 K

3. Solubility. The lower aliphatic amines are soluble in water because they are capable of forming hydrogen bonds with water. However, solubility decreases with increase in molar mass of amines due to increase in size of the hydrophobic alkyl part. Therefore, the higher amines containing six or more carbon atoms are insoluble. Because of their weaker hydrogen bonds, the solubility of amines in water is less than that of alcohols. This is because electronegativity of nitrogen is lower (3.0) than that of oxygen (3.5) and therefore, amines form weaker hydrogen bonds as compared to alcohols and carboxylic acids. For example, butan-1-amine is less soluble than butan-1-ol. The amines are also soluble in less polar solvents like ether, alcohol or benzene, etc.



Aromatic amines, on the other hand, are insoluble in water. This is due to larger hydrocarbon part which tends to retard the formation of hydrogen bonds. For example, aniline is insoluble in water. However, it is quite soluble in organic solvents such as ether, alcohols or benzene.

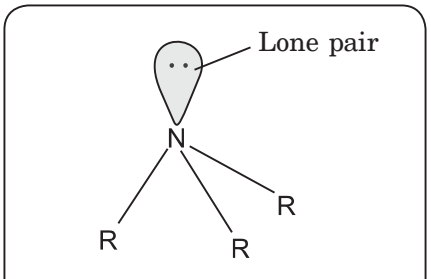


Fig. 1. Pyramidal shape of amine (R may be H).

CHEMICAL PROPERTIES OF AMINES

The difference in electronegativity between nitrogen and hydrogen atoms and the presence of lone pair of electrons on the nitrogen atom make amines very reactive organic compounds. Due to the presence of lone pair of electrons on N-atom, amines behave as nucleophiles. The number of hydrogen atoms attached to nitrogen atom also decide the course of reactions of amines. Therefore 1°, 2° and 3° amines differ in many reactions as discussed below :

1. Reaction with water—basic character of amines

Amines have a lone pair of electrons on nitrogen atom. Due to the presence of lone pair on N atom of the $—NH_2$ group, the amines are generally basic in nature. These are more basic than water and therefore, get protonated by water to form alkyl ammonium or aryl ammonium hydroxides which ionize to furnish —OH ions in solutions.

$$\underset{\text{1°-Amine}}{R\ddot{N}H_2} + H_2O \longrightarrow \underset{\text{Alkyl ammonium hydroxide}}{RNH_3^+\ OH^-} \rightleftharpoons RNH_3^+ + OH^-$$

This reaction is similar to the reaction of ammonia with water.

$$\ddot{N}H_3 + H_2O \longrightarrow NH_4^+OH^- \rightleftharpoons NH_4^+ + OH^-$$

Similarly,

$$R_2\ddot{N}H + H_2O \longrightarrow R_2NH_2^+OH^- \rightleftharpoons R_2NH_2^+ + OH^-$$

2°Amine

$$R_3\ddot{N} + H_2O \longrightarrow R_3NH^+OH^- \rightleftharpoons R_3NH^+ + OH^-$$

3°Amine

Due to the presence of hydroxide ions, the aqueous solutions of amines are **basic in nature**.

The basic strength of an amine is expressed in terms of **dissociation constant, K_b**. For the reaction,

$$RNH_2 + H_2O \rightleftharpoons RNH_3^+ + OH^-$$

$$K_{eq} = \frac{[RNH_3^+][OH^-]}{[RNH_2][H_2O]}$$

Since $[H_2O]$ is constant, it is convenient to incorporate it into equilibrium constant as :

$$K_{eq}[H_2O] = \frac{[RNH_3^+][OH^-]}{[RNH_2]}$$

$$\text{or } K_{eq}[H_2O] = K_b = \frac{[RNH_3^+][OH^-]}{[RNH_2]}$$

$$\text{Thus, dissociation constant, } K_b = \frac{[RNH_3^+][OH^-]}{[RNH_2]}$$

Greater the K_b value, the stronger is the base.

The basic strength of amines can also be expressed in terms of pK_b values which is defined as

$$pK_b = -\log K_b$$

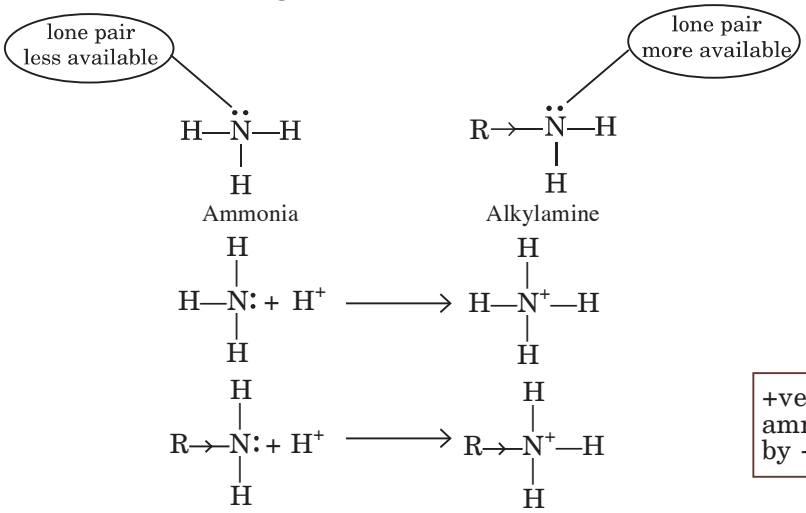
The smaller the value of pK_b, more is the basic strength of amine.

Struture - Basicity Relationship of Amines : Comparison of Basic Character of Amines

The basicity of any amine depends upon the ease with which it accepts a proton from the acid to form the ammonium cation. In other words, the basic character of an amine depends upon the stability of the ammonium cation it forms after accepting a proton. *The more stable the ammonium cation is relative to the amine, more basic is the amine.*

(*a*) Comparison of aliphatic amines and ammonia

Aliphatic amines are stronger bases than ammonia. This is due to the reason that alkyl groups are electron releasing (+ I inductive effect). As a result of electron releasing effect of alkyl group, it increases the electron density on the nitrogen atom and therefore, they can donate electron pair of electrons more easily than ammonia. Moreover, the substituted ammonium ion formed from the amine gets stabilised due to dispersal of positive charge by the +I inductive effect of the alkyl group. Thus, **alkylamines are more basic than ammonia.** For example, K_b value of NH_3 (1.8×10^{-5}) and ethylamine ($K_b = 5.5 \times 10^{-4}$) shows that ethylamine is stronger base. The pK_b value of NH_3 is 4.75 while pK_b values of amines lies in the range of 3 to 4.22.



+ve charge on substituted ammonium ion gets dispersed by +I effect of R group

(*b*) Comparison of basic strength of primary, secondary and tertiary amines.

Due to the presence of lone pair of electrons in amines, they are basic in character. The alkyl group is electron releasing group (+ I inductive effect) and it will increase the electron density on nitrogen and therefore, its basic character should increase. Moreover, the basic character of aliphatic amines should increase with increase in number of alkyl groups. As a result, the basic character should decrease in the order :

tertiary amine > secondary amine > primary amine.

This trend is followed in the gaseous phase.

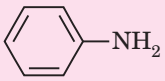
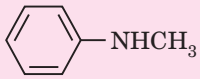
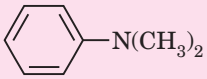
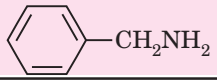
However in aqueous solutions, it has been observed that tertiary amines are **unexpectedly less basic than the others**. For example, the correct order of methylamines and ethylamines is :

$(CH_3)_2NH_2 > CH_3NH_2 > (CH_3)_3N$ and

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

The K_b values of some amines are given in Table 1.

Table 1. Basicity constants of some amines.

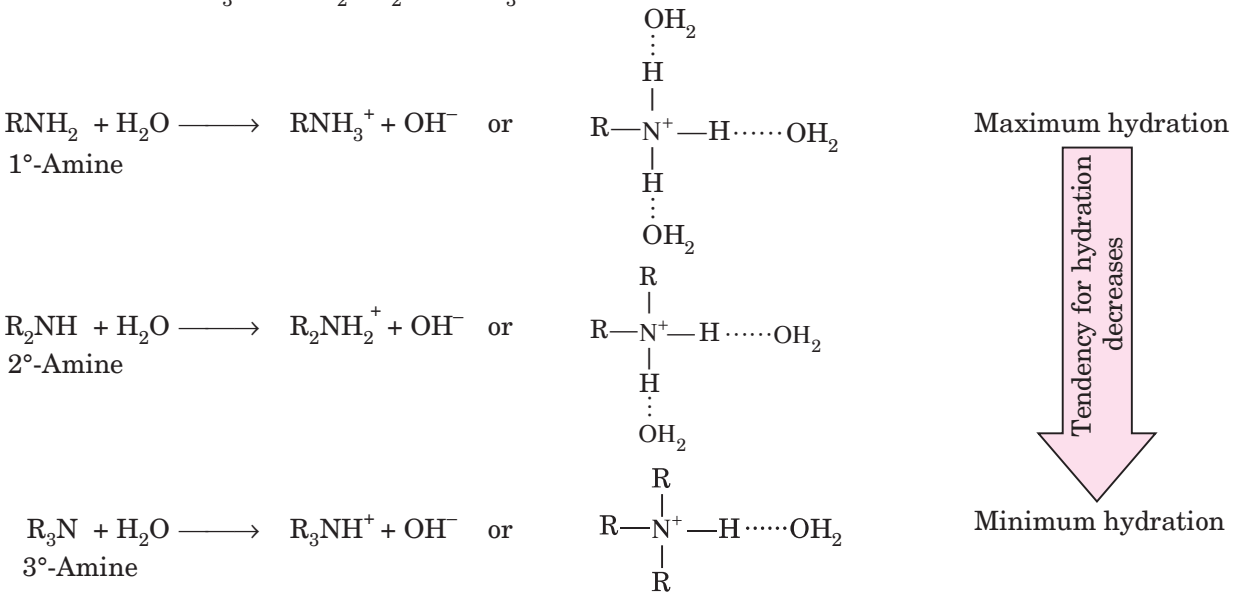
Amine		K_b	pK_b	Amine		K_b	pK_b
Ammonia	NH_3	1.8×1^{-5}	4.75	niline		4.2×10^{-10}	9.38
Methylamine	CH_3NH_2	4.5×1^{-4}	3.3				
Dimethylamine	$(H_3)_2NH$	5.4×10^{-4}	3.2	N-Methylaniline		5.0×10^{-10}	9.30
Trimethylamine	$(CH_3)_3N$	6.0×10^{-5}	4.22				
Ethylamine	$CH_3CH_2NH_2$	5.1×10^{-4}	3.29	N, N-Dimethylaniline		1.15×10^{-9}	8.92
Diethylamine	$(CH_3CH_2)_2NH$	10.0×10^{-4}	3.0				
Triethylamine	$(CH_3CH_2)_3N$	5.6×10^{-4}	3.25	Benzylamine		2.0×10^{-5}	4.70

This may be explained on the basis of following factors :

1. Steric factor. The size of alkyl group is more than that of hydrogen and therefore, it hinders the attack of acid on the amine and therefore, basic strength decreases. Now crowding of alkyl group increases from primary to tertiary amines. As a result, their basic strength decreases. This is called **steric hindrance.** According to this effect, tertiary alkyl amines should be least basic.

2. Solvation of ions. When amines are dissolved in water, they undergo hydration through hydrogen bonding. The substituted ammonium cations form hydrogen bonds with water molecules and release energy called *hydration energy* and therefore, get stabilised. Now, greater the extent of hydrogen bonding in ammonium cations, more will be its stabilization and consequently greater will be the tendency of amine to change into cation and *greater will be the strength of the corresponding amine.* The stability of ammonium cation due to hydrogen bonding depends upon the number of H-atoms present on the N-atom. As can be seen below, the hydration of protonated amine due to hydrogen bonding decreases as :

$RNH_3^+ > R_2NH_2^+ > R_3NH^+$



Thus, tertiary ammonium ion is less hydrated than secondary ammonium ion, which is less hydrated than primary ammonium ion. Thus, tertiary amines have less tendency to form ammonium ion and consequently, they are least basic.

Thus, the order of basicity of aliphatic amines should be :

1°-amine > 2°-amine > 3°-amine

This order is opposite to the order based on inductive effect.

As a consequence of combined effects of inductive effect and solvation, *the secondary amines are the strongest bases among amines and basic strength varies as* :

2°-amine > 3°-amine > 1°-amine

Further, when the alkyl group is small such as $—CH_3$ group, there is no steric hindrance to hydrogen bonding. But, in case the alkyl group is bigger than $—CH_3$ group, there will be steric hindrance to hydrogen bonding. Thus, the change of nature of the alkyl group e.g., from $—CH_3$ to $—C_2H_5$ results in change of the order of basic strength.

It may be noted that in the gas phase, where the solvent effect is missing, the basic trend is as expected *i.e.*,

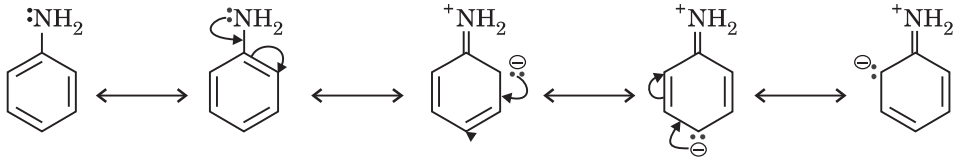
3°-amine > 2°-amine > 1°-amine > ammonia

(*c*) Comparison of basic strength of aromatic amines or arylamines and aliphatic amines.

Aromatic amines or arylamines are less basic than aliphatic amines and ammonia. For example, ethylamine is basic in nature due to the presence of lone pair on N-atom. But aniline is less basic than ammonia as well as ethylamine as shown by K_b values :

Aniline : $K_b = 4.2 \times 10^{-10}$	Ammonia : $K_b = 1.8 \times 10^{-5}$	Ethylamine : $K_b = 5.1 \times 10^{-4}$
pK_b = **9.38**	pK_b = **4.75**	pK_b = **3.29**

In aniline or other aryl amines, the $—NH_2$ group is attached directly to the benzene ring. As a result, the unshared electron pair on nitrogen atom is present in conjugation with the benzene ring and becomes less available for protonation because of resonance. Aniline may be regarded as resonance hybrid of the following resonating structures:



(I) (II) (III) (IV) (V)

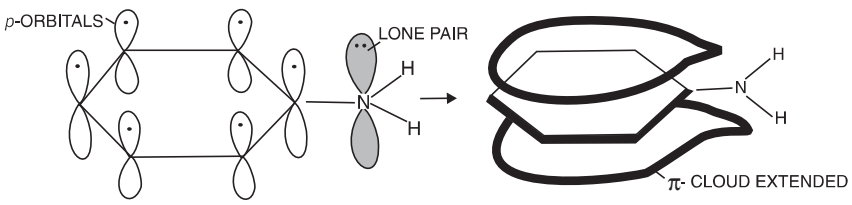
It is clear from the above resonating structures that three of these structures (III, IV and V) acquire some positive charge on nitrogen. As a result, the pair of electrons become less available for protonation. Hence, aniline is less basic than ethylamine in which there is no such resonance.

This can also be understood by comparing the relative stability of aniline and anilinium ion obtained by accepting a proton. Anilinium ion can have only two resonating structures :

(VI) (VII)

We know, greater the number of resonating structures, greater is the stability. Now, we observed that whereas aniline has five resonating structures, but anilinium ion has only two resonanting structures. Therefore, aniline is more stable than anilinium ion. In other words, aniline has lesser tendency to combine with a proton to form anilinium ion and therefore, aniline is less basic.

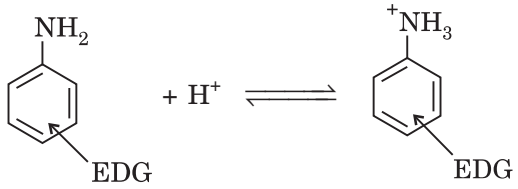
The basic character of aniline can also be understood in terms of **orbital theory**. According to this concept, the orbital containing the lone pair of electrons on the nitrogen atom interacts with π-bonding of the benzene ring system. The delocalised π-cloud gets extended as shown in adjacent structure.



As a result, the lone pair of electrons is not readily available for protonation and therefore, aniline is less basic than ethylamine (alkyl amines).

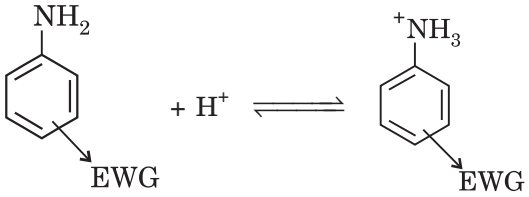
Effect of Substituents on the Basic Character of Aromatic Amines

(*i*) Electron donating or releasing groups like —OCH_3, —CH_3 increase the basic strength, while electron withdrawing groups like —X (halogen), —NO_2, —CN, —SO_3, —COOH, etc. decrease the basic strength;



EDG → released electrons, stabilized the cation and increases basic strength

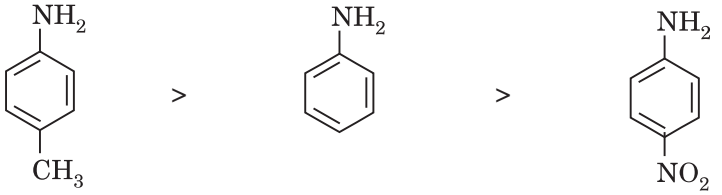
EDG = —CH_3, —OCH_3, —NH_2



EWG → withdraws electrons, destabilized the cation and decreases basic strength

EWG = —NO_2, —CN, —X (halogen)

For example,

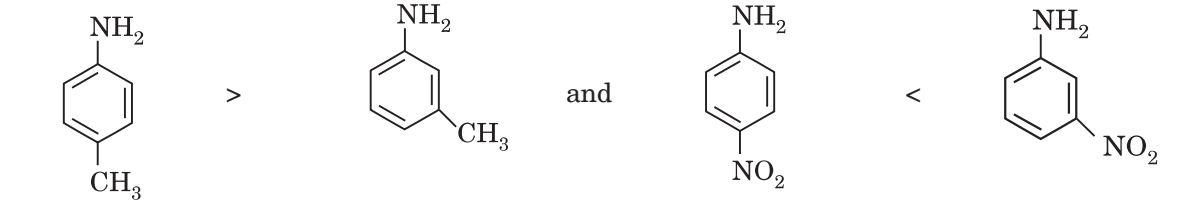


$[K_b = 1.2 \times 10^{-9}, pK_b = 8.92]$ $[K_b = 4.2 \times 10^{-10}, pK_b = 9.38]$ $[K_b = 1.0 \times 10^{-13}, pK_b = 13.0]$

The basicity constants (pK_b) of some aromatic amines are given below :

ctivating group		**eactivating group**	
Amine	pK_b	Amine	pK_b
p–$C_6H_4(CH_3)NH_2$	8.92	p– $C_6H_4(Cl)\ NH_2$	10.02
p–$C_6H_4(OCH_3)NH_2$	8.66	p–$C_6H_4(Br)NH_2$	10.14
p–$C_6H_4(NH_2)NH_2$	7.85	p–$C_6H_4(CN)NH_2$	12.26
Aniline	**9.38**	p–$C_6H_4(NO_2)NH_2$	13.00

(*ii*) The base weakening effect of electron withdrawing group and base strengthening effect of electron releasing group is more marked at *p*-position than at *m*-position.

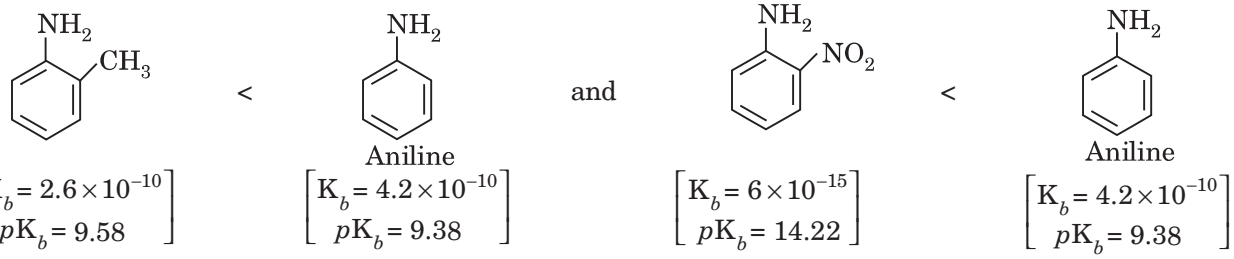


$[K_b = 1.2 \times 10^{-9}, pK_b = 8.92]$ $[K_b = 5 \times 10^{-10}, pK_b = 9.30]$ $[K_b = 1 \times 10^{-13}, pK_b = 13]$ $[K_b = 2.9 \times 10^{-12}, pK_b = 11.54]$

Electron releasing group — CH_3 makes *p*-isomer **more stronger basic** than *m*-isomer

Electron withdrawing group —NO_2 makes *p*-isomer **more weaker base** than *m*-isomer

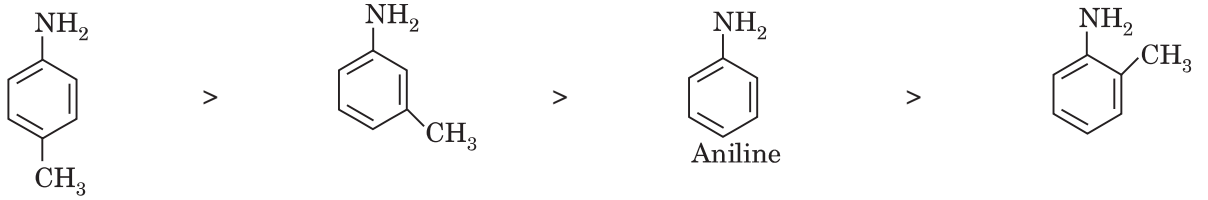
(*iii*) Every *o*-substituted aniline (electron releasing or electron withdrawing) is less basic than aniline. This is due to **ortho effect** which is probably due to combination of steric and electronic factors.



$[K_b = 2.6 \times 10^{-10}, pK_b = 9.58]$ $[K_b = 4.2 \times 10^{-10}, pK_b = 9.38]$ $[K_b = 6 \times 10^{-15}, pK_b = 14.22]$ $[K_b = 4.2 \times 10^{-10}, pK_b = 9.38]$

It may be noted that the base weakening effect of electron withdrawing group is **very large** when present at *o*-position than from the *m*- or *p*-position (note aniline and *o*-nitro aniline).

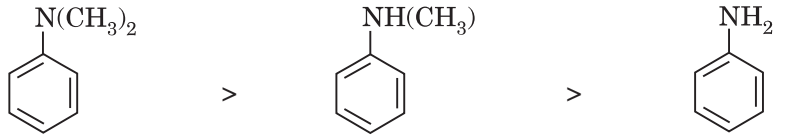
Similarly,



$[K_b = 1.2 \times 10^{-9}, pK_b = 8.92]$ $[K_b = 5 \times 10^{-10}, pK_b = 9.30]$ $[K_b = 4.2 \times 10^{-10}, pK_b = 9.38]$ $[K_b = 2.6 \times 10^{-10}, pK_b = 9.59]$

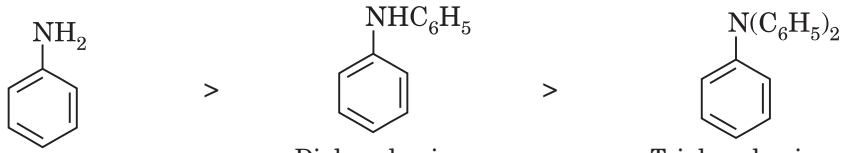
Effect of substituents on the nitrogen atom (N-substituted anilines)

When hydrogen atoms of the amino group of arylamines are replaced by electron donating alkyl groups, the basic character of the resulting arylamine increases. For example, N-methylaniline is a stronger base than aniline and N, N-dimethylaniline is even stronger than N-methylaniline. Thus,



N, N-Dimethylaniline ($pK_b = 8.92$) > N-Methylaniline ($pK_b = 9.30$) > Aniline ($pK_b = 9.38$)

On the other hand, when the hydrogen atoms of amino group are replaced by electron withdrawing groups (such as phenyl group), the basic character of the resulting arylamine decreases. For example,



Aniline ($pK_b = 9.38$) > Diphenylamine ($pK_b = 13.2$) > Triphenylamine

(*d*) Comparison of basic character of aralkylamines. As already learnt, the lone pair of electrons on N-atom of aniline is delocalised over the benzene ring. However, in case of aralkylamines, the lone pair of electrons on the N-atom is not conjugated with the benzene ring and therefore, it is not delocalized. Hence, the lone pair of electrons on the N-atom in aralkylamines is more readily available for protonation than that on the N-atom of aniline. Thus, *the aralkylamines are more basic than arylamines.* For example, benzylamine is a stronger base than aniline:

Benzylamine ($pK_b = 4.70$) > Aniline ($pK_b = 9.38$)

Further *aralkylamines are less basic than alkylamines*. This is because aryl group has electron-withdrawing inductive effect (-I effect) while alkyl group in alkylamines is electron donating group (+I effect). As a result, the lone pair of electrons on the N-atom of aralkylamines is less easily available for protonation than that on the N-atom of alkylamines. However, they are stronger bases than ammonia. For example,

CH_3NH_2	>	$C_6H_5CH_2NH_2$	>	NH_3
Methylamine		Benzylamine		Ammonia
($pK_b = 3.28$)		($pK_b = 4.70$)		($pK_b = 4.75$)

2. Reaction with acids

Amines being basic react with acids to form salts.

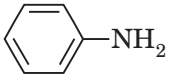
$$RNH_2 + HX \longrightarrow \underset{\text{Alkylammonium halide}}{RNH_3^+X^-}$$

$$\underset{\text{Methyl amine}}{CH_3NH_2} + HCl \longrightarrow \underset{\text{Methyl ammonium chloride}}{CH_3NH_2HCl \text{ or } CH_3NH_3^+Cl^-}$$

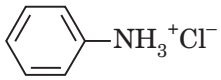
$$\underset{\text{Dimethylamine}}{2(CH_3)_2NH} + H_2SO_4 \longrightarrow \underset{\text{Dimethylammonium sulphate}}{[(CH_3)_2\overset{+}{N}H_2]_2\,SO_4^{2-}}$$

$$\underset{\text{Dimethylamine}}{(CH_3)_2NH} \quad HNO_3 \longrightarrow \underset{\text{Dimethylammonium nitrate}}{[(CH_3)_2\overset{+}{N}H_2]NO_3^-}$$

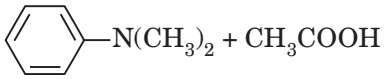
$$\underset{\text{Triethylamine}}{(C_2H_5)_3N} \quad HCl \longrightarrow \underset{\text{Triethylammonium chloride}}{(C_2H_5)_3NH^+Cl^-}$$



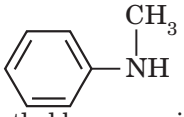
$$+ HCl \longrightarrow$$



Aniline — Aniline hydrochloride nilinium chloride)

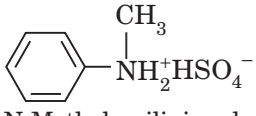


N, N-Dimethylaniline — N, N-Dimethylanilium acetate



N-Methyl benzenamine

$$+ H_2SO_4 \longrightarrow$$



N-Methyl anilinium hydrogen sulphate

The salts of amines are ionic compounds and are soluble in water. On treatment with aqueous hydroxide, amines are regenerated.

$$RNH_3^+X^- + NaOH \longrightarrow RNH_2 + H_2O + NaX$$

These amine salts are non-volatile solids and generally decompose before their melting points are reached. These are soluble in water but insoluble in non-polar solvents such as benzene, ether, chloroform, etc. This difference in solubility behaviour of amines and their salts is often used to detect amines and seperate (or purify) them from other non-basic impurities.

The amines react with chloroplatinic acids (H_2PtCl_6) to form insoluble salts called chloroplatinates.

$$2RNH_2 + H_2PtCl_6 \longrightarrow \underset{\text{Amine chloroplatinate}}{(RNH_3^+)_2\,PtCl_6^{2-}}$$

The salts chloroplatinates are used for the determination of equivalent and molecular masses of amines.

3. Reaction of amines with transition metal ions

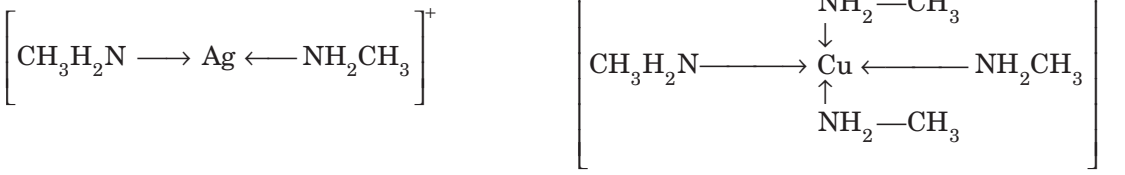
Like ammonia, amines combine with metal ions such as Ag^+ and Cu^{2+} ions to form complex compounds. The lone pair of electrons in NH_3 is used to form a co-ordinate bond of amine with metal ions. For example, silver chloride dissolves in methylamine to form a soluble silver amine complex.

$$AgCl + 2CH_3NH_2 \longrightarrow \underset{\text{Soluble complex}}{[Ag(CH_3NH_2)_2]^+Cl^-}$$

Similarly, copper sulphate reacts with methylamine to give deep blue coloured complex.

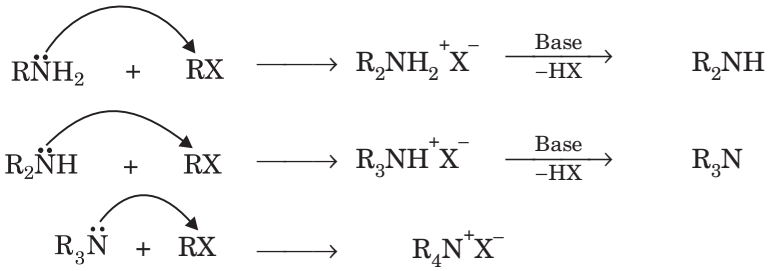
$$CuSO_4 + 4CH_3NH_2 \longrightarrow \underset{\text{Soluble complex}}{[Cu(CH_3NH_2)_4]^{2+}SO_4^{2-}}$$

In these complexes, there is a co-ordinate bond between metal ion and amine molecules as shown below :

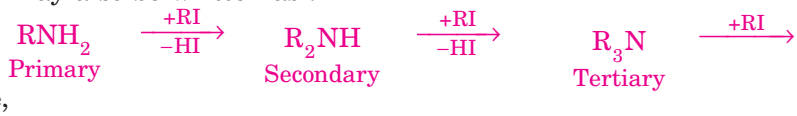


4. Reaction with alkyl halides: Alkylation

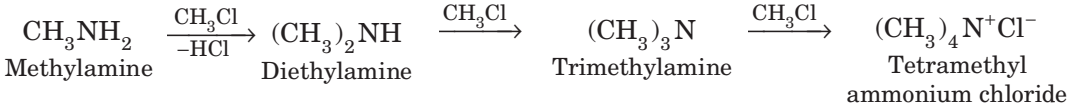
Primary and secondary amines react with alkyl halides to form tertiary amines. The primary or secondary amine acts as nucleophile and perform nucleophilic substitution at an alkyl halide. On removal of HX, secondary or a tertiary amine is regenerated respectively. The secondary amine being a more powerful nucleophile again reacts similarly with another alkyl halide forming tertiary amine. At each stage of the reaction, an equivalent amount of a strong acid is formed. This can protonate the amine making lone pair on nitrogen not available for nucleophilic attack and therefore, stop the reaction before completion. Therefore, for the neutralisation of the acid and for liberating the nucleophile, a base such as carbonate is added. Finally, the tertiary amine react with alkyl halides to form quaternary ammonium salts.

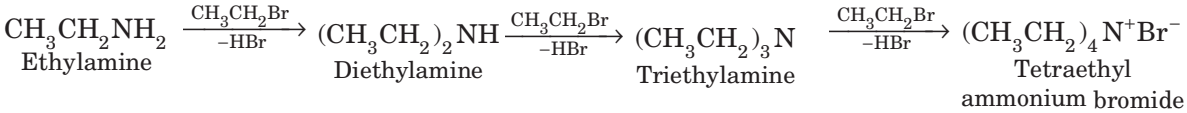


The reaction may also be written as :



For example,

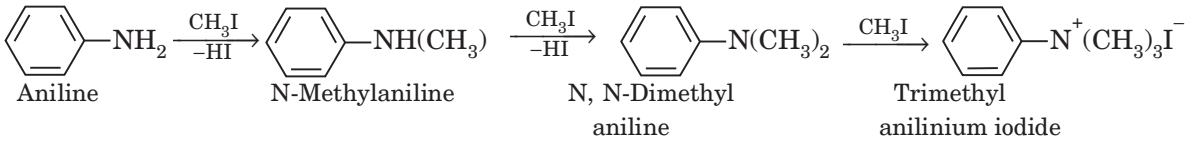




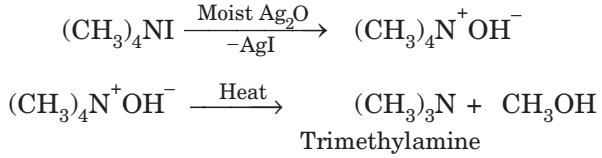
The process of converting an amine (1°, 2° or 3°) into its quaternary ammonium salt on treatment with excess of alkyl halide is called **exhaustic alkylation.**

If the alkyl halide used is methyl iodide, the process is commonly called **exhaustic methylation.**

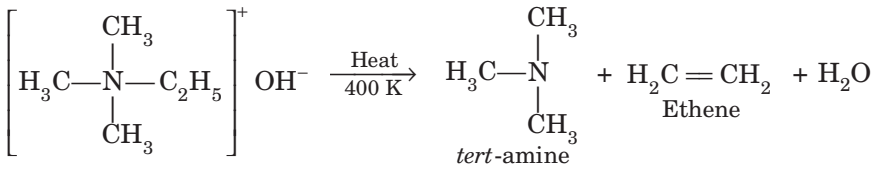
Aromatic amines also undergo similar reactions. For example, when aniline is treated with methyl iodide under pressure, quaternary ammonium salts are formed.



The tetramethyl ammonium salt or quaternary ammonium halide on reaction with moist silver oxide forms tetramethyl ammonium hydroxide and silver halide gets precipitated. This on heating (400 K) decomposes to give tertiary amine and alcohol.



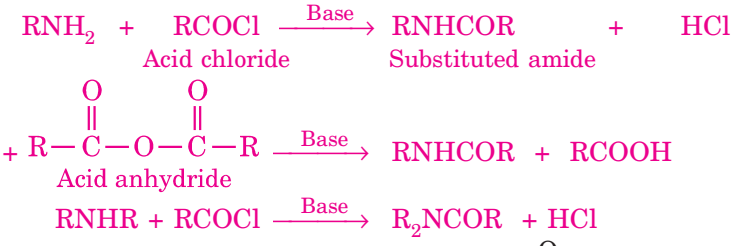
If one of the alkyl groups is other than methyl, the quaternary ammonium hydroxide, *gives a tertiary amine, an alkene and water on heating*. For example,



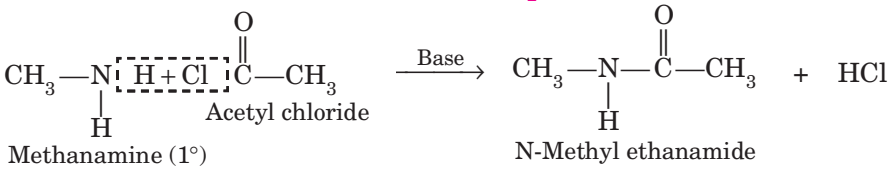
This pyrolysis of quaternary ammonium hydroxide to give alkenes is called **Hoffmann's elimination reaction.** This can be used for the elucidation of the structure of amines.

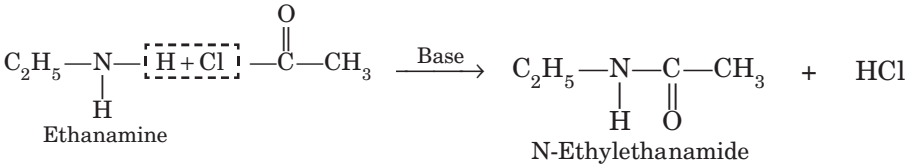
5. Acylation (reaction with acid chlorides and acid anhydrides)

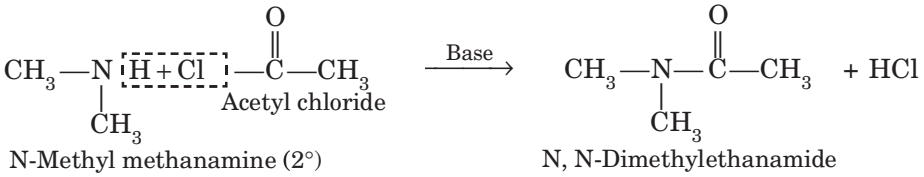
Aliphatic and aromatic primary and secondary amines (which contain replaceable hydrogen atoms) react with acid chloride, acid anhydride and esters to form substituted amides. *The process of introducing an acyl group* (R—C(=O)—) *into a molecule is called* ***acylation.*** The reaction may be considered as the replacement of hydrogen atom of —NH_2 or >N—H group by the acyl group. It is **nucleophilic substitution reaction**. The reaction is carried out in the presence of a base stronger than amine like pyridine which removes HCl so formed and shifts the equilibrium to the right hand side. For example,



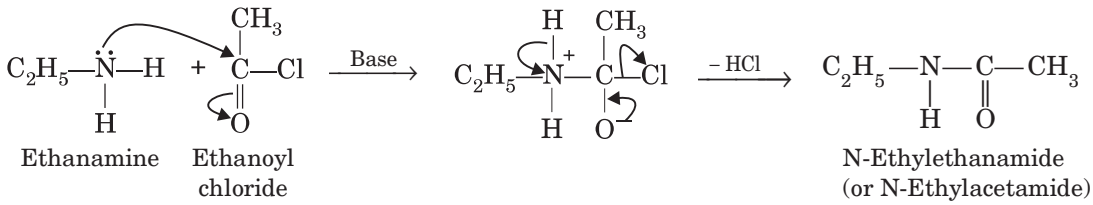
The process of introducing an acyl group (R—C(=O)—) into a molecule is called **acylation**.



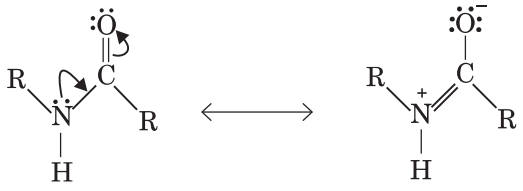




The reaction occurs as :

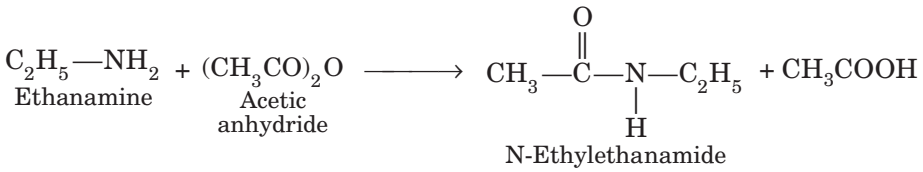


During the reaction, the acid generated can form salt of the amine which will then lose nucleophilic character and therefore, the reaction will not go to completion. Therefore, a base is added to facilitate the reaction. Unlike alkylation, the amide formed does not react further with organic halide because amide is non-basic. The lone pair of electrons on nitrogen is in conjugation with carbonyl group and therefore, it is a poor nucleophile.

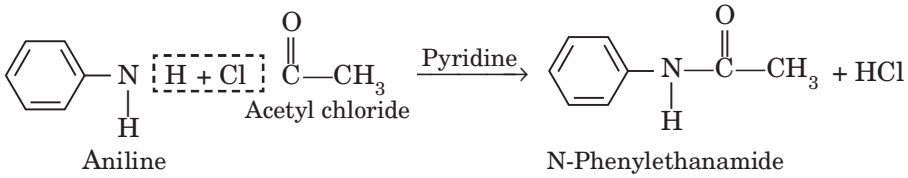


Amongst the acid derivatives the acid chlorides are stronger acylating agents than the anhydrides and esters which react very slowly.

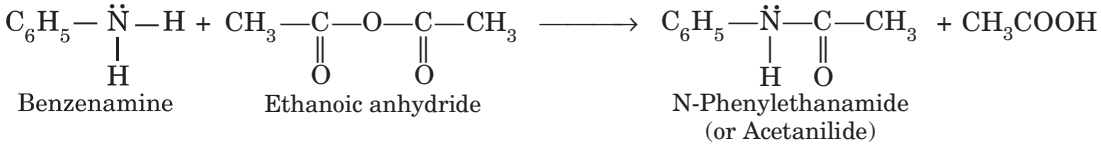
Since tertiary amines do not contain replaceable hydrogen atom, they do not react with acetyl chloride. Therefore, in acylation reaction of an amine, in addition to its nucleophilic character, the presence of an H atom on nitrogen is also necessary. Acylation can also take place with acid anhydride.



Aniline or benzenamine reacts in a similar manner. However, acylation of aromatic amines is usually carried out in the presence of a base stronger than the amine such as aqueous NaOH or pyridine. This base removes HCl formed.

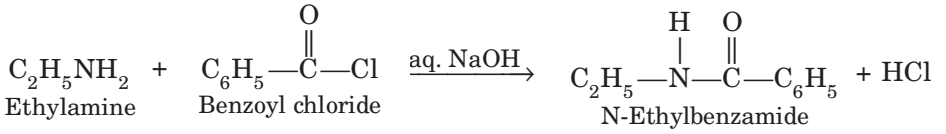


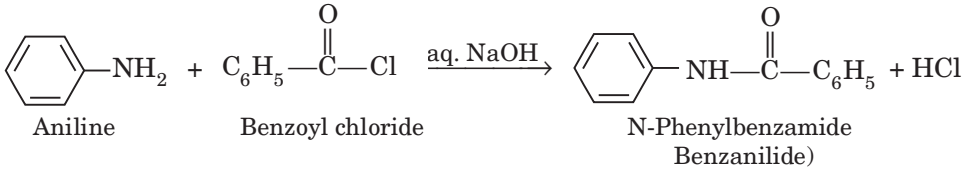
Similarly,



6. Benzoylation

Aliphatic and aromatic amines react with benzoyl chloride in the presence of a base such as pyridine or aqueous NaOH to form benzoyl derivatives in which C_6H_5CO— group is introduced. This reaction is called **benzoylation.**



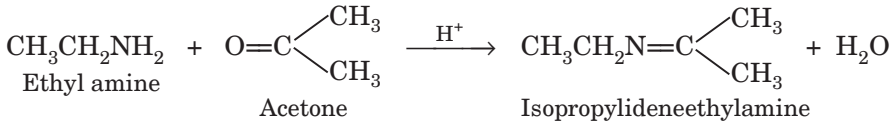


Benzoylation of compounds containing an active hydrogen such as alcohols, phenols or amines with benzoyl chloride in the presence of dilute aqueous NaOH solution is called **Schotten Baumann reaction.**

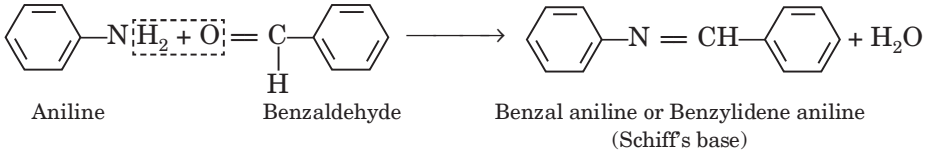
7. Schiff's base formation (reaction with aldehydes and ketones)

Both aliphatic and aromatic primary amines react with aldehydes and ketones to form imines also called **Schiff's bases** or **anils**

e.g.,



Benzaldehyde reacts with aniline to give a typical Schiff's base known as **benzal aniline.**



Schiff's base on reduction gives secondary amine.

$$\underset{\text{Ethylideneethylamine}}{CH_3CH_2N{=}CHCH_3} \xrightarrow[\text{or } NaBH_4]{H_2,\ \text{Raney Ni}} \underset{\text{Diethylamine}}{CH_3CH_2NHCH_2CH_3}$$

$$C_6H_5N{=}CH{-}C_6H_5 + H_2 \xrightarrow{\text{Raney Ni}} \underset{\substack{\text{N-Benzylaniline}\\ \text{(Secondary amine)}}}{C_6H_5NH{-}CH_2{-}C_6H_5}$$

Therefore, this method can be used to prepare secondary amines.

Aldehydes and ketones which have alpha hydrogen react with secondary amines both acyclic (*e.g.*, N, N-dimethylamine) as well as cyclic (*e.g.*, pyrrolidene, piperidine etc.) to form carbinolamines. These carbinolamines are unstable and readily lose a molecule of water to form stable **α, β-unsaturated amines** commonly called **enamines** (ene – e + amine = enamine).

$$\underset{\substack{\\ (R' = \text{alkyl or H})}}{R{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}R'} + R_2NH \underset{PTS}{\overset{C_6H_6}{\rightleftharpoons}} \underset{\substack{\text{Carbinolamine}\\ \text{(Unstable)}}}{\left[R{-}CH_2{-}\overset{\overset{OH}{|}}{\underset{\underset{NR_2}{|}}{C}}{-}R'\right]} \overset{-H_2O}{\rightleftharpoons} \underset{\text{Enamine}}{R{-}CH{=}C\begin{matrix}R'\\ \diagup\\ \diagdown\\ NR_2\end{matrix}}$$

e.g.,

$$\underset{\text{Acetone}}{\begin{matrix}CH_3\\ \diagup\\ \diagdown\\ CH_3\end{matrix}C{=}O} + (CH_3)_2NH \underset{PTS}{\overset{C_6H_6}{\rightleftharpoons}} \left[CH_3{-}\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}{-}N\begin{matrix}CH_3\\ \diagup\\ \diagdown\\ CH_3\end{matrix}\right] \xrightarrow{-H_2O} \underset{\text{N, N-Dimethylprop-1-en-2-amine}}{CH_2{=}\underset{\underset{CH_3}{|}}{C}{-}N\begin{matrix}CH_3\\ \diagup\\ \diagdown\\ CH_3\end{matrix}}$$

It may be noted that the equilibrium is shifted in the forward direction by removing water as an azeotrope with benzene. Thus, enamine formation is usually carried out by refluxing the benzene solution of an aldehyde or ketone with a secondary amine in the presence of trace amount of an acid such as PTS (*p*-toluene sulphonic acid).

Enamines can also be reduced by catalytic hydrogenation (Ni/H_2) or sodium borohydride ($NaBH_4$) to form corresponding amines.

$$\underset{\text{N, N-Dimethylprop-1-en-2-amine}}{CH_2{=}\underset{\underset{CH_3}{|}}{C}{-}N\begin{matrix}CH_3\\ \diagup\\ \diagdown\\ CH_3\end{matrix}} \xrightarrow[\text{or } NaBH_4]{H_2,\ \text{Raney Ni}} \underset{\text{N, N-Dimethyl-2-propanamine}}{CH_3{-}\underset{\underset{CH_3}{|}}{CH}{-}N\begin{matrix}CH_3\\ \diagup\\ \diagdown\\ CH_3\end{matrix}}$$

8. Reaction with chloroform : Carbylamine reaction (or isocyanide test)

Aliphatic and aromatic primary amines when warmed with chloroform and an alcoholic solution of KOH, form isocyanide or carbylamine which have very unpleasant or foul smell.

$$\underset{\substack{1^\circ \text{ amine}}}{R{-}NH_2} + CHCl_3 + 3KOH\ (alc.) \xrightarrow{\text{Warm}} \underset{\text{Alkyl isocyanide}}{R{-}NC} + 3KCl + 3H_2O$$

$$\underset{\text{Ethylamine}}{CH_3CH_2NH_2} + \underset{\text{Chloroform}}{CHCl_3} + 3KOH\ (alc.) \xrightarrow{\text{Warm}} \underset{\text{Ethyl isocyanide}}{CH_3CH_2NC} + 3KCl + 3H_2O$$

$$\underset{\text{Aniline}}{C_6H_5NH_2} + \underset{\text{Chloroform}}{CHCl_3} + 3KOH\ (alc.) \xrightarrow{\text{Warm}} \underset{\text{Phenyl isocyanide}}{C_6H_5NC} + KCl + 3H_2O$$

HELP

Carbylamine test is an important test to distinguish primary amines from secondary and tertiary amines.

Secondary and tertiary amines do not give this test. Therefore, this test can be used to distinguish between *primary amines from secondary and tertiary amines.*

9. Reaction with nitrous acid

Nitrous acid (HNO_2) is an unstable acid therefore, it must be freshly prepared (in situ) by treatment of sodium nitrite with cold dilute HCl or H_2SO_4.

$$\underset{\text{Sodium nitrite}}{NaNO_2} + HCl \longrightarrow NaCl + \underset{\text{Nitrous acid}}{HONO}$$

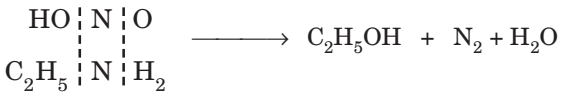
Nitrous acid is a source of electrophilic nitrosonium ion ($O = N^+$) which reacts with amines.

Different classes of amines react differently with nitrous acid. This reaction serves as an important reaction to distinguish between primary, secondary and tertiary amines.

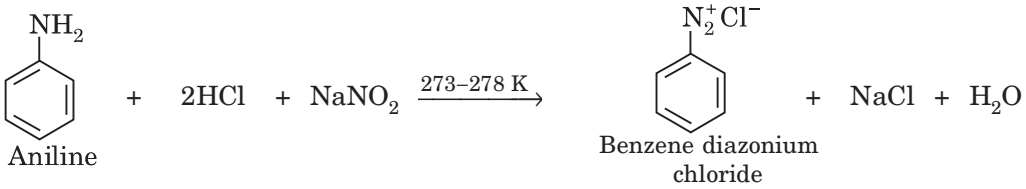
(*i*) **Primary amines.** Primary aliphatic amines react rapidly with nitrous acid to form aliphatic diazonium salt, which is unstable and decomposes to give alcohol and **evolve nitrogen**.

$$\underset{\text{Primary amine}}{RNH_2} + HNO_2 \xrightarrow[HCl]{NaNO_2} [R{-}N_2^+Cl^-] \xrightarrow{H_2O} \underset{\text{Alcohol}}{ROH} + HCl + N_2$$

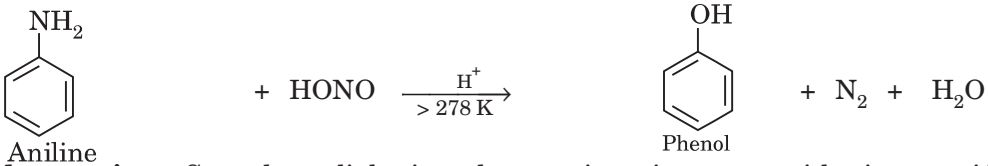
e.g.,



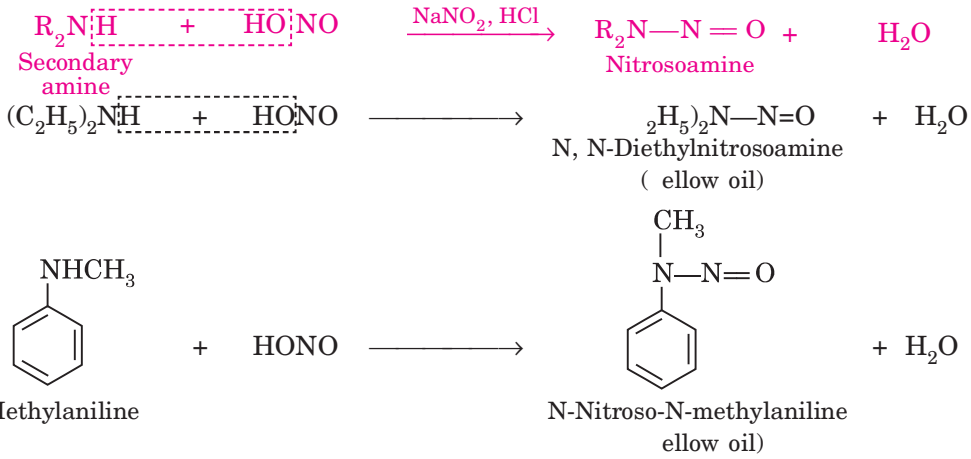
Primary aromatic amines react with nitrous acid in the cold (273–278 K) to form diazonium salts. *The process of formation of diazonium salts by the reaction of aromatic amino compound and nitrous acid* is called **diazotisation.** For example,



However, if the temperature is more than 278 K, aromatic amines form phenol with the evolution of N_2 gas.

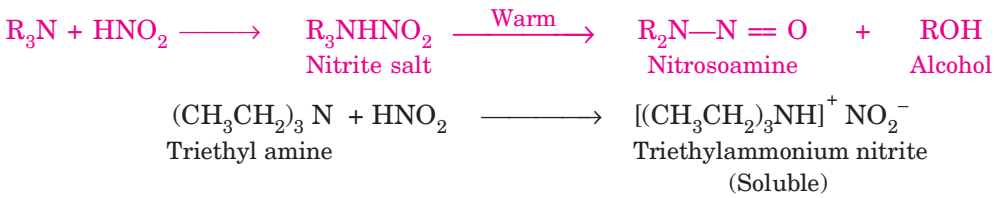


***(ii)* Secondary amines.** Secondary aliphatic and aromatic amines react with nitrous acid slowly in the cold to form yellow oily **nitroso amines.**

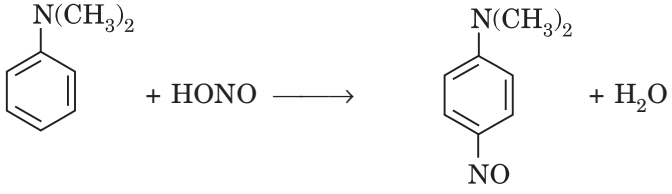


The yellow oily nitrosoamine gives a **green solution** when warmed with phenol and conc. sulphuric acid. On dilution with water, the colour changes to **red,** but it changes to **greenish blue to violet** on the addition of sodium hydroxide. The overall reaction is called **Libermann's nitroso reaction.** This test is used for secondary amines.

***(iii)* Tertiary amines.** Tertiary amines dissolve in cold nitrous acid to form salts which decompose on warming to **nitrosoamine** and **alcohol.**



Aromatic tertiary amines react with nitrous acid to give coloured substituted nitroso compound. These undergo electrophilic substitution of nitrosonium ion ($N = O^+$) at the para position of the phenyl ring.



R U Curious...

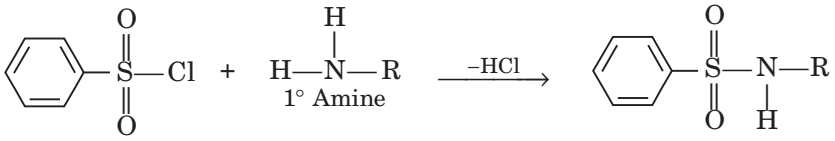
❑ **Cigarette smoking is injurious to health. Do you know why?**

◆ In addition to nicotine, cigarette smoke contains N-nitrosodimethylamine which is a powerful carcinogen and very harmful.

10. Reaction with aryl sulphonyl chloride

Benzene sulphonyl chloride ($C_6H_5SO_2Cl$) which is also known as **Hinsberg's reagent** reacts with primary and secondary amines to form sulphonamides.

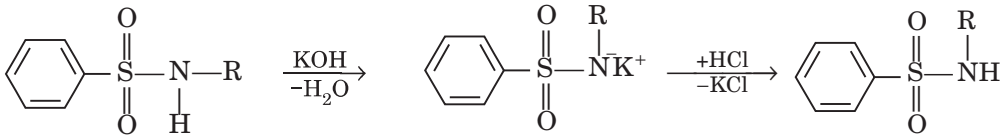
(*i*) Primary amines react with benzene sulphonyl chloride to give N-alkyl benzene sulphonamide.



Benzenesulphonylchloride N-Alkylbenzenesulphonamide

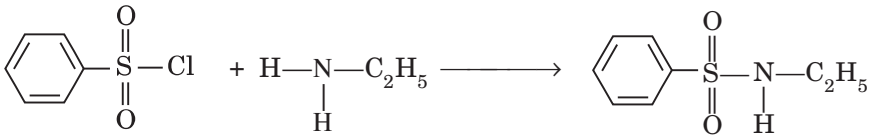
(Soluble in alkali)

The hydrogen attached to nitrogen in sulphonamide is strongly acidic due to the presence of strongly electron withdrawing sulphonyl group. Therefore, it is soluble in alkali. On acidification, it gives an insoluble material.



(Water soluble salt) (Insoluble)

e.g.,

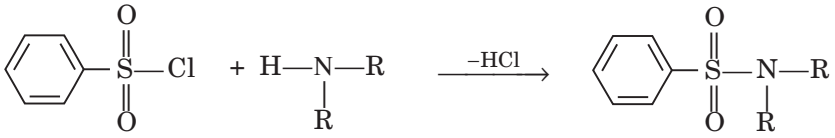


N-Ethylbenzenesulphonamide

(Soluble in alkali)

(*ii*) Secondary amines react with benzene sulphonyl chloride to form N, N-dialkyl benzene sulphonamide.

e.g.,

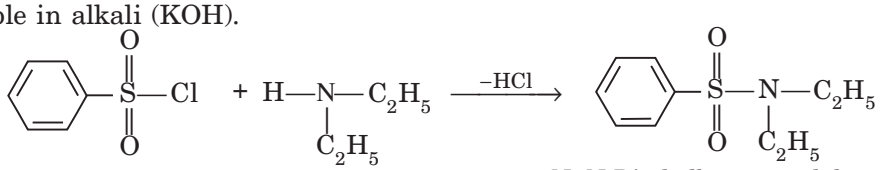


N, N-Dialkylbenzenesulphonamide

(Insoluble in KOH)

Since the sulphonamide does not contain any hydrogen atom attached to nitrogen atom, so it is not acidic. Hence it is not soluble in alkali (KOH).

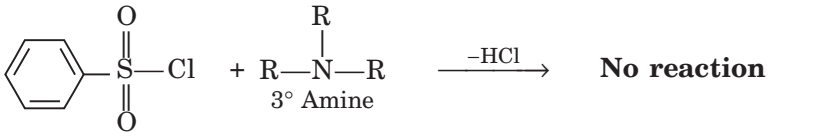
e.g.,



N, N-Diethylbenzenesulphonamide

(Insoluble in KOH)

(*iii*) Tertiary amines do not react with benzene sulphonylchloride.



No reaction

Since different amines react differently with benzene sulphonyl chloride, this reaction can be used **for the distinction between 1°, 2° and 3° amines** and also for the separation of their mixtures.

However, these days, benzene sulphonyl chloride has been replaced by *p*-toluenesulphonyl chloride.

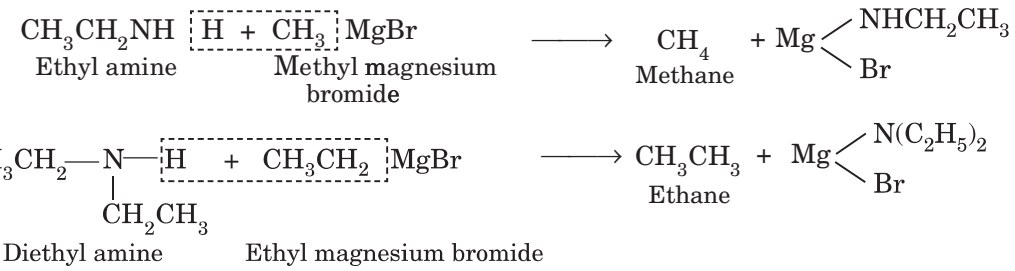
11. Reaction with Grignard reagent

Primary and secondary amines react with Grignard reagents to form *alkanes*.

NOTE

It may be noted that alkane is obtained from the alkyl part of Grignard reagent.

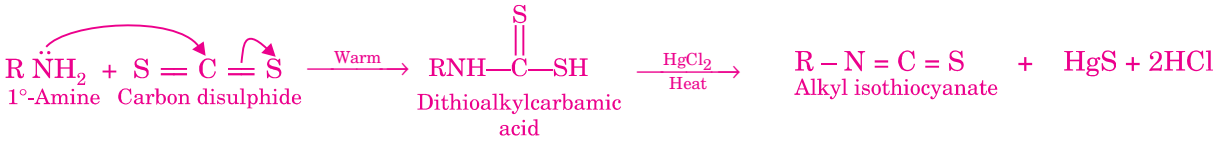
For example,

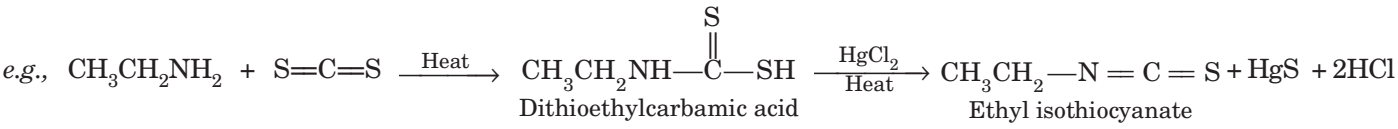


Tertiary aliphatic amines do not react with Grignard reagent because they do not have hydrogen atom attached to the nitrogen atom.

12. Reaction with carbon disulphide

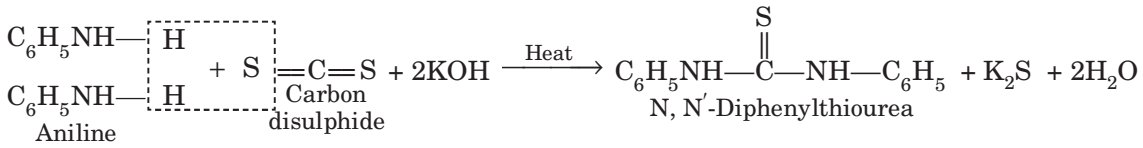
Primary amines react with carbon disulphide to form dithioalkyl carbamic acids which decompose on heating with mercuric chloride ($HgCl_2$) to give *alkyl isothiocyanates*. These have characteristic smell like mustard oil. For example,

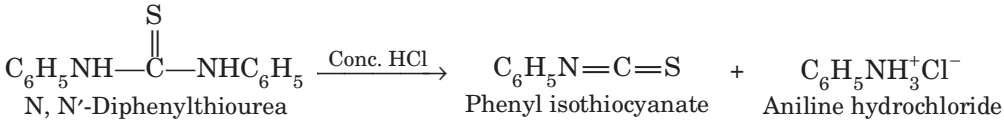




This reaction is called ***Hoffmann mustard oil* reaction** and is **used as a *test for primary amines.***

However, aromatic amines react in slightly different manner. For example, when aniline is heated with ethanolic CS_2 and solid KOH, it forms N, N′-diphenyl thiourea which on treatment with conc. HCl gives phenyl isothiocyanate.

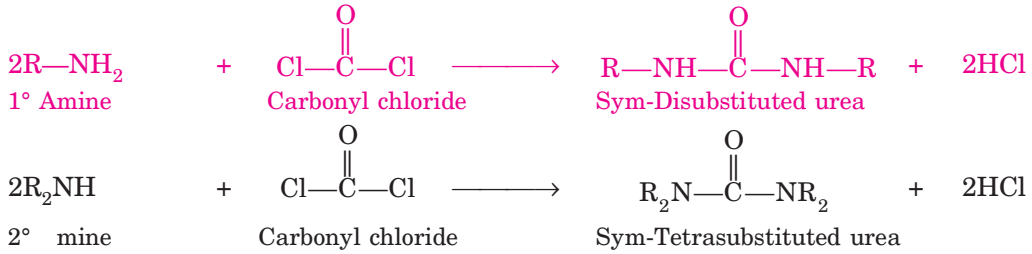




N, N′- Diphenyl thiourea (or thiocarbanilide) is used as an accelerator during vulcanization of rubber.

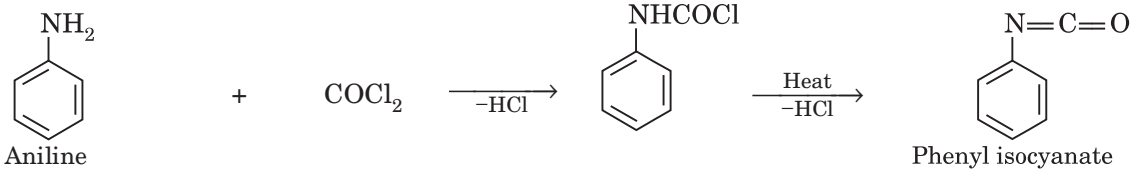
13. Reaction with carbonyl chloride (phosgene)

Primary and secondary aliphatic amines react with carbonyl chloride to form substituted ureas.



Tertiary aliphatic amines form salts.

Aromatic 1° amines react with $COCl_2$ to form aryl isocyanate. For example,



14. Oxidation

Oxidation of amines give different products depending upon the nature of amine and oxidising agent. Amines undergo oxidation by powerful oxidising agents such as Caro's acid (H_2SO_5), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2) etc. The products of oxidation depend upon the nature of amine and oxidising agent. For example,

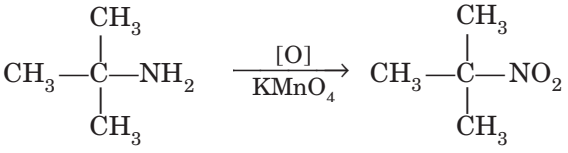
(*a*) Oxidation of primary amines

(*i*) Primary aliphatic amines on oxidation with potassium permanganate give nitro compounds through a sequence of reactions as shown below :

$$\underset{\text{1° Amine}}{RNH_2} \xrightarrow{[O]} \underset{\text{Hydroxylamine}}{RNHOH} \xrightarrow[-H_2O]{[O]} \underset{\text{Nitroso compound}}{R{-}N{=}O} \xrightarrow{[O]} \underset{\text{Nitro compound}}{R{-}NO_2}$$

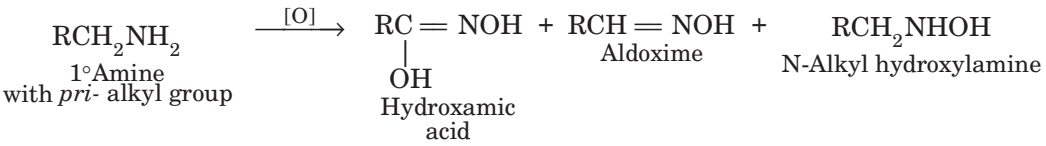
Depending upon the nature of the oxidising agent, various products such as hydroxylamine, nitroso or nitro compounds can be isolated.

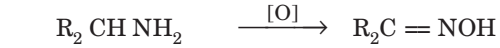
Primary amines in which $-NH_2$ group is attached to the tertiary carbon atom can be oxidised with $KMnO_4$ to the corresponding nitro compound in excellent yield (about 83%).

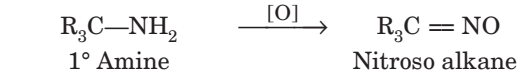


2-Methyl-2-propanamine → 2-Methyl-2- nitropropane (excellent yield 83%)

(*ii*) Primary amines react with Caro's acid (H_2SO_5) or H_2O_2 in the following ways :

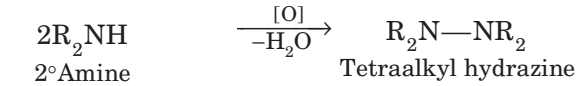




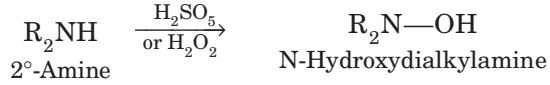


(*b*) Oxidation of secondary amines

(*i*) Secondary aliphatic amines on oxidation with potassium permanganate give *tetra* alkyl hydrazines.

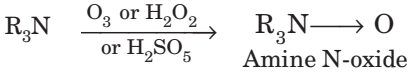


(*ii*) Secondary amines with Caro's acid give corresponding N-hydroxy amine.



(*c*) Oxidation of tertiary amines

Tertiary amines are not oxidised by $KMnO_4$ but are oxidised by Caro's acid, ozone or H_2O_2 to corresponding N-oxides.

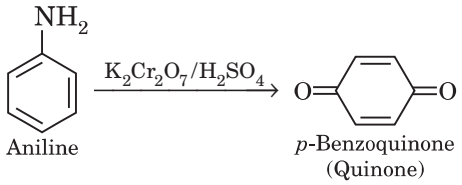


(*d*) Oxidation of aromatic amines

Aromatic amines, because of high electron density on the benzene ring, are readily oxidised on exposure to air or oxidising agents forming a complex coloured product.

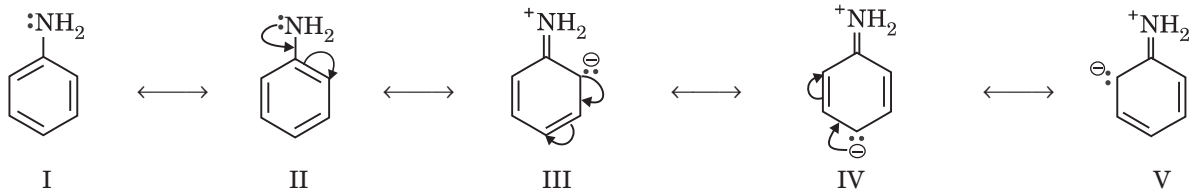
$$C_6H_5NH_2 + K_2Cr_2O_7 + H_2SO_4 \longrightarrow \text{A black product called aniline black.}$$

However, controlled oxidation of aniline with $K_2Cr_2O_7$ and H_2SO_4, gives *p*-benzoquinone.

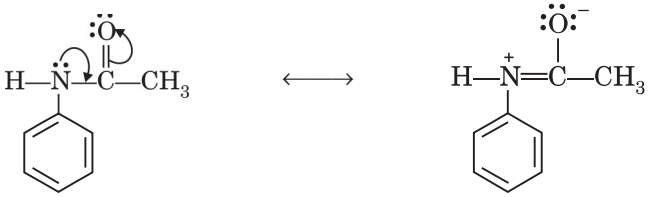


15. Ring substitution in aromatic amines

Aromatic amines give the aromatic substitution reactions as given by benzene. *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. This is clear from the following resonating structures in which electron density is more at *ortho* and *para* positions (structures III to IV).



Therefore, substitution mainly occurs at *ortho* and *para* positions. Due to strong activating effect of $—NH_2$, aromatic amines undergo electrophilic substitution reactions readily. Therefore, it is difficult to stop the reaction to monosubstitution stage. However, in order to stop the reaction to monosubstitution stage, the activating effect of the amino group has to be reduced. This can be done by *acetylation* with acetic anhydride in the presence of pyridine. Acetyl group is electron withdrawing group and therefore, the electron pair of N-atom is withdrawn towards the carbonyl group as shown by the following resonating structures :

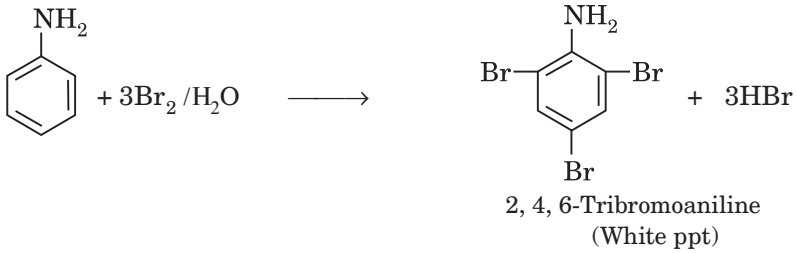


Therefore, the lone pair of electrons on nitrogen is less available and the activating power of $—NH_2$ group is decreased. This method is called the **protection** of the amino group by acetylation and can be used to control the rate of electrophilic substitution reaction. This also prevents the formation of *di* and *tri* substituted products.

The acetyl group is then removed by hydrolysis to get back the amine.

Some of these reactions are given below :

***(i)* Halogenation.** Aniline reacts with bromine water readily to give a white precipitate of 2, 4, 6-tribromoaniline.

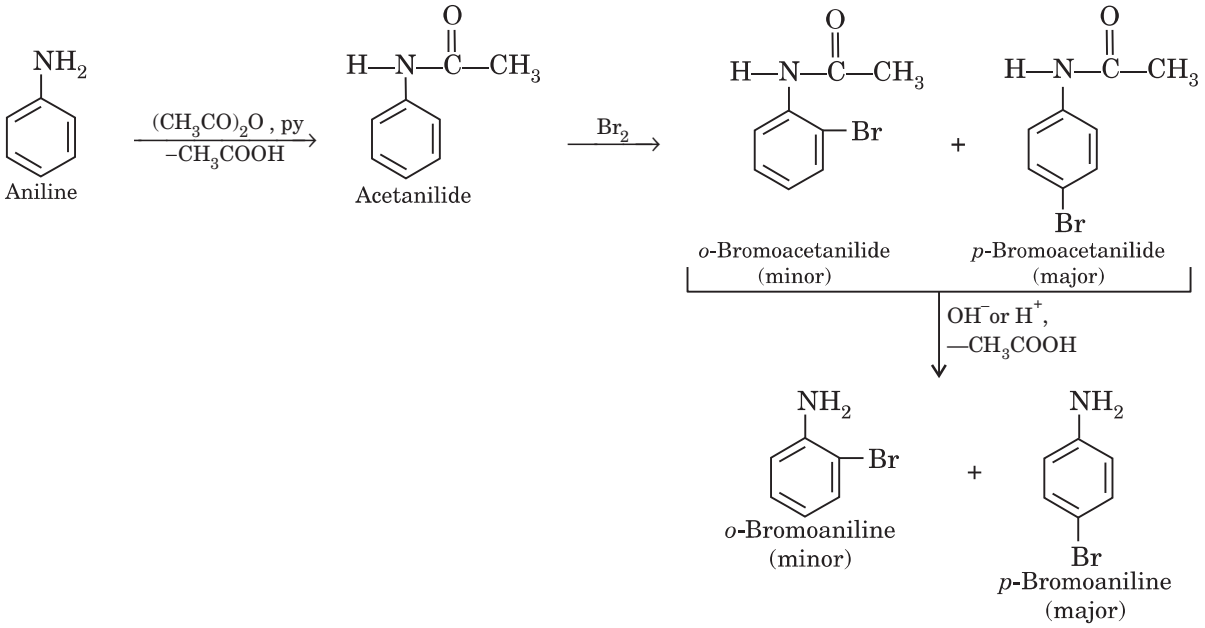


NOTE

This reaction is used as a test for aniline.

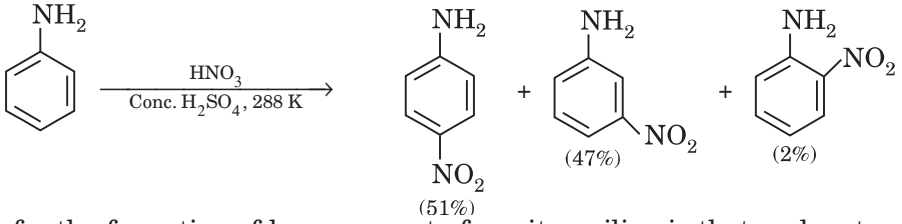
However, if monosubstituted derivative is desired, aniline is first acetylated with acetyl chloride and then halogenation is carried out. After halogenation, the acetyl group is removed by hydrolysis and only monosubstituted halogen derivative is obtained.

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.

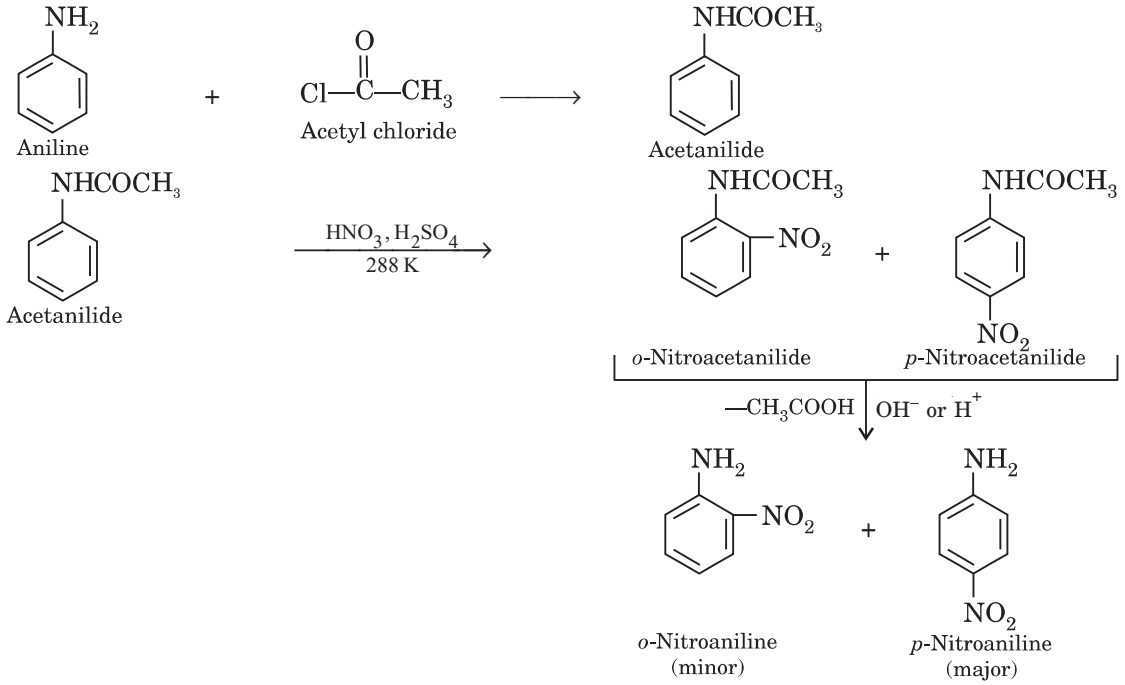


As already explained ***acetylation deactivates the ring and controls the reaction to monosubstitution stage only.***

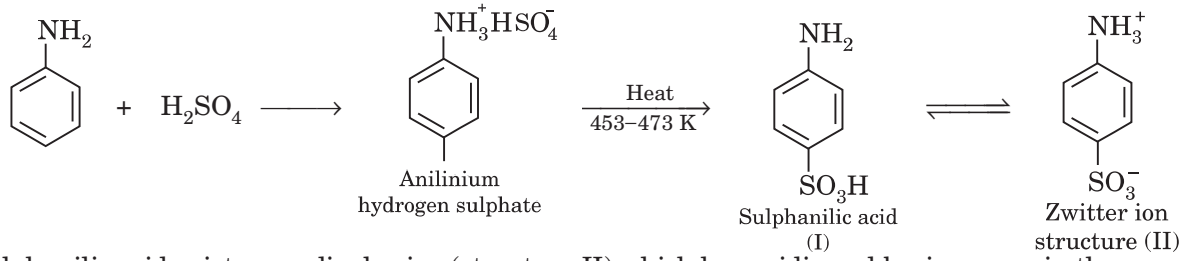
***(ii)* Nitration.** Aromatic amines cannot be nitrated directly because they are readily oxidized. This is because, HNO_3 is a strong oxidising agent and results in partial oxidation of the ring to form a black mass. However, under controlled conditions, nitration of aniline gives unexpectedly 47% *m*-nitro aniline in addition to *o*- and *p*-nitroaniline



The reason for the formation of large amount of *m*-nitroaniline is that under strongly acidic conditions aniline gets protonated to anilinium ion (– NH_3^+ group). This is deactivating group and is meta directing. Therefore, to solve this problem, nitration is carried out by protecting the —NH_2 group by acetylation. *The acetylation deactivates the ring and therefore, controls the reaction (already explained).* The hydrolysis of nitroacetanilides removes the protecting acyl group and gives back amines.



***(iii)* Sulphonation.** Sulphonation of aniline is carried out by heating aniline with sulphuric acid. The product formed is anilinium hydrogen sulphate which on heating gives sulphanilic acid.



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.**

NOTE

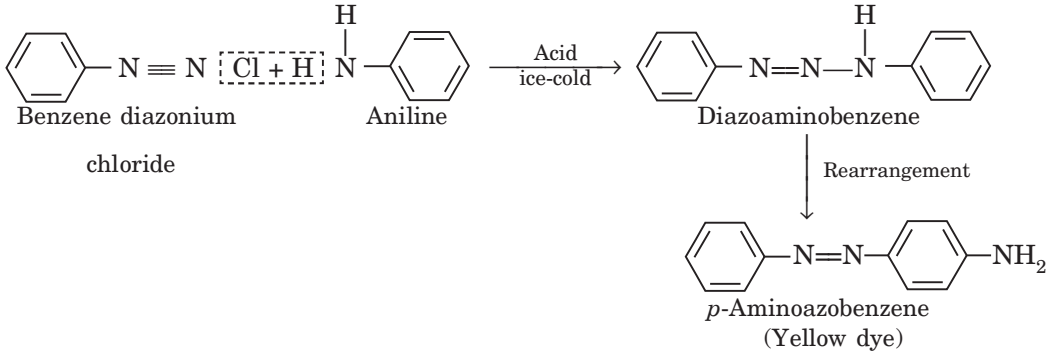
Aniline does not undergo Friedel Craft reaction (alkylation and acetylation) because of the salt formation with aluminium chloride (Lewis acid which is used as a catalyst).

$$C_6H_5NH_2 + AlCl_3 \longrightarrow C_6H_5\overset{+}{N}H_2\ AlCl_3^-$$

Nitrogen of aniline aquires positive charge and hence acts as a strong electron withdrawing group. As a result, it reduces the electron density in the benzene ring and therefore, deactivates it. Hence, aniline does not undergo Friedel-Crafts alkylation or acylation reaction.

16. Coupling with diazonium salts

Aromatic amines react with diazonium salts to form azo compounds in acidic medium called dyes. The reaction is known as **coupling** or **diazo reaction.** For example, aniline couples with benzene diazonium chloride to form diazo amino benzene which ultimately changes to *p*-amino azo benzene on warming with a small quantity of hydrochloric acid.



Tests for amines

1. **Solubility test:** All amines are basic in nature and hence are soluble in dil HCl. These amines can be regenerated from acidic medium by adding excess of alkali.

2. **Carbylamine test:** Primary amines (aliphatic or aromatic) can be detected easily by heating the amine with chloroform and alkali, when characteristic foul smell of isocyanides is produced. This test is called carbylamine test (Reaction 8).

3. **Liebermann's nitroso test.** Secondary amines (aliphatic or aromatic, can be detected by **Liebermann's nitroso reaction,** reaction 9).

4. **Dye test**. Aromatic primary amines give azo dye test (reaction 16).

Uses of amines

The important uses of aliphatic and aromatic amines are given below :

1. Aliphatic amines of low molecular mass are used as solvents.

2. Amines are also used as intermediates in drug manufacture and as reagents in organic synthesis.

3. Aromatic amines are used for the manufacture of polymers, dyes and as intermediates for additives in the rubber industry.

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

5. Aromatic amines are converted into arene diazonium salts which are used for the preparation of variety of aromatic compounds via substitution and coupling reactions.

DISTINCTION BETWEEN PRIMARY, SECONDARY AND TERTIARY AMINES

The following tests can be used to distinguish between primary, secondary and tertiary amines :

1. Carbylamine test. Both aromatic and aliphatic **primary amines** on heating with chloroform in the presence of alcoholic KOH form carbylamines or isocyanides having extremely unpleasant smell. This test is called **carbylamine test** and is used to distinguish primary amines from secondary and tertiary amines (see reaction 8); page 28.

2. Reaction with nitrous acid. The three types of amines react differently with nitrous acid (reaction 9 page 1490–1491).

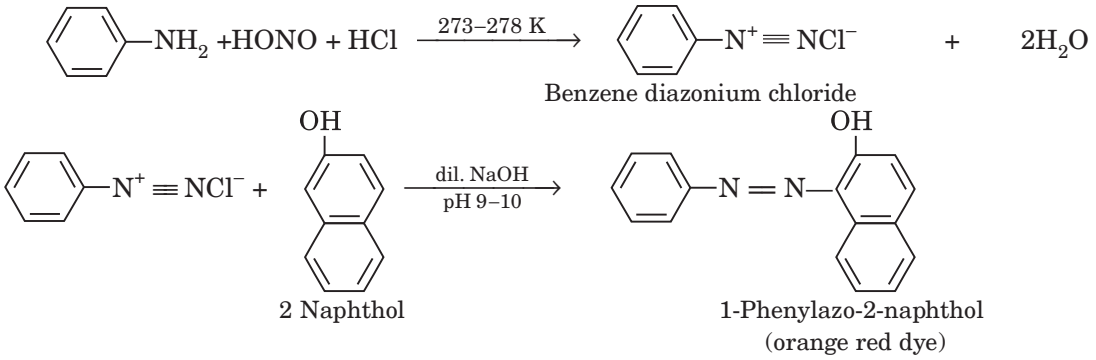
3. Hinsberg's test for amines. This test is used to distinguish primary, secondary and tertiary amines. In this test, the amine is heated with benzene sulphonyl chloride $C_6H_5SO_2Cl$ (known as **Hinsberg's reagent**) in the presence of excess of alkali. Different amines give different observations (reaction 10).

(*i*) Primary amines give *clear solution* which on acidification yields an insoluble material.

(*ii*) Secondary amines give an *insoluble substance* which remains unaffected on addition of acid.

(*iii*) Tertiary amines do not react and remain insoluble in alkali and can be dissolved in acids.

4. Azo dye test. Aromatic primary amines can be distinguished from aliphatic primary amines by azo dye test. To perform this test, dissolve the primary amine in dil. HCl and cool it to 273–278 K. Treat this solution with ice cold solution of HNO_2 ($NaNO_2$ + dil. HCl) at 273–278 K. Add the resulting solution to cold alkaline solution of 2-naphthol (β-naphthol). Appearance of an orange or red dye confirms the presence of a primary aromatic amine.



The above tests are summarized below :

Characteristic Reaction	Primary	Secondary	Tertiary
1. Action with nitrous acid ($NaNO_2$ + HCl)	N_2 is given out with the formation of alcohols : $RNH_2 + HONO \longrightarrow N_2\uparrow$ + alcohols	Nitrosoamines are formed which give *Libermann's Nitroso test* : $R_2NH + HONO \longrightarrow R_2N{-}N{=}O + H_2O$ Nitrosoamine	They remain dissolved forming amine nitrite salt which decomposes on warming to nitrosoamines and alcohol $R_3N + HONO \longrightarrow R_3NHNO_2 \xrightarrow{\text{Warm}} R_2N.NO + ROH$
2. Carbylamine reaction *i.e.*, with $CHCl_3$ and alcoholic KOH	Give foul smelling carbylamine. $RNH_2 + CHCl_3 + 3KOH \longrightarrow RNC + 3KCl + 3H_2O$ Carbylamine	No reaction	No reaction
3. cylation *i.e.*, reaction with acetyl chloride	Form amides RCONH.R	Form amides $RCON\langle^{R}_{R}$	No reaction
4. Hinsberg's test	Give clear solution which on acidification gives insoluble material $RNH_2 + C_6H_5SO_2Cl \longrightarrow C_6H_5SO_2NHR \underset{HCl}{\overset{KOH}{\rightleftharpoons}} C_6H_5SO_2N^-K^+R$ (soluble in alkali)	Give insoluble substance which is not affected by acid $R_2NH + C_6H_5SO_2Cl \xrightarrow{KOH} C_6H_5SO_2NR_2$ (Insoluble in alkali)	Does not react.
5. Azo dye test.	Primary aromatic amines give coloured dyes.	No reaction	No reaction

SOLVED EXAMPLES

❑ Example 6.

Give the structures of A, B and C in the following reactions:

(i) $CH_3Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[273\ K]{HNO_2} C$

(ii) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{Br_2+KOH} B \xrightarrow{CHCl_3+NaOH} C$ *(D.S.B. 2013, 2014)*

(iii) $CH_3CN \xrightarrow{H_2O/OH^-} A \xrightarrow[\Delta]{NH_3} B \xrightarrow{Br_2+KOH} C$ *(A.I.S.B. 2014)*

Solution:

(i) $CH_3Br \xrightarrow{KCN} \underset{(A)}{CH_3CN} \xrightarrow{LiAlH_4} \underset{(B)}{CH_3CH_2NH_2} \xrightarrow[273\ K]{HNO_2} \underset{(C}{CH_3CH_2OH}$

(ii) $CH_3COOH \xrightarrow[\Delta]{NH_3} \underset{(A)}{CH_3CONH_2} \xrightarrow{Br_2+KOH} \underset{(B)}{CH_3NH_2} \xrightarrow{CHCl_3+KOH} \underset{(C)}{CH_3NC}$

(iii) $CH_3CN \xrightarrow{H_2O/OH^-} \underset{(A)}{CH_3COOH} \xrightarrow[\Delta]{NH_3} \underset{B)}{CH_3CONH_2} \xrightarrow{Br_2+KOH} \underset{(C)}{CH_3NH_2}$

❑ Example 7.

Write structures and IUPAC names of

(i) the amide which gives propanamine by Hoffmann bromamide reaction ***N.C.E.R.T***

(ii) the alkyl halide used in Garbriel phthalimide synthesis to give ethanamine

(iii) amine obtained by reduction of propanamide

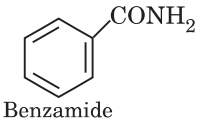
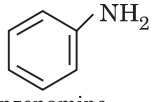
(iv) the amine produced by the Hoffmann degradation of benzamide. ***N.C.E.R.T***

Solution : *(i)* Since propanamine contains 3 carbon atoms, the amide molecule must contain four carbon atoms.

$CH_3—CH_2—CH_2—\underset{\underset{O}{\|}}{C}—NH_2$ (Butanamide) $\xrightarrow[\text{bromide reaction}]{\text{Hoffmann}}$ $CH_3CH_2CH_2NH_2$ (Propanamine)

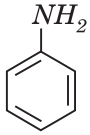
(ii) Ethanamine will be obtained by treating the potassium phthalimide salt with bromoethane (ethyl bromide) $CH_3—CH_2Br$

(iii) $CH_3—CH_2—\overset{\overset{O}{\|}}{C}—NH_2$ (Propanamide) $\xrightarrow[LiAlH_4,\ H_2O]{\text{Reduction}}$ $CH_3CH_2CH_2NH_2$ (Propanamine)

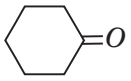
(iv)  (Benzamide) $\xrightarrow[\text{degradation}]{\text{Hoffmann}}$  (Benzenamine)

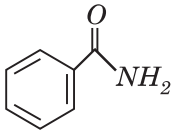
❑ Example 8.

Complete the following reactions :

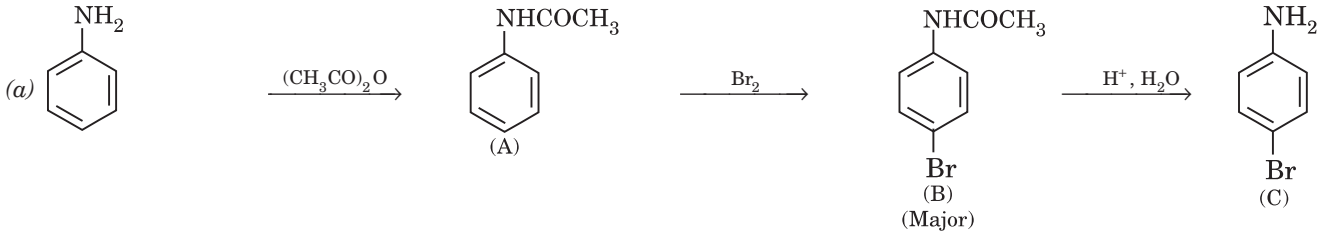
(a)  $\xrightarrow{(CH_3CO)_2O}$ *A* $\xrightarrow[CH_3COOH]{Br_2}$ *B* $\xrightarrow{H_2O,\ OH^-}$ *C* *(Meghalaya S.B. 2018)*

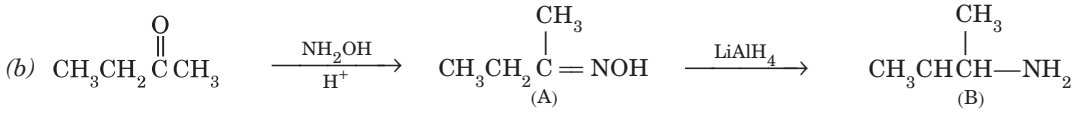
(b) $CH_3CH_2\overset{\overset{O}{\|}}{C}CH_3 \xrightarrow[H^+]{NH_2OH}$ *A* $\xrightarrow{LiAlH_4}$ *B*

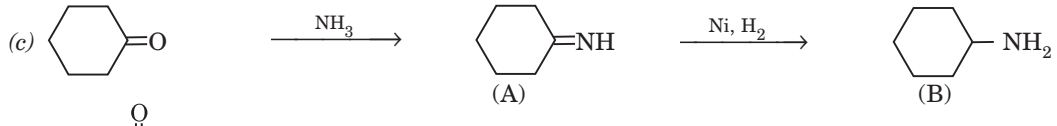
(c)  $\xrightarrow{NH_3}$ *A* $\xrightarrow{Ni,\ H_2}$ *B*

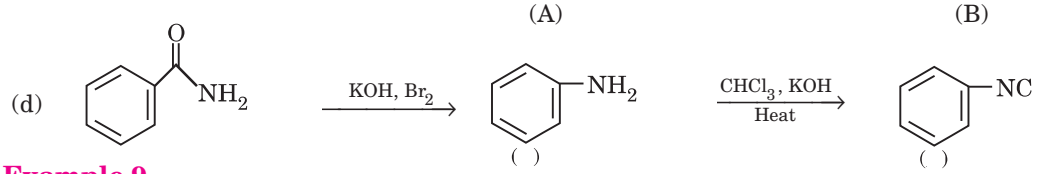
(d)  $\xrightarrow{KOH,\ Br_2}$ *A* $\xrightarrow{CHCl_3,\ KOH}$ *B*

Solution :

(a) 

(b) 

(c) 

(d) 

❑ Example 9.

(a) How will you convert an alkyl halide into a primary amine having one more carbon atom than the alkyl halide uses.
(b) How can a carboxylic acid be converted into an amine having one more carbon atom than the carboxylic acid used?

Solution : (a) By heating with KCN followed by teatment with Na, C_2H_5OH. For example

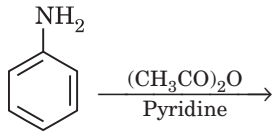
$$C_2H_5Cl \xrightarrow{KCN} C_2H_5CN \xrightarrow[4H]{Na,\ C_2H_5OH} C_2H_5CH_2NH_2$$

(b) By forming amide which on reacting with Br_2 and KOH gives amine having one carbon atom less.

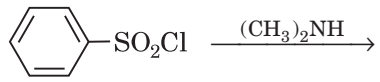
$$CH_3COOH \xrightarrow[Heat]{NH_3} CH_3CONH_2 \xrightarrow{Br_2,\ KOH} CH_3NH_2$$

❑ Example 10.

Complete the following reactions:

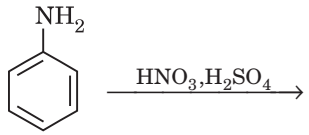
(i) 

(A.I.S. B. 2018)

(ii) 

(A.I.S. B. 2018)

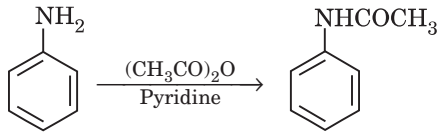
(iii) $CH_3CONH_2 + 4\ [H] \xrightarrow{LiAlH_4/ether}$ *(Nagaland S.B. 2018)*

(iv) 

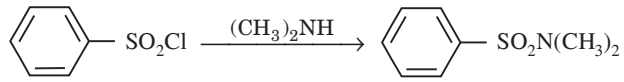
(Nagaland S.B. 2018)

(v) $C_6H_5NH_2 + CHCl_3 + KOH \longrightarrow$ *(H.P.S.B. 2018)*

Solution :

(i) 

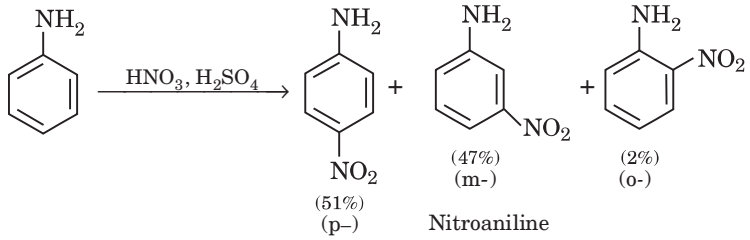
Acetanilide

(ii) 

N,N – Dimethylbenzenesulphonamide

(*iii*) $CH_3CONH_2 + 4[H] \xrightarrow[\text{Ether}]{LiAlH_4} CH_3CH_2NH_2$

Ethylamine

(*iv*) 

Nitroaniline

(*v*) $C_6H_5NH_2 + CHCl_3 + 3KOH \longrightarrow C_6H_5NC + 3KCl + 3H_2O$

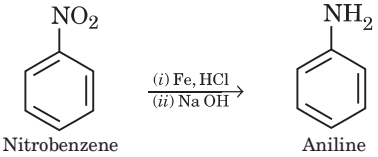
Phenyl isocyanide

❑ Example 11.

How will you convert the following :

(*i*) *Nitrobenzene into aniline* (*ii*) *Ethanoic acid into methanamine,* (*iii*) *Aniline into N-phenylethanamide. Write the chemical equations involved.* (*D.S.B. 2014*)

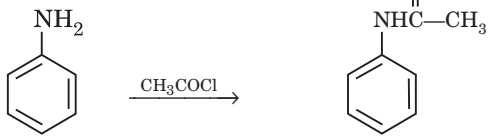
Solution :

(*i*) 

Nitrobenzene Aniline

(*ii*) $CH_3COOH \xrightarrow[\Delta]{NH_3} CH_3CONH_2 \xrightarrow[\Delta]{Br_2, KOH} CH_3NH_2$

Ethanoic acid Methanamine

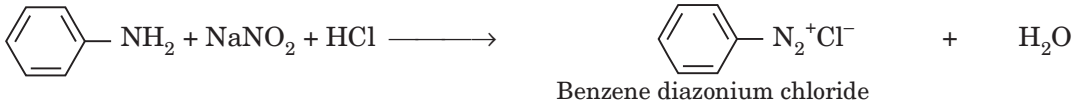
(*iii*) 

Aniline N-Phenylethanamide

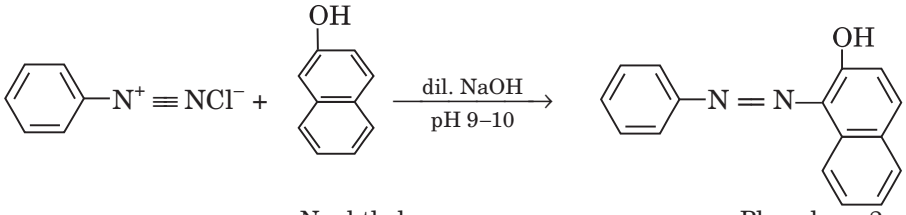
DISTINCTION BETWEEN PAIRS OF COMPOUNDS

1. Ethylamine and Aniline

Azo dye test. Dissolve the compound in conc. HCl and add ice-cold solution of HNO_2 ($NaNO_2$ + dil. HCl) at 273 K and then treat it with an alkaline cold solution of 2-naphthol. Appearance of brilliant orange or red dye indicates aromatic amine *i.e.,* aniline.



Benzene diazonium chloride



Naphthol Phenyl azo-2-naphthol (orange red dye)

Aliphatic amines *i.e.,* ethylamine does not form dye. It will give brisk effervescence due to the evolution of N_2 but solution remains clear.

2. Ethylamine ($CH_3CH_2NH_2$) and Diethylamine

(*i*) Carbylamine test. When heated with an alcoholic solution of KOH and $CHCl_3$, ethylamine gives foul smelling ethyl isocyanide.

$$CH_3CH_2NH_2 + CHCl_3 + 3KOH \longrightarrow \underset{\text{Foul smell}}{CH_3CH_2NC} + 3KCl + 3H_2O$$
(alc.)

Diethylamine does not give this test.

$$(CH_3CH_2)_2NH \xrightarrow[\text{Heat}]{CHCl_3/KOH} \text{No reaction.}$$

***(ii)* Hinsberg's test.** When treated with **Hinsberg's reagent** [benzene sulphonyl chloride ($C_6H_5SO_2Cl$)], ethylamine gives N-ethyl benzene sulphonamide which is soluble in aqueous KOH solution.

$$C_6H_5SO_2Cl + CH_3CH_2NH_2 \xrightarrow{-HCl} C_6H_5SO_2NHCH_2CH_3 \xrightarrow{KOH} \underset{\text{Soluble in aq. KOH}}{C_6H_5SO_2NKCH_2CH_3} + H_2O$$

Diethylamine gives N, N-diethylbenzene sulphonamide which is insoluble in aqueous KOH.

$$C_6H_5SO_2Cl + (CH_3CH_2)_2NH \xrightarrow{-HCl} \underset{\substack{\text{N, N-Diethyl benzene sulphonamide}\\ \text{insoluble in aq. KOH}}}{C_6H_5SO_2N(CH_2CH_3)_2} + HCl$$

3. Aniline and N-ethylaniline

Aniline is a primary amine. Therefore, it gives carbylamine test. When heated with an alcoholic solution of KOH and $CHCl_3$, it gives offensive smell of phenylisocyanide.

$$\underset{\text{Aniline}}{C_6H_5NH_2} + CHCl_3 + \underset{\text{alc.}}{3KOH} \longrightarrow \underset{\substack{\text{Phenylisocyanide}\\ \text{(Foul smell)}}}{C_6H_5NC} + KCl + 3H_2O$$

But N-ethyl aniline is a secondary amine and hence does not give carbylamine test.

4. N-Methylpropane-2-amine and N-Ethyl-N-methylethanamine

N-methylpropane-2-amine is a secondary amine. On adding Hinsberg's reagent, compound formed is insoluble in aqueous NaOH.

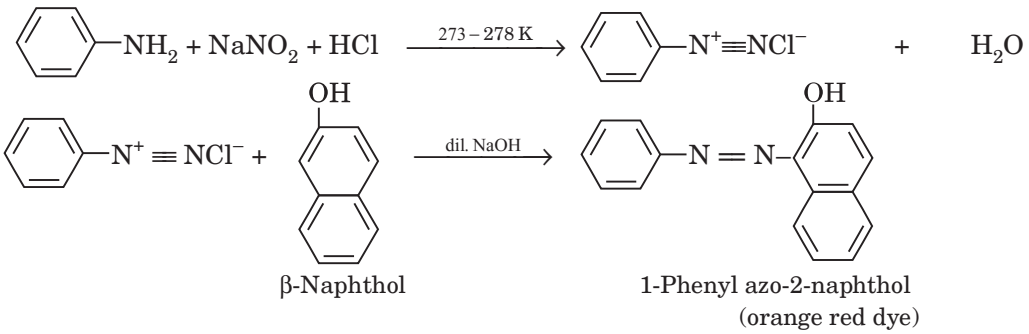
$$\underset{\substack{|\\ NHCH_3}}{CH_3CHCH_3} + C_6H_5SO_2Cl \xrightarrow{-HCl} \underset{\substack{\text{insoluble in aq. NaOH}}}{C_6H_5SO_2-\underset{\substack{|\\ CH_3}}{N}-CH(CH_3)_2}$$

N-Methylpropan-2-amine

But N-ethyl-N-methylethanamine does not react with Hinsberg's reagent.

5. Aniline and Benzylamine

Azo dye test. On treatment with nitrous acid ($NaNO_2$ + dil HCl) at 273–278 K followed by reaction with an alkaline solution of β-naphthol, aniline gives orange red coloured dye.



β-Naphthol

1-Phenyl azo-2-naphthol
(orange red dye)

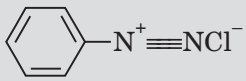
PART B

DIAZONIUM SALTS

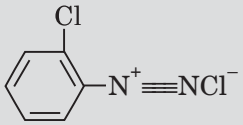
The diazonium salts were discovered by John Peter Greiss in 1858. These have the general formula $ArN_2^+X^-$, where X^- may be an anion like Cl^-, Br^-, HSO_4^-, BF_4^- etc. and the group N_2^+ ($-N \equiv N^+$) is called diazonium group or diazo group. These are obtained when aromatic primary amines react with nitrous acid.

NOMENCLATURE

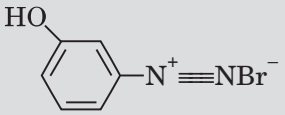
The diazonium salts are named by suffixing the word diazonium to the name of the parent aromatic compound to which they are related followed by the name of the anion. For example,



Benzenediazonium chloride

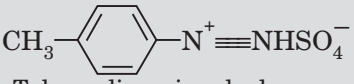


o-Chlorobenzenediazonium chloride

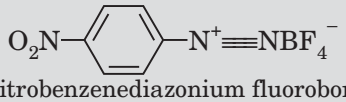


m-Hydroxybenzenediazonium bromide

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



p-Toluenediazonium hydrogen sulphate



p-Nitrobenzenediazonium fluoroborate

PREPARATION OF DIAZONIUM SALTS

Aromatic diazonium salts are prepared by heating an ice cold solution of aromatic primary amine in excess of mineral acid like HCl or H_2SO_4 with an ice cold solution of sodium nitrite dissolved in water. The temperature is maintained between 273–278 K because most of the diazonium salts decompose at higher temperature.

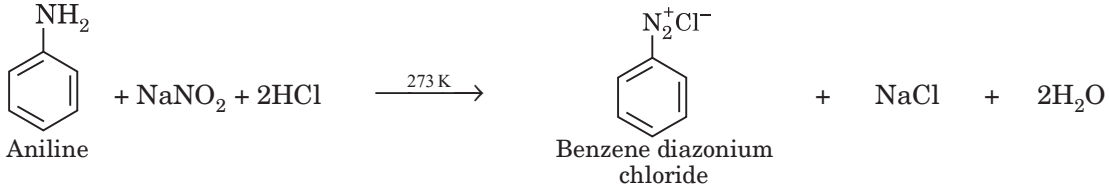
The diazonium salt so formed remains in the solution. Since the diazonium salts are unstable and explosive substances, they are not isolated in solid form but are used directly in the solution.

$$NaNO_2 + HCl \longrightarrow NaCl + HONO$$

$$\underset{\text{Aromatic amine}}{ArNH_2} \xrightarrow[HCl,\ 273\ K]{NaNO_2} Ar - N^+ \equiv NCl^- + NaCl + H_2O$$

For example, benzene diazonium chloride is prepared by treating an ice-cold solution of aniline in hydrochloric acid with an ice-cold solution of sodium nitrite at about 0°C. **The reaction of converting aromatic primary amine to diazonium salt** is called **diazotisation.**

$$NaNO_2 + HCl \longrightarrow NaCl + HONO$$

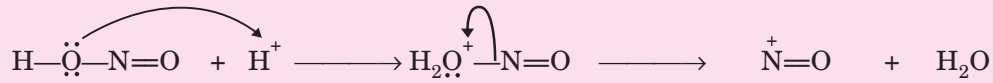


Aniline

Benzene diazonium chloride

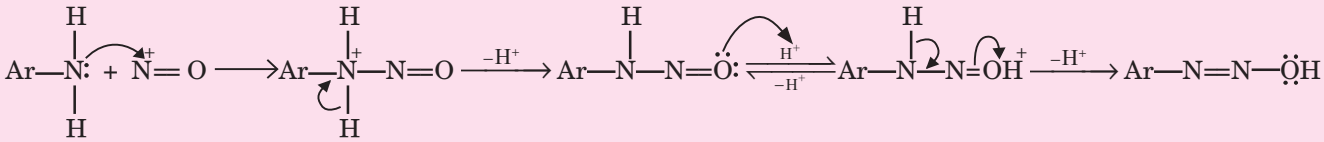
Mechanism : Diazotisation of amines

The diazotisation of amines is believed to occur by the following mechanism. Nitrous acid formed by the reaction of sodium nitrite and mineral acid, takes up a proton from the acid and undergoes heterolysis to form nitrosonium ion.

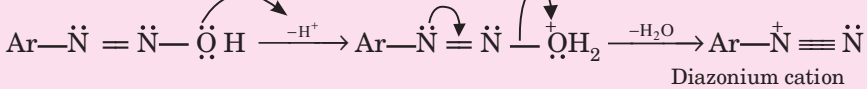


Nitrous acid — Nitrosonium ion

The electrophilic nitrosonium ion reacts with the nitrogen of the amine and combines with the lone pairs of electrons at N to form N-nitroso derivative, which by protonic shift rearranges to diazohydroxide.



The diazohydroxide in acidic solution takes up a proton and by the elimination of water molecule forms diazonium ion, which may take up acid anion X to form diazonium salt.

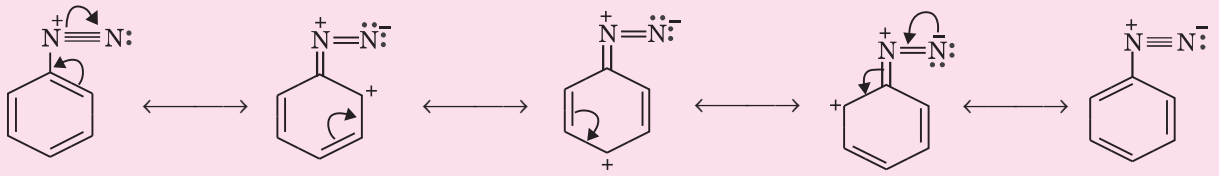


Diazonium cation

Diazonium salt

Stability of Diazonium salt

Aromatic diazonium salts are stable due to the dispersal of positive charge over the benzene ring as shown below:



R U Curious...

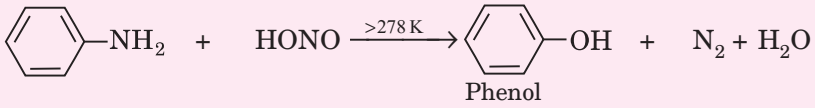
❒ **Are primary aliphatic diazonium salts formed ?**

➤ Primary aliphatic diazonium salts are highly unstable alkane diazonium salts. These readily decompose even at low temperature (273–278 K) forming carbocation and nitrogen gas.

$$R{-}N^{+}{\equiv}NX^{-} \xrightarrow{\text{Decompose}} \underset{\text{Carbocation}}{R^{+}} + N_2 + X^{-}$$

❒ **Why is it important to keep the temperature very low (273–278 K) during the formation of diazonium salts ?**

➤ Aromatic diazonium salts are formed only in ice cold solution (273–278 K). However, if temperature is more than 278 K amines form phenol with the evolution of N_2 gas.



PHYSICAL PROPERTIES OF DIAZONIUM SALTS

The general physical properties of diazonium salts are :

1. Diazonium salts are generally colourless, crystalline solids.
2. These are readily soluble in water and are stable in cold but react with water when warmed. They are less soluble in alcohol.
3. They are unstable and explode in dry state. Therefore, they are generally used in solution state.
4. Certain diazonium salts such as fluoroborates are water insoluble and are stable enough to be dried and stored.
5. Their aqueous solutions are neutral to litmus and conduct electricity due to the presence of ions.

CHEMICAL PROPERTIES OF DIAZONIUM SALTS

The reactions of benzene diazonium salts can be broadly divided into two types :

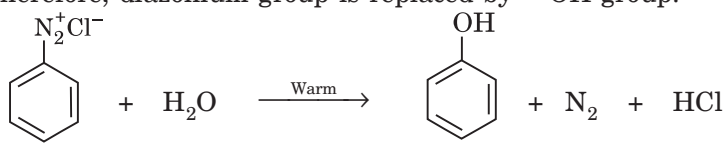
A. Reactions involving displacement of diazo group

B. Reactions involving retention of diazo group

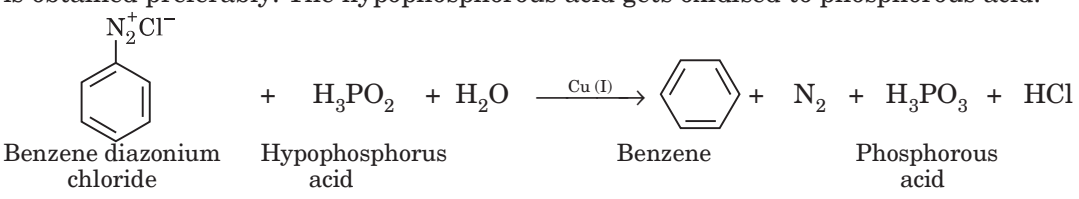
A. Reactions involving displacement of nitrogen

Diazo group being a very good leaving group, is readily substituted or replaced by other groups. In these reactions, nitrogen of diazonium salts is lost as N_2 and different groups are introduced in its place. Some of the important replacement reactions are :

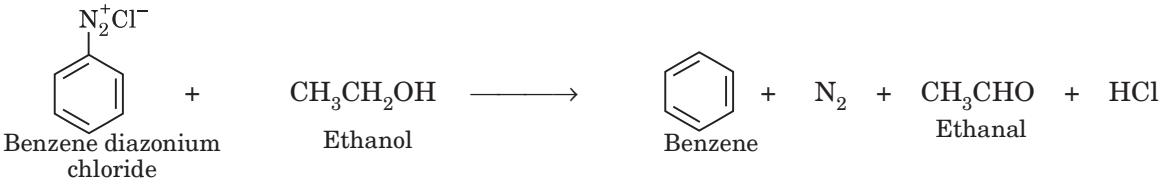
***(i)* Replacement by —OH group.** When an aqueous solution of diazonium salt is boiled (upto 283 K) or steam distilled, it gives phenols, therefore, diazonium group is replaced by —OH group.



***(ii)* Replacement by hydrogen or deamination.** When diazonium salt is treated with mild reducing agents such as hypophorous acid (phosphinic acid) *i.e.*, H_3PO_2, in the presence of Cu(I) salt as a catalyst at room temperature benzene is obtained preferably. The hypophosphorous acid gets oxidised to phosphorous acid.



The diazo group can also be replaced by hydrogen by heating diazonium salt with ethanol.

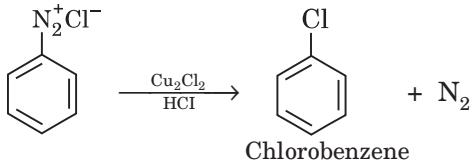


Benzene diazonium chloride

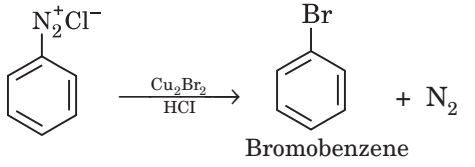
Benzene

This complete process involving diazotisation of an amine followed by reduction of diazonium salt or replacement of the diazo group by hydrogen is called **deamination**.

***(iii)* Replacement by Cl and Br group.** When a diazonium salt solution is warmed with cuprous chloride in hydrochloric acid or cuprous bromide in hydrobromic acid the corresponding halide is formed.



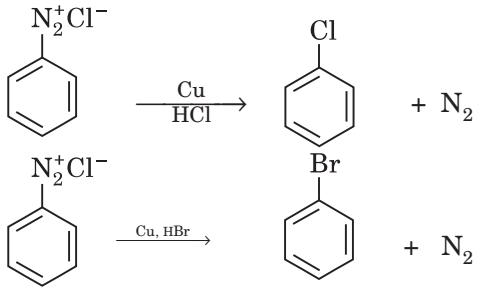
Chlorobenzene



Bromobenzene

This reaction is called **Sandmeyer reaction.**

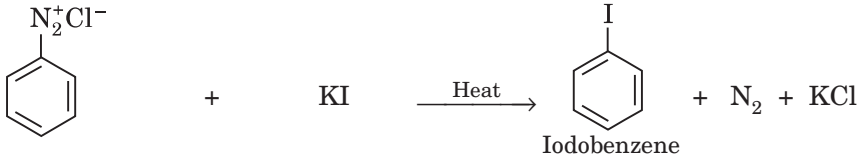
When the diazonium salt solution is warmed with copper powder and the corresponding halogen acid, the respective halogen is introduced. The reaction is a modified form of Sandmeyer reaction and is known as **Gattermann reaction.**



Gattermann reation is modification of Sandmeyer reaction.

The yield of Sandmeyer reaction is found to be better than Gattermann reaction.

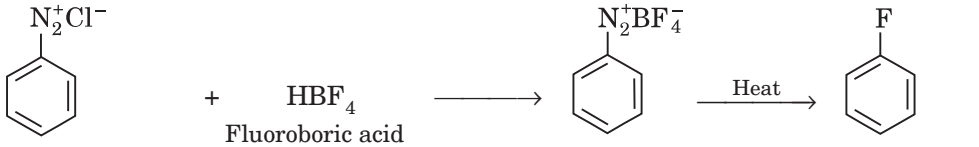
***(iv)* Replacement by iodo (—I) group.** When aqueous solution of benzene diazonium salt is warmed with excess of potassium iodide, aryl iodide is formed.



Iodobenzene

Iodine is not easily introduced into the benzene ring directly, therefore, this reaction provides an indirect method for preparing iodo compounds.

***(v)* Replacement by fluoro (—F) group.** When diazonium salt is treated with fluoroboric acid (HBF_4), benzene diazonium fluoroborate is precipitated, which on heating decomposes to fluorobenzene. This reaction is called **Balz-Schiemann reaction.**



Fluoroboric acid

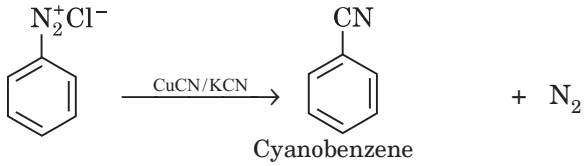
Benzene diazonium fluoroborate

Fluorobenzene

NOTE

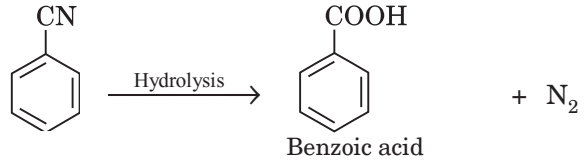
The preparation of aryl halides from diazonium salts is a good method and has many advantages. Aryl chlorides and bromides when obtained by direct halogenation of aromatic compounds give mixtures of products which are difficult to separate. However, in the diazonium salt replacement method, a pure single product is formed. This also provides good synthetic route for the preparation of aryl iodides and fluorides which are not obtained by direct halogenation.

***(vi)* Replacement by cyano (—CN) group.** When benzene diazonium salt is treated with copper cyanide dissolved in aqueous KCN, cyanobenzene is formed.



Cyanobenzene

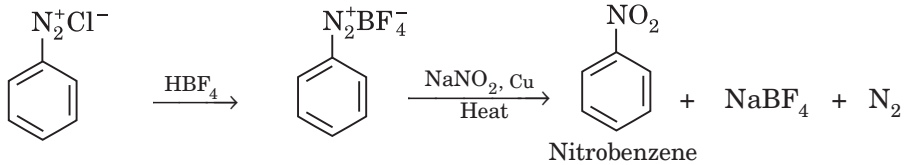
The nitriles can be hydrolysed to acids



Benzoic acid

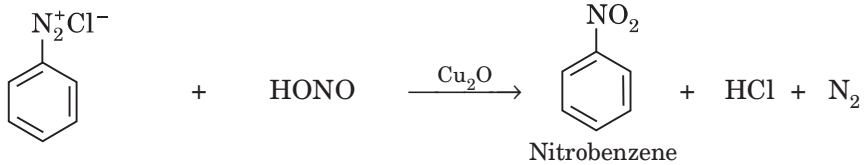
This method of preparing carboxylic acids is more useful than carbonation of **Grignard reagents.**

***(vii)* Replacement by nitro (—NO_2) group.** Nitrobenzene is prepared by heating diazonium fluoroborate with aqueous $NaNO_2$ in the presence of copper powder.



Nitrobenzene

Alternatively, nitro compounds may be prepared by treating diazonium salt with nitrous acid in the presence of cuprous oxide.



Nitrobenzene

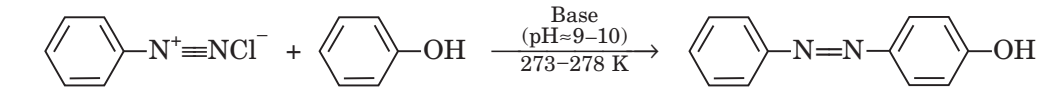
***(viii)* Replacement by thio (—SH) group.** When diazonium salt is treated with potassium hydrosulphide, thiophenol is produced.

Thiophenol

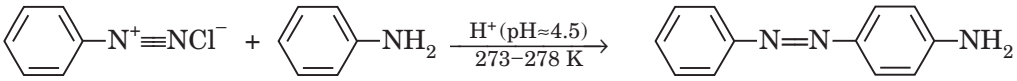
B. Reactions involving retention of diazo group

(*i*) **Coupling reactions:** Benzene diazonium salts react with highly reactive (i.e. electron rich) aromatic compounds such as phenols and amines to form azo compounds, Ar—N=N—Ar. The reaction is known as **coupling reaction.** These azo compounds are generally coloured and are used as dyes. The colour of azo compounds is due to extended conjugate system involving the double bond of both the aromatic rings through —N=N— double bond.

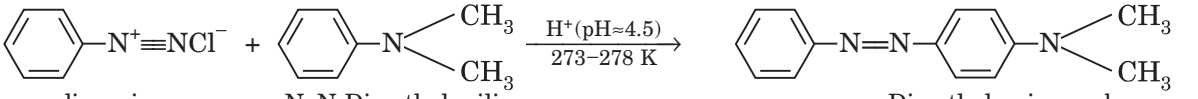
It may be noted that coupling with phenol occurs in basic medium (pH ≈ 9–10) while that of amines occurs in faintly acidic medium (pH ≈ 4–5) at 273–278 K. The coupling reaction is an example of **electrophilic substitution reaction** in which the diazonium cation with a positive charge on the terminal nitrogen acts as the electrophile and the electron rich compounds such as phenols and amines act as nucleophiles.



Benzenediazonium chloride — Phenol — *p*-Hydroxyazobenzene (orange dye)

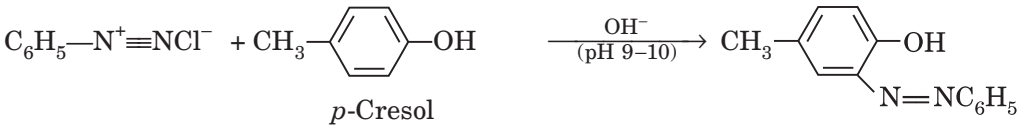


Benzenediazonium chloride — Aniline — *p*-Aminoazobenzene (ellow dye)



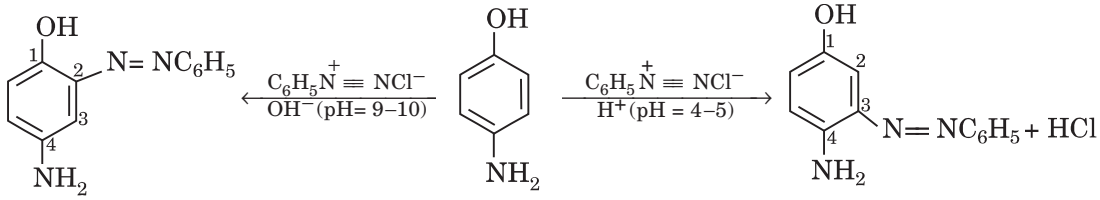
Benzenediazonium chloride — N, N-Dimethylaniline — *p*-Dimethylamine azobenzene (orange)

Coupling occurs para to hydroxy or amino group. However, if the *para* position is blocked with respect to hydroxy or amino group it occurs at *ortho* position. For example,



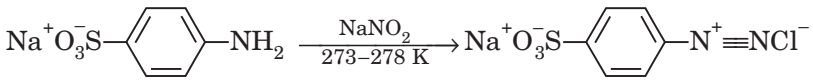
p-Cresol — 2-Phenylazo-4-methylphenol

In case of aromatic compounds containing both hydroxy or amino groups the coupling occurs in the alkaline medium at *p*- or *o*-position with respect to hydroxy group and in acidic medium at *p*- or *o*-position with respect to amino group.

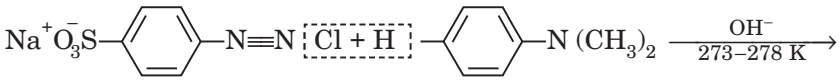


4-Amino-2-phenylazo phenol (*ortho* w.r.t. –OH group) — *p*-Amino phenol — 4-Amino-3-phenylazophenol (*ortho* w.r.t. —NH_2 group)

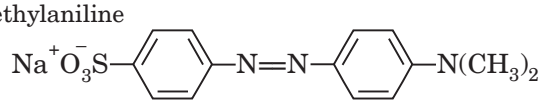
All azo compounds are strongly coloured and are used as dyes. Methyl orange is an important dye obtained by coupling the diazonium salt of sulphanilic acid with N, N-dimethylaniline.



Sodium salt of sulphanilic acid

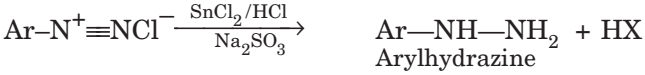


N, N-Dimethylaniline



Methyl orange

(*ii*) **Reduction to arylhydrazines:** Arene diazonium salts are reduced to aryl hydrazines upon treatment with stannous chloride and hydrochloric acid or zinc dust and acid or sodium sulphide or even by electrolytic method.



Arylhydrazine

Phenylhydrazine, which is an important reagent for organic synthesis can be easily prepared in good yield from benzene diazonium chloride as :

Phenylhydrazine

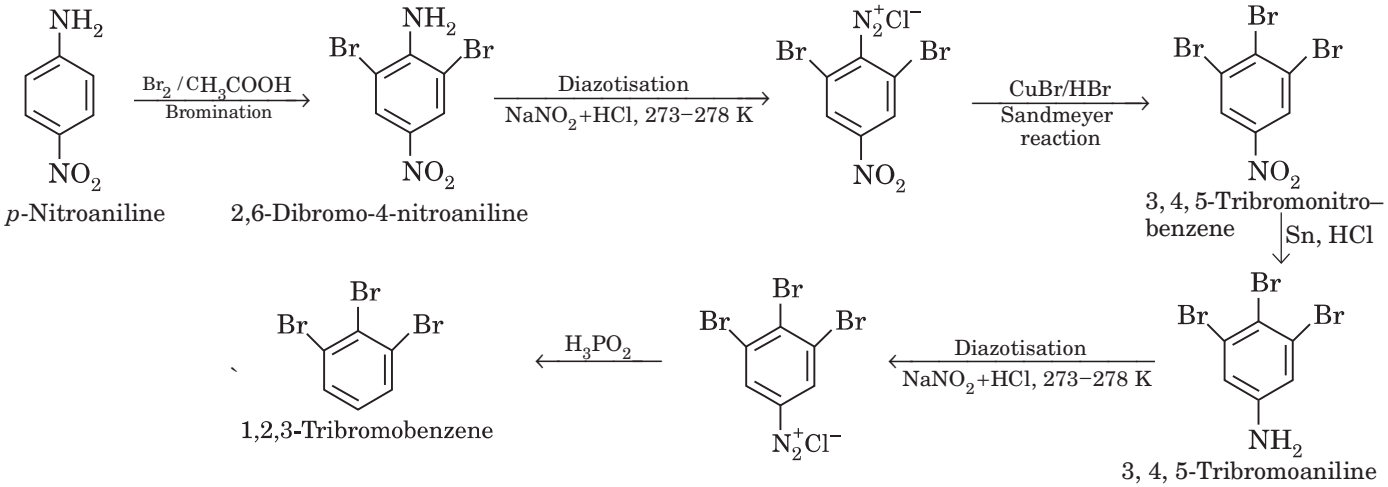
However, if vigorous reducing agent such as Zn/HCl is used, the product is aromatic amine.

$$\underset{\text{Benzene diazonium chloride}}{C_6H_5N^+{\equiv}NCl^-} \xrightarrow{Zn/HCl} \underset{\text{Phenylhydrazine}}{[C_6H_5NHNH_2]} \xrightarrow{Zn/HCl} \underset{\text{Aniline}}{C_6H_5NH_2} + NH_3$$

IMPORTANCE OF BENZENE DIAZONIUM SALTS IN SYNTHETIC ORGANIC CHEMISTRY

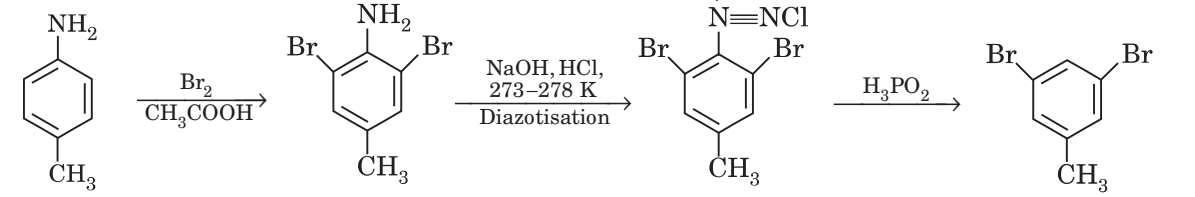
Diazonium salts are highly **useful intermediates** in the synthesis of large variety of aromatic compounds. Therefore, these are regarded as good synthetic tools in the hands of a chemist. These can be used to prepare many classes of organic compounds especially aryl halides in pure state. Some common examples are :

1. Synthesis of 1, 2, 3-tribromo benzene. 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 reactions starting from *p*-nitroaniline through the formation of diazonium salt as :



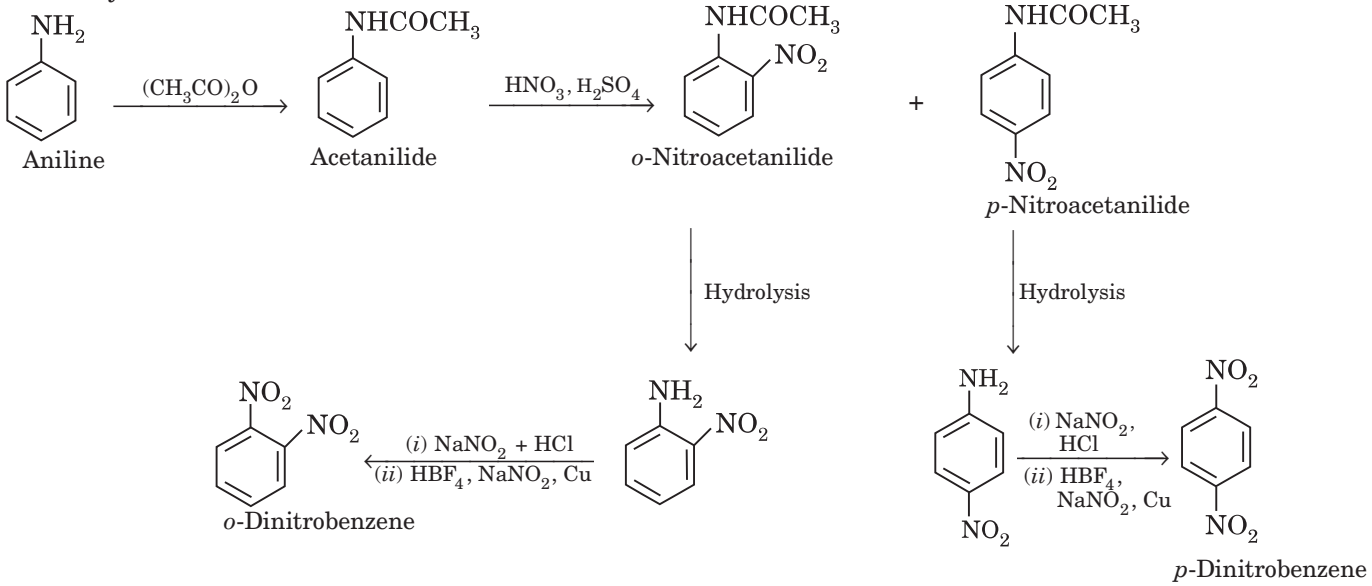
p-Nitroaniline — 2,6-Dibromo-4-nitroaniline

2. Synthesis of 3, 5-dibromotoluene. Direct bromination of toluene with $Br_2/FeBr_3$ gives, 2, 4-dibromotoluene. But 3-5, dibromotoluene may by synthesised as :

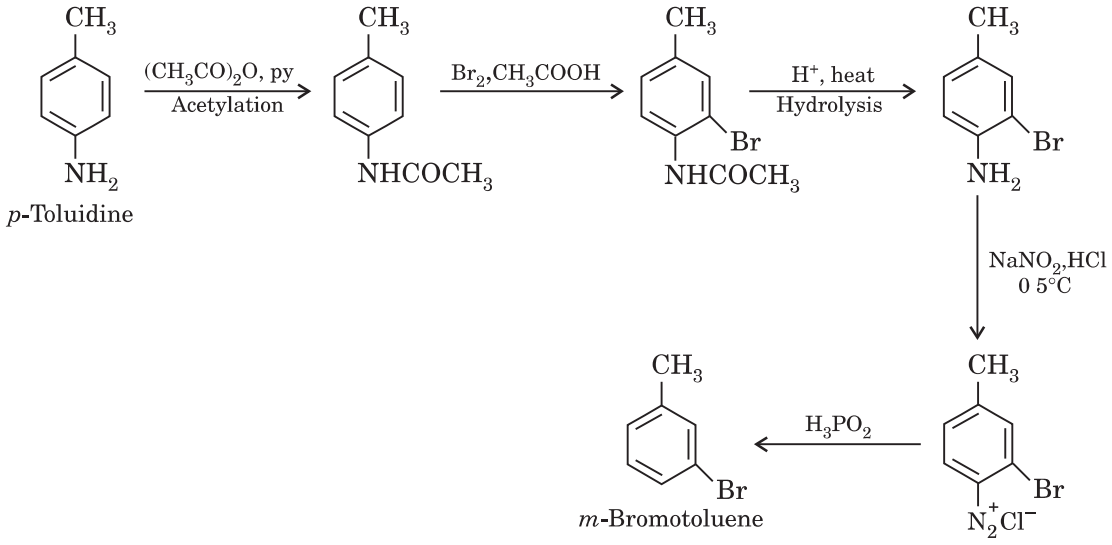


p-Toluidine — 3, 5-Dibromotoluene

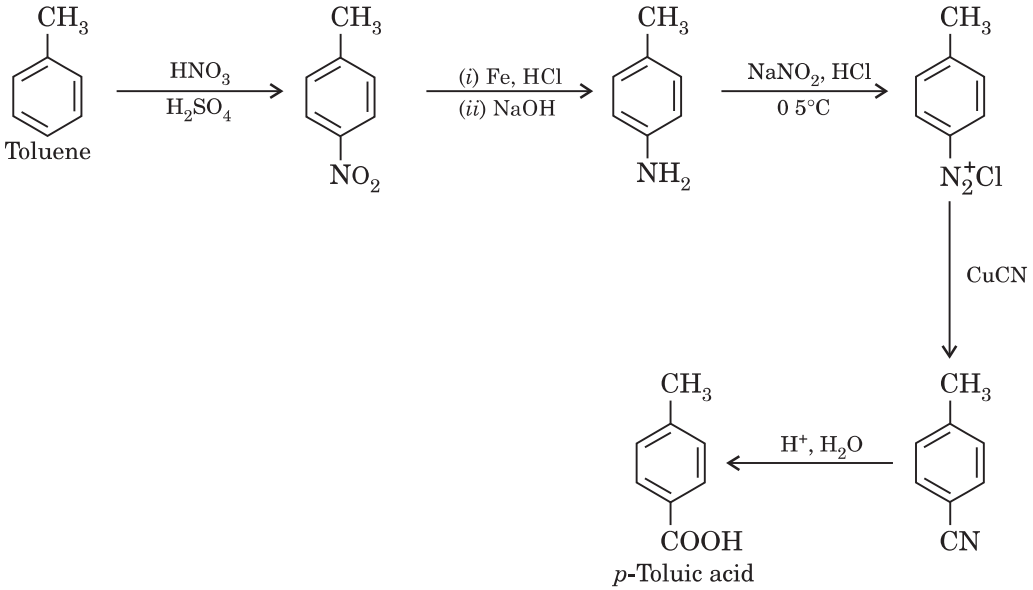
3. Synthesis of *o*- and *p*-dinitrobenzenes. These cannot be prepared by direct substitution. However, diazonium salts route may be followed as :



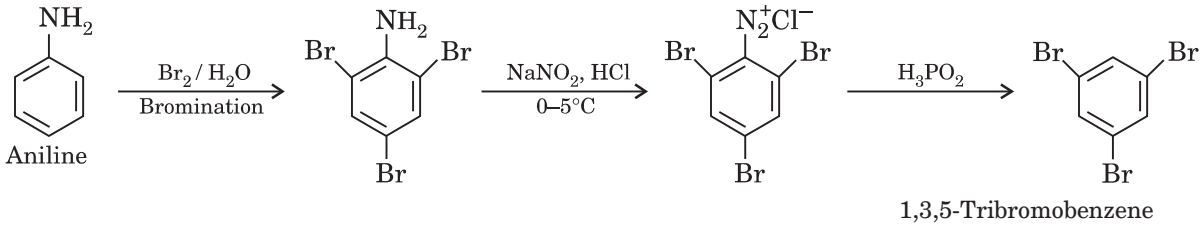
4. Synthesis of *m*-bromotoluene. It cannot be prepared by direct bromination of toluene or Friedel Crafts alkylation of bromobenzene because of *o*, *p*-directing nature of methyl group. It can be synthesised as :



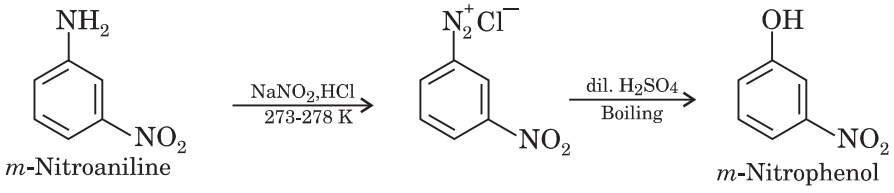
5. Synthesis of *p*-toluic acid. This can be synthesised as :



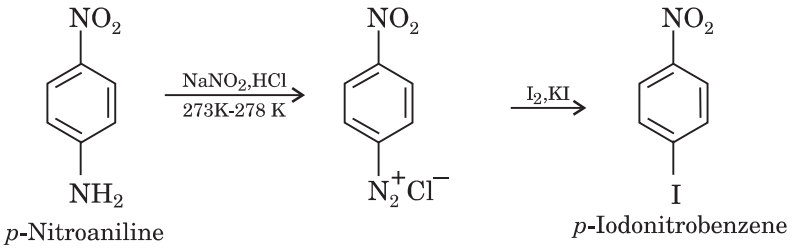
6. Synthesis of 1,3,5-tribromobenzene. It can be synthesised as :



7. Synthesis of *m*-nitrophenol from *m*-nitroaniline. It can be synthesised as :

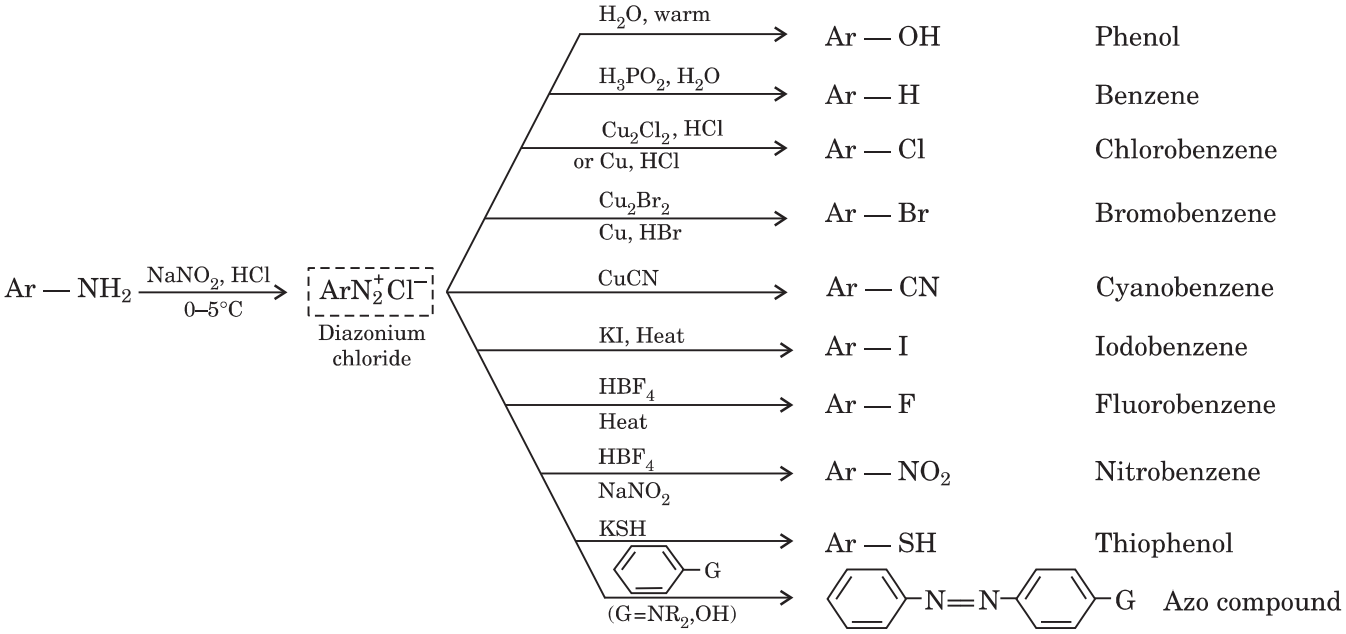


8. Synthesis of *p*-iodonitrobenzene. It can be synthesised from *p*-nitroaniline as :



p-Nitroaniline *p*-Iodonitrobenzene

Some of the important chemical reactions and the important products formed are summarized below.



Uses of diazonium salts. Diazonium salts are used

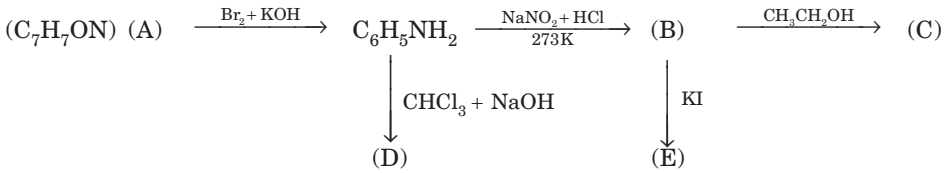
1. for the manufacture of azo dyes.
2. for the industrial preparation of important organic compounds like *m*-bromotoluene, *m*-bromophenol, etc.
3. for the preparation of a variety of useful halogen substituted arenes.

SOLVED EXAMPLES

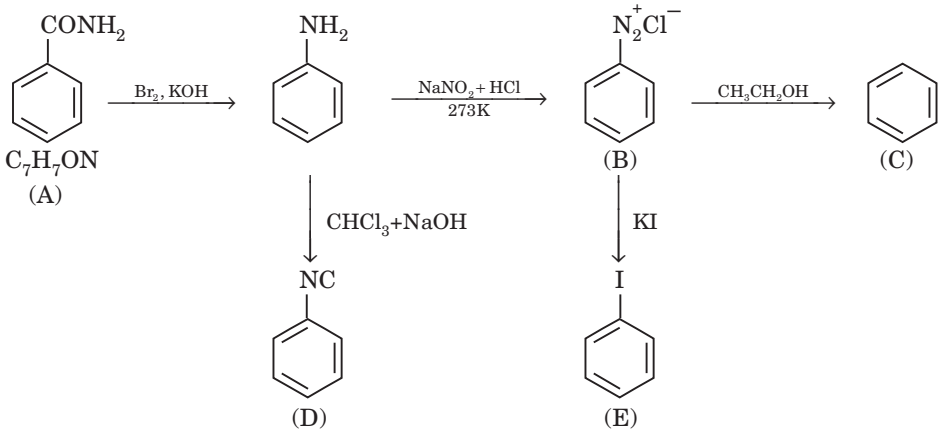
❑ Example 12.

An aromatic compound 'A' of molecular formula C_7H_7ON undergoes a series of reactions as shown below. Write the structures of A, B, C, D and E in the following reactions :

(D.S.B. 2015)



Solution :



❑ Example 13.

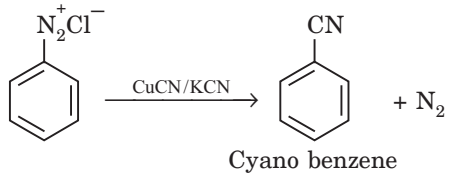
Write the main products when benzene diazonium chloride ($C_6H_5N_2^+Cl^-$) reacts with the following:

(i) CuCN/KCN *(ii) H_2O* *(Pb.S.B. 2018)* *(iii) CH_3CH_2OH* *(A.I.S.B. 2015, 2018)*

(iv) Copper powder/HCl *(Pb.S.B. 2016)*

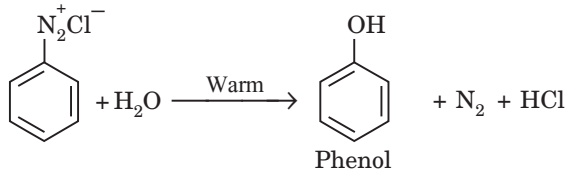
Solution :

(i)



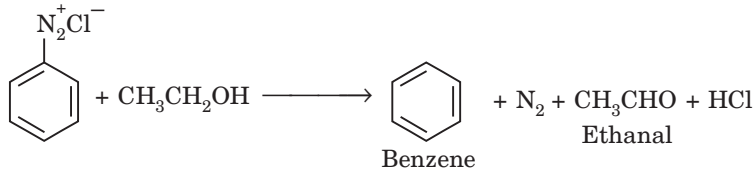
Cyano benzene

(ii)



Phenol

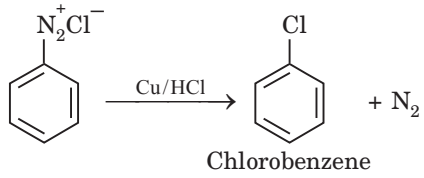
(iii)



Benzene

Ethanal

(iv)



Chlorobenzene

❑ Example 14.

How will you convert

(a) propionamide to ethylamine *(H.P.S.B. 2015)*

(b) aniline to phenol *(Tripura S.B. 2016)*

(c) p-toluidine into 2-bromo-4-methylaniline *(H.P.S.B. 2015)*

(d) aniline to acetanilide *(Pb. S.B. 2015)*

(e) aniline to benzene *(H.P.S.B. 2015)*

(f) aniline to bromobenzene *(H.P.S.B. 2015)*

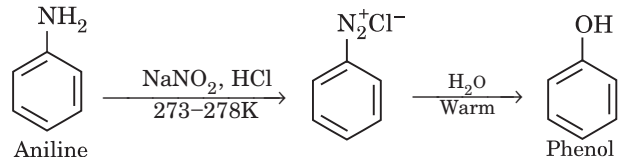
(g) aniline into benzonitrile ? *(Pb.S.B. 2015)*

(h) methylamine to ethylamine *(H.P.S.B. 2015, 2016)*

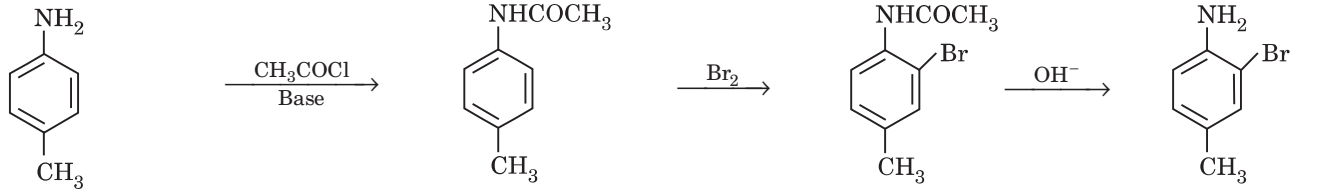
Solution :

(*a*) $CH_3CH_2CONH_2$ —(Br_2,KOH, Hoffmann bromamide reaction)→ $CH_3CH_2NH_2$

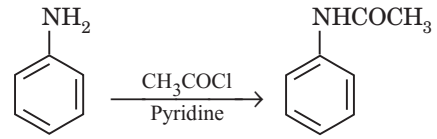
Propionamide → Ethylamine

(*b*) 

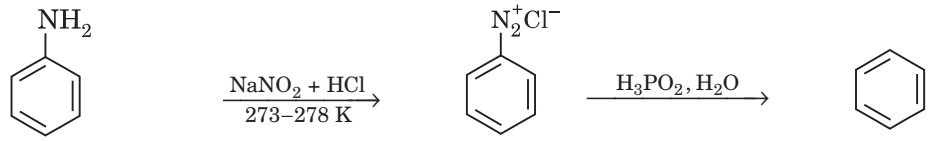
Aniline → Phenol

(*c*) 

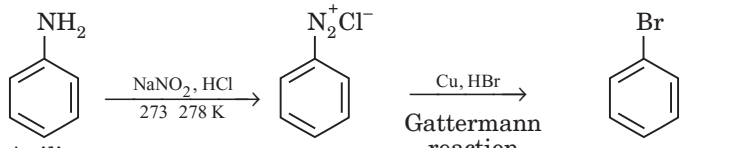
p-toluidine → 2-Bromo-4-methylaniline

(*d*) 

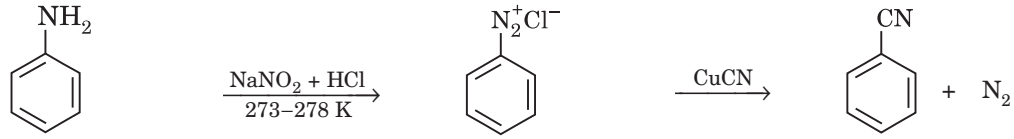
Aniline → Acetanilide

(*e*) 

Aniline → Benzene

(*f*) 

Aniline → Bromobenzene

(*g*) 

Aniline → Benzonitrile

(*h*) CH_3NH_2 —(HONO)→ CH_3OH —(P, I_2)→ CH_3I —(KCN)→ CH_3CN —(Na, C_2H_5OH, Reduction)→ $CH_3CH_2NH_2$

Methylamine → Ethylamine

❑ Example 15.

Complete the following chemical equations :

(*a*) $CH_3CH_2Cl \xrightarrow{NaCN} ? \xrightarrow[Ni/H_2]{reduction}$ *(D.S.B. 2011)*

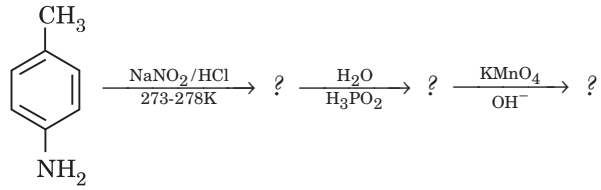
(*b*) $C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow$ *(D.S.B. 2011)*

(*c*) $R{-}\overset{\overset{O}{\|}}{C}{-}NH_2 \xrightarrow[H_2O]{LiAlH_4}$ *(D.S.B. 2011)*

(*d*) $CH_3CH_2NH_2 + CHCl_3 + alc.\ KOH \longrightarrow$ *(A.I.S.B. 2013)*

(*e*) $C_6H_5N_2^+Cl^- \xrightarrow[room\ temp.]{H_2O}$ *(A.I.S.B. 2013)*

(*f*) $C_6H_5NH_2 + HCl(aq) \longrightarrow$ *(A I.S.B. 2013)*

(*g*) 

(Hr.S.B. 2018)

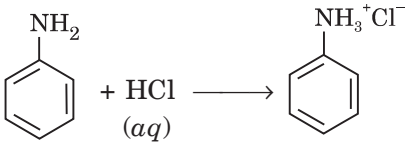
Solution : (*a*) $CH_3CH_2Cl \xrightarrow{NaCN} \underset{(A)}{CH_3CH_2CN} \xrightarrow[Ni/H_2]{reduction} \underset{(B)}{CH_3CH_2CH_2NH_2}$

(*b*) $C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow \underset{\text{Benzene}}{C_6H_6} + N_2 + H_3PO_3 + HCl$

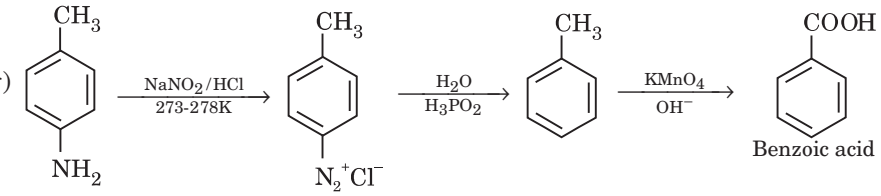
(*c*) $R{-}\overset{\overset{O}{\|}}{C}{-}NH_2 \xrightarrow[H_2O]{LiAlH_4} RCH_2NH_2$

(*d*) $CH_3CH_2NH_2 + CHCl_3 + 3KOH \xrightarrow{Warm} \underset{\text{Ethyl isocyanide}}{CH_3CH_2NC} + 3KCl + 3H_2O$

(*e*) $C_6H_5N_2^+\ Cl^- \xrightarrow[\text{Room temp.}]{H_2O} \underset{\text{Phenol}}{C_6H_5OH} + N_2 + HCl$

(*f*) 

Aniline hydrochloride

(*g*) 

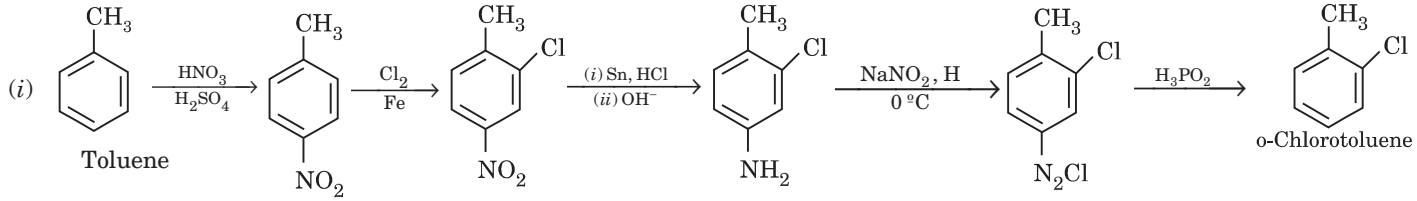
Benzoic acid

❑ Example 16.

Starting from toluene prepare

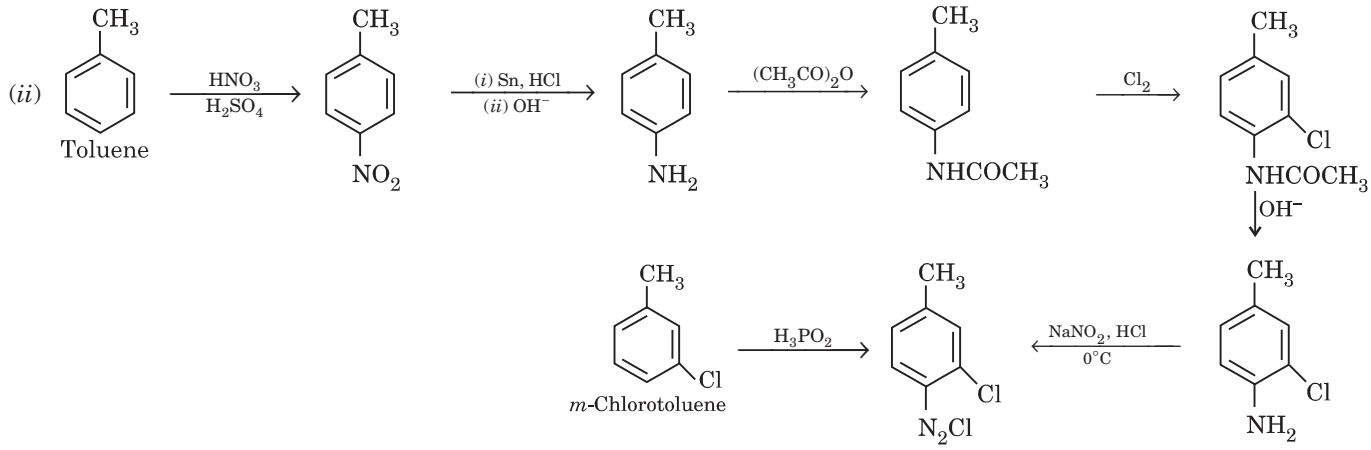
(i) o-chlorotoluene (ii) m-chlorotoluene (iii) p-iodotoluene (iv) p-cyanobenzoic acid.

Solution :

(*i*) 

Toluene → o-Chlorotoluene

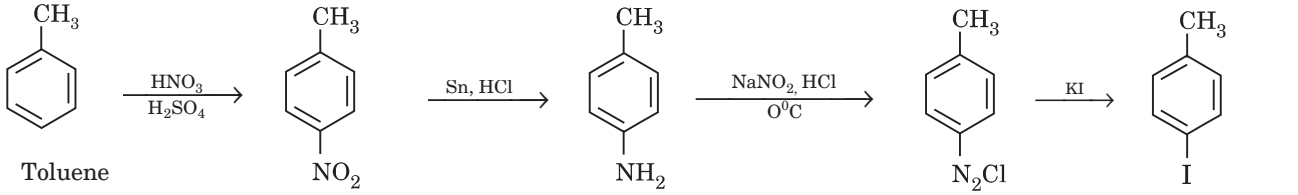
In this case, the *para* position is blocked by NO_2 to prepare only *ortho* product.

(*ii*) 

Toluene → *m*-Chlorotoluene

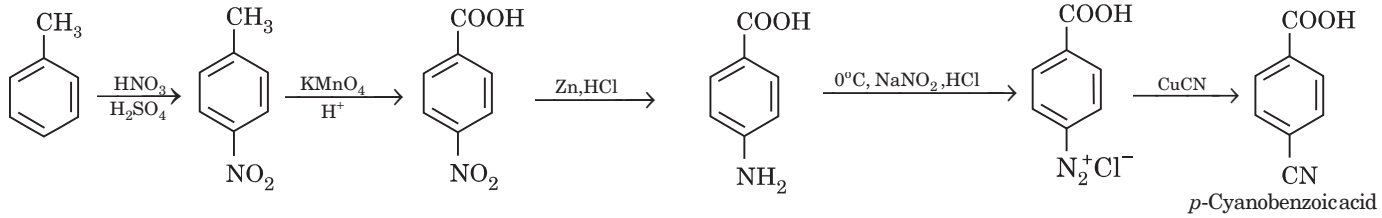
The $-NHCOCH_3$ group helps Cl to orient at ortho position, which is meta to CH_3. It is then removed.

(*iii*)



Toluene — *p*-Iodotoluene

(*iv*)



p-Cyanobenzoic acid

❑ Example 17.

Give the structures of A, B and C in the following reactions :

(*a*) $CH_3-COOH \xrightarrow{NH_3/\Delta} A \xrightarrow{Br_2/KOH(aq)} B \xrightarrow{CHCl_3+alc.KOH} C$ *(A.I.S.B. 2017)*

(*b*) $C_6H_5N_2^+BF_4^- \xrightarrow[\Delta]{NaNO_2/Cu} A \xrightarrow{Fe/HCl} B \xrightarrow{CH_3COCl/\,pyridine} C$ *(A.I.S.B. 2017)*

(*c*) $C_6H_5CONH_2 \xrightarrow{Br_2/aq\cdot KOH} A \xrightarrow[0-5^\circ C]{NaNO_2+HCl} B \xrightarrow{KI} C$ *(D.S.B. 2016)*

(*d*) $CH_3-Cl \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[\Delta]{CHCl_3/Alc.KOH} C$ *(D.S.B. 2016)*

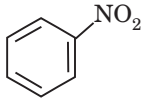
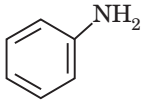
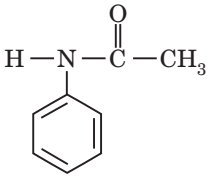
(*e*) $C_6H_5COO^-NH_4^+ \xrightarrow{\Delta} A \xrightarrow{Br_2/KOH} B \xrightarrow[Pyridine]{CH_3COCl} C$ *(A.I.S.B. 2016)*

(*f*) $C_6H_5N_2^+BF_4^- \xrightarrow[\Delta]{NaNO_2/Cu} A \xrightarrow{Sn/HCl} B \xrightarrow{CHCl_3+alc.KOH} C$ *(A.I.S.B. 2016)*

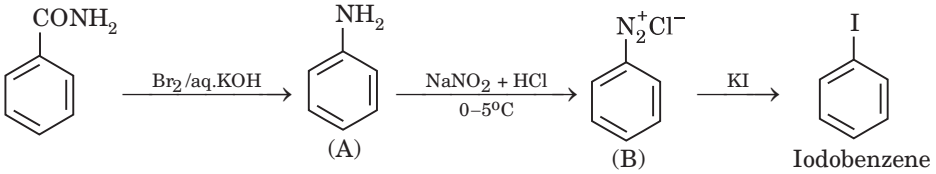
(*g*) $ArNH_2 \xrightarrow[0-5\ C]{NaNO_2/HCl} A \xrightarrow{CuCN} B$ *(Mizoram S.B. 2018)*

Solution :

(*a*) $CH_3COOH \xrightarrow{NH_3/\Delta} \underset{(A)}{CH_3CONH_2} \xrightarrow{Br_2/KOH(aq)} \underset{(B)}{CH_3NH_2} \xrightarrow[alc.KOH]{CHCl_3+} \underset{(C)}{CH_3NC}$

(*b*) $C_6H_5N_2^+BF_4^- \xrightarrow[\Delta]{NaNO_2/Cu}$  $\xrightarrow{Fe/HCl}$  $\xrightarrow[pyridine]{CH_3COCl/}$ 

(A) (B) (C)

(*c*) 

(A) (B) Iodobenzene (C)

(d) $CH_3Cl \xrightarrow{KCN} \underset{(A}{CH_3CN} \xrightarrow{LiAlH_4} \underset{B)}{CH_3CH_2NH_2} \xrightarrow[\Delta]{CHCl_3/Alc.KOH} \underset{\text{Ethyl isocyanide (C)}}{CH_3CH_2NC}$

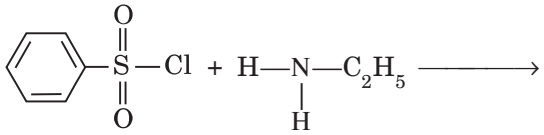
(e) $C_6H_5COO^-NH_4^+ \xrightarrow{\Delta} \underset{(A)}{C_6H_5CONH_2} \xrightarrow{Br_2/KOH} \underset{(B)}{C_6H_5NH_2} \xrightarrow[Pyridine]{CH_3COCl} \underset{\text{N-phenylethanamide (C)}}{C_6H_5NHCOCH_3}$

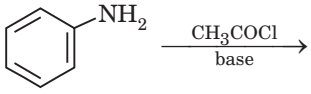
(f) $C_6H_5N_4^+BF_4^- \xrightarrow[\Delta]{NaNO_2/Cu} \underset{(A)}{C_6H_5NO_2} \xrightarrow{Sn/HCl} \underset{B)}{C_6H_5NH_2} \xrightarrow{CHCl_3+alc.KOH} \underset{\text{Phenyl isocyanide (C)}}{C_6H_5NC}$

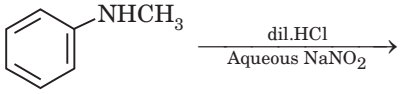
(g) $ArNH_2 \xrightarrow[0-5\ C]{NaNO_2/HCl} ArN_2^+Cl^- \xrightarrow{CuCN} ArCN$

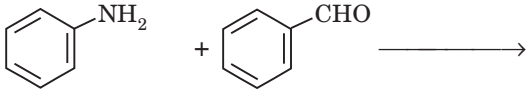
❑ Example 18.

(a) Write the products of the following reactions :

(i)  *(Hr. S.B. 2016)*

(ii)  *(A.I.S.B. 2016, H.P.S.B. 2018)*

(iii)  *(Kolkata S.B. 2016)*

(iv)  *(Kolkata S.B. 2016)*

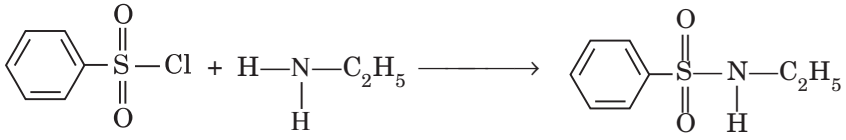
(v) $C_6H_5N_2Cl + C_2H_5OH \longrightarrow$ *(Jharkhand S.B. 2016)*

(b) How will you convert :

(i) benzene to aniline *(H.P.S.B. 2016)*

(ii) benzoic acid to aniline *(H.P.S.B. 2016)*

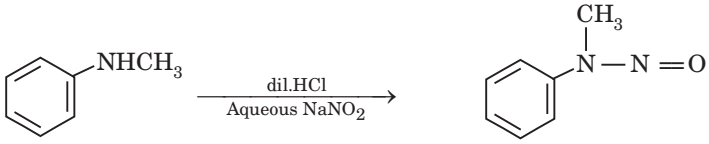
Solution :

(a) (i) 

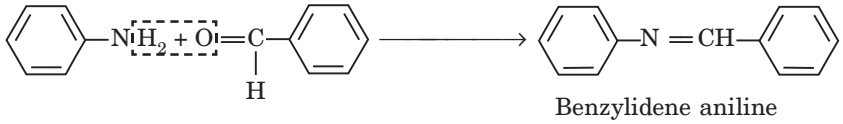
N-Ethylbenzenesulphonamide

(ii) 

N-Phenylethanamide

(iii) 

N-Nitroso-N-methylaniline

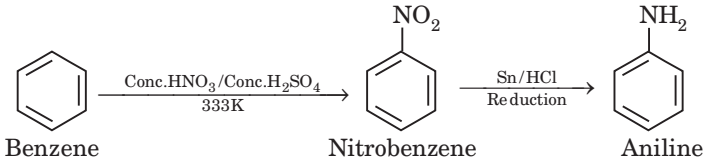
(iv) 

Benzylidene aniline
(Schiff's base)

(v) $C_6H_5N_2Cl + C_2H_5OH \longrightarrow C_6H_6 + N_2 + CH_3CHO + HCl$

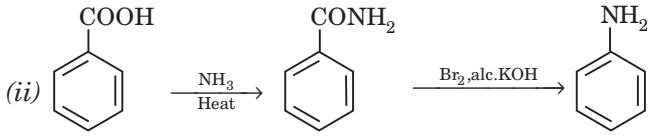
Benzene Ethanal

(b) (i)



Benzene Nitrobenzene Aniline

(ii)

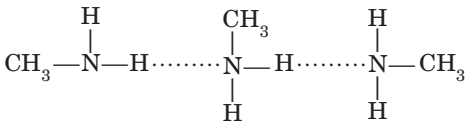


Aniline

add on Conceptual Questions

Q.1. Why does methylamine has lower boiling point than methanol ?

Ans. Methylamine is polar and can form intermolecular hydrogen bonds However, its tendency to form intermolecular hydrogen bonds is less than that of methanol (CH_3OH), which has highly electronegative oxygen atom. As a result, CH_3NH_2 has lower boiling point than CH_3OH.



Q.2. Why is methylamine stronger base than ammonia ?

Ans. Both ammonia and CH_3NH_2 have a lone pair of electrons and therefore, behave as Lewis bases. The alkyl group in CH_3NH_2 has + I inductive effect and is electron releasing in nature. As a result, its electron releasing tendency becomes more. Thus, CH_3NH_2 is more basic than ammonia.

CONCEPTUAL QA

Q.3. Aniline dissolves in aqueous HCl. Why ?

Ans. Aniline dissolves in aqueous HCl due to the formation of water soluble salt :

$$C_6H_5NH_2 + HCl \longrightarrow C_6H_5NH_3^+Cl^-$$

Anilinium chloride (water soluble)

Q.4. Why is it difficult to prepare pure amines by ammonolysis of alkyl halides ?

Ans. By ammonolysis of alkyl halides, a mixture of primary, secondary and tertiary amines is formed.

$$NH_3 \xrightarrow{RX} \underset{1^\circ\text{Amine}}{R{-}NH_2} \xrightarrow{RX} \underset{2^\circ\text{Amine}}{R_2NH} \xrightarrow{RX} \underset{3^\circ\text{Amine}}{R_3N} \xrightarrow{RX} \underset{\text{Quaternary salt}}{R_4N^+X^-}$$

The separation of these amines is very difficult. Thus, it is very difficult to prepare pure amines by ammonolysis of alkyl halides.

Q.5. Methylamine in water reacts with ferric chloride to precipitate ferric hydroxide. Explain.

Ans. Methylamine in water gives OH^- ions which react with ferric chloride to give the precipitate of ferric hydroxide as:

$$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3OH \rightleftharpoons CH_3NH_3^+ + OH^-$$

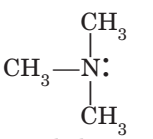
$$Fe^{3+} + 3OH^- \longrightarrow \underset{\text{Precipitate}}{Fe(OH)_3}$$

Q.6. Electrophilic substitution in case of aromatic amines takes place more readily than benzene. Explain.

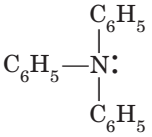
Ans. NH_2 group in aromatic amines strongly activates the aromatic ring through delocalisation of the lone pair of electrons on N-atom over the aromatic ring. However, no such delocalisation occurs in case of benzene.

Q.7. Although boron trifluoride adds on trimethylamine but it does not add on triphenylamine. Explain.

Ans. Trimethylamine has three electron donating alkyl groups and therefore acts as a Lewis base and reacts with BF_3 (a Lewis acid).



Trimethylamine



Triphenylamine

On the other hand, in triphenylamine, the lone pair of N gets delocalised over three benzene rings. Thus, the lone pair is not readily available to BF_3 for reaction.

Q.8. Why does silver chloride dissolve in methylamine solution ?

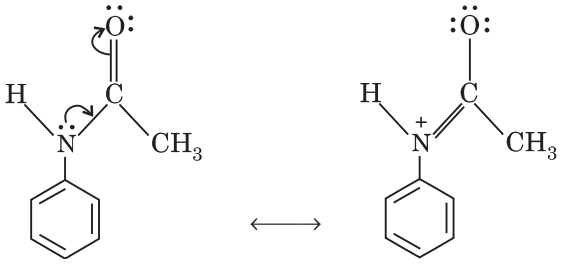
Ans. Silver chloride dissolves in methylamine solution because it forms soluble complex.

$$2CH_3NH_2 + AgCl \longrightarrow [Ag(CH_3NH_2)_2]^+Cl^-$$

Soluble complex

Q.9. Why does the reactivity of NH_2 get reduced in acetanilide ? *(Pb. S.B. 2018)*

Ans. In acetanilide, the amide group withdraws electrons from NH_2 group as shown below :



As a result, the electron pair on nitrogen gets displaced to the carboxyl group. Therefore, the unshared pair of electrons on nitrogen is less available for donation to the aromatic ring. Consequently, the electron density at *ortho* and *para* position in the benzene ring gets reduced which in turn results in reduced reactivity towards electrophilic substitution of benzene.

Q.10. Although trimethyl amine and *n*-propylamine have the same molecular mass, the former boils at a lower temperature (276 K) than the latter (322 K). Why ?

Ans. *n*-Propylamine $CH_3CH_2CH_2NH_2$ has two hydrogen atoms on the nitrogen atom and therefore, forms intermolecular hydrogen bonding. Hence, its boiling point is high. On the other hand, trimethylamine, $(CH_3)_3N$ does not have hydrogen atom on the nitrogen atom. As a result, it does not undergo hydrogen bonding and hence its boiling point is low.

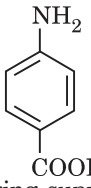
Q.11. Sulphanilic acid is soluble in dil. NaOH but not in dil. HCl. Explain.

Ans. Sulphanilic acid exists as a zwitter ion, NH_3^+–C$_6$H$_4$–SO_3^-. In the presence of dil. NaOH, the weakly acidic NH_3^+ group transfers its H^+ to OH^- to form a soluble *p*-$NH_2C_6H_4SO_3^-Na^+$. On the other hand, SO_3^- group is very weak base and therefore, does not accept a proton from dil. HCl to form *p*-$NH_3^+C_6H_4SO_3H$. Hence, it does not dissolve in dil. HCl.

Q.12. Glycine exists as $NH_3^+CH_2COO^-$, zwitter ion but anthranilic acid (*p*-amino benzoic acid) does not exist as zwitter ion. Why ?

Ans. Glycine exists as zwitter ion because the acidic group –COOH donates proton to basic –NH_2 group as :

$CH_2(NH_2)$–COOH $\longrightarrow$ $CH_2(NH_3^+)$–COO^- (Zwitter ion)



Anthranilic acid

However, in anthranilic acid, the electron withdrawing benzene ring suppresses the tendency of a weak acidic group (–COOH) to transfer its proton to –NH_2 group.

Q.13. Tertiary amines do not undergo acylation. Explain. ***(Pb.S.B. 2014, H.P.S.B. 2016)***

Ans. Amines containing replaceable hydrogen atom react with acid chloride or acid anhydride to form substituted amides. This reaction is called acylation reaction. In case of tertiary amines, there is no replaceable H atom and therefore, these do not react with acetyl chloride or acetic anhydride and hence do not undergo acylation.

Q.14. Arrange the following sets in order of their basic strength in aqueous solution :

(*i*) NH_3, $C_6H_5NH_2$, CH_3NH_2, $(CH_3)_3N$, $(CH_3)_2NH$ ***(Kerala S.B. 2013)***

(*ii*) Aniline, *p*-nitroaniline, *p*-methylaniline. ***(Hr. S.B. 2013, A.I.S.B. 2015)***

Ans. (*i*) $C_6H_5NH_2 < NH_3 < (CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$

(*ii*) *p*-nitroaniline < aniline < *p*-methylaniline

Q.15. Account for the following order of increasing basicity :

$RC{\equiv}N$ < $R'CH=NR$ < RNH_2

Nitrile Imine Amine

Ans. In RC≡N, the N atom is *sp* hybridised, in R′CH = NR, the N atom is sp^2 hybridised while in RNH_2, the N-atom is sp^3 hybridised. The more *s*-character in the hybrid orbital of N with the lone pair of electrons, greater will be its tendency to be strongly held by the nucleus. Therfore, it will have lesser tendency to donate its electron pair and hence will behave as weak base. Thus, as *s*-character decreases from RCN, to RCH = NR to RNH_2 its basic character increases.

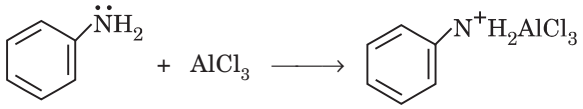
CONCEPTUAL QA

Q.16. Why do amines react as nucleophiles ? ***(A.I.S.B. 2007)***

Ans. Amines have a lone pair of electrons on N atom and therefore, react as nucleophiles.

Q.17. Aniline does not undergo Friedel Crafts alkylation. Explain. ***(Pb. S.B. 2013, Hr. S.B. 2015)***

Ans. Aniline does not undergo Friedel Craft alkylation reaction because of the formation of salt with aluminium chloride (Lewis acid) which is used as a catalyst. Due to this, nitrogen of aniline acquires positive charge and hence acts as a strong deactivating group for further reaction.



Q.18. lthough —NH_2 group is an *ortho* and *para* directing group, nitration of aniline gives along with *ortho* and *para* derivatives, *meta* derivative also. ***(C.B.S.E. Sample Paper 2007)***

Ans. Under strong acidic conditions of nitration, most of the aniline is converted into anilinium ion having NH_3^+ group. This group is a *m*-directing group, therefore, *m*-nitro aniline is also obtained along with *o*- and *p*-products.

Q.19. The presence of a base is needed in the ammonolysis of alkyl halides. ***(C.B.S.E. Sample Paper 2007)***

Ans. The ammonolysis of alkyl halides gives quaternary ammonium salt. The free amine can be obtained from ammonium salt by using a strong base.

$$RNH_3^+X^- + NaOH \longrightarrow RNH_2 + H_2O + Na^+X^-$$

Q.20. Aromatic primary amines cannot be prepared by Gabriel pthalimide synthesis. ***(C.B.S.E. Sample Paper 2007)***

Ans. Aromatic amines cannot be prepared by Gabriel phthalimide synthesis because aryl halides donot undergo nucleophilic substitution with the anion formed by phthalimide.

Q. 21. Suggest a structural formula of a compound having molecular formula $C_8H_{11}N$ (A) which is optically active, dissolves in dil. aqueous HCl and release N_2 with nitrous acid.

Ans. $C_6H_5\underset{\displaystyle NH_2}{\underset{|}{C}}HCH_3$

Q. 22. Arrange the following in the increasing order of boiling points $C_2H_5NH_2$, C_2H_5OH, $(CH_3)_3N$ ***(D.S.B. 2015, A.I.S.B. 2015)***

Ans. $(CH_3)_3N < C_2H_5NH_2 < C_2H_5OH$

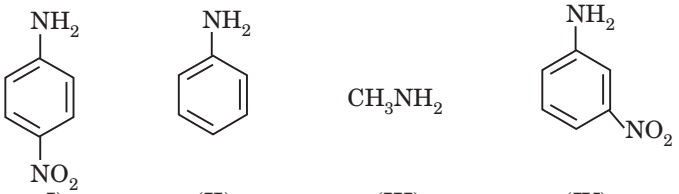
Q. 23. Identify A, B, C and D in the following conversions: ***(Assam S.B. 2016)***

$$A \xrightarrow[0-5^oC]{NaNO_2/HCl} CH_3OH \xrightarrow{PCl_3} B \xrightarrow{KCN} C \xrightarrow{LiAlH_4} D$$

Ans. $CH_3NH_2 \xrightarrow[0-5^oC]{NaNO_2/HCl} CH_3OH \xrightarrow{PCl_3} CH_3Cl \xrightarrow{KCN} CH_3CN \xrightarrow{LiAlH_4} CH_3CH_2NH_2$

Methanamine (A) — B) — (C) — Ethanamine (D)

Q. 24. Arrange the following compounds in the decreasing order of basicity :



I) (II) (III) (IV) ***(W.B.S.B. 2016)***

Ans. III > II > IV > I

Q. 25. Name the following reactions:

(i) $C_6H_5N_2^+Cl^- \xrightarrow{CuCl/HCl} C_6H_5Cl + N_2$

(ii) $C_6H_5N_2^+Cl^- \xrightarrow{Cu/HCl} C_6H_5Cl + N_2 + CuCl$ ***(Assam S.B. 2017)***

Ans. *(i)* Sandmeyer reaction *ii)* Gattermann reaction.

Q. 26. rrange the following in the increasing order of their pK_b values.

$C_6H_5NH_2$, $C_2H_5NH_2$, $C_6H_5NHCH_3$ ***(A.I.S.B. 2018)***

Ans. $C_2H_5NH_2 < C_6H_5NHCH_3 < C_6H_5NH_2$

CONCEPTUAL QA

Chapter Summary

Key Terms and Name Reactions

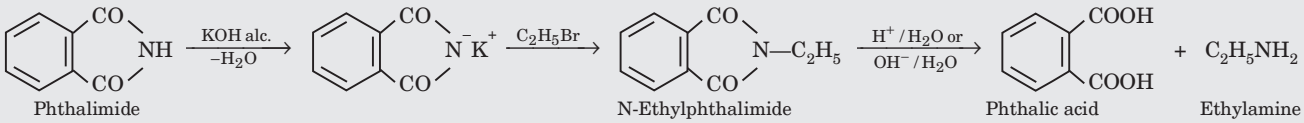
- **Exhaustic alkylation.** The process of converting an amine (1°, 2° or 3°) into its quaternary ammonium salt on treatment with excess alkyl halide.
- **Deamination.** The process involving diazotisation of an amine followed by reduction of diazonium salt or replacement of diazo group by hydrogen.
- **Mendius reaction.** The reduction of cyanide with sodium and alcohol.

$$CH_3CN \xrightarrow[C_2H_5OH]{Na(Hg)} CH_3CH_2NH_2$$

- **Hoffmann bromamide degradation.** Primary amines can be prepared from amides by treatment with Br_2 and KOH solution. **The amine formed contains one carbon atom less than the parent amide.**

$$RCONH_2 + Br_2 + 4KOH \longrightarrow RNH_2 + K_2CO_3 + 2KBr + H_2O$$

- **Gabriel phthalimide synthesis.** Phthalimide is treated with alcoholic KOH to give potassium phthalimide, which is treated with alkyl halide or benzyl halide to form N-alkyl or aryl phthalimide. The hydrolysis of N-alkyl phthalimide with 20% HCl under pressure or refluxing with NaOH gives primary amine.

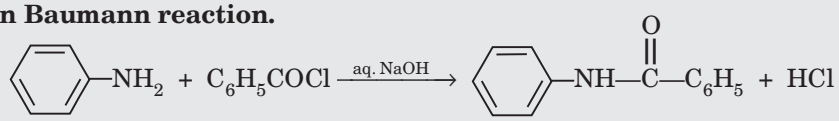


Phthalimide → N-Ethylphthalimide → Phthalic acid + Ethylamine

- **Sabatier and Mailhe method.**

$$C_2H_5OH + NH_3 \xrightarrow[Al_2O_3]{723\ K} C_2H_5NH_2 \xrightarrow[Al_2O_3]{C_2H_5OH} (C_2H_5)_2NH \xrightarrow[Al_2O_3]{C_2H_5OH} (C_2H_5)_3N$$

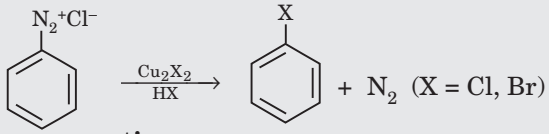
- **Schotten Baumann reaction.**



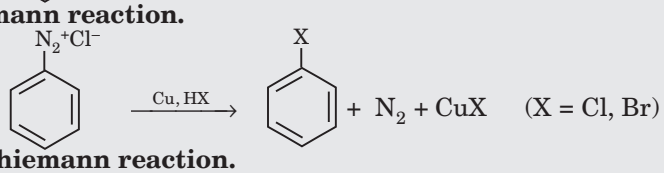
- **Carbylamine reaction.**

$$RNH_2 + CHCl_3 + 3KOH \longrightarrow \underset{\text{Alkyl isocyanide}}{RNC} + 3KCl + H_2O$$

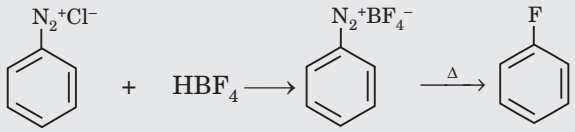
- **Sandmeyer's reaction.**



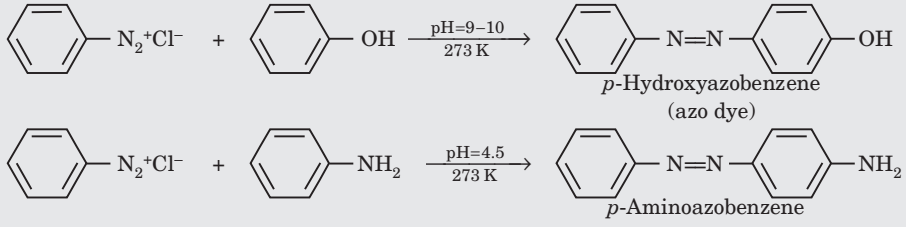
- **Gattermann reaction.**



- **Balz Schiemann reaction.**



- **Coupling reaction.**



QUICK CHAPTER ROUND UP

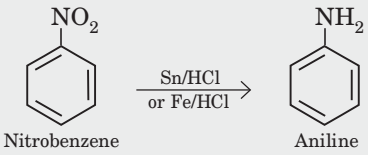
Preparation of amines

- **By ammonolysis of alkyl halides**

$$RNH_2 \xrightarrow[373\ K]{RX} R_2NH \xrightarrow[373\ K]{RX} R_3N \xrightarrow[373\ K]{RX} R_4N^+X^-$$

- **Reduction of nitro compounds**

$$RNO_2 + 6[H] \xrightarrow[Pt\ or\ Pd]{Raney\ Ni} RNH_2 + 2H_2O$$



Nitrobenzene Aniline

$$CH_3CH_2NO_2 \xrightarrow{LiAlH_4} CH_3CH_2NH_2$$

- **Reduction of cyanides**

$$CH_3CN + 4[H] \xrightarrow[Na,\ C_2H_5OH]{H_2/Ni,LiAlH_4} CH_3CH_2NH_2$$

$\Rightarrow$ Reaction of cyanides with Na, C_2H_5OH is **Mendius reaction.**

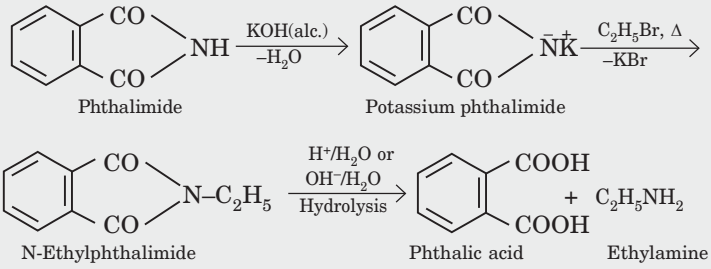
- **Reduction of amides**

$$R{-}\overset{\overset{O}{\|}}{C}{-}NH_2 \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4,\ ether} RCH_2NH_2$$

- **Hoffmann bromamide degradation**

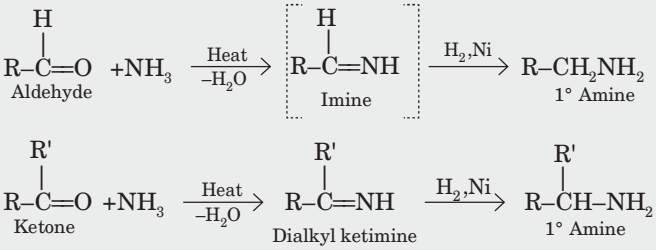
$$RCONH_2 + Br_2 + 4KOH \longrightarrow \underset{(one\ C\ less)}{RNH_2} + K_2CO_3 + 2H_2O$$

- **Gabriel Phthalimide Synthesis**



Aryl halides cannot be converted to aryl amines by Gabriel synthesis.

- **Reductive amination of aldehydes and ketones**



- **Schmidt reaction**

$$\underset{\text{Carboxylic acid}}{R{-}\overset{\overset{O}{\|}}{C}{-}OH} \xrightarrow[Conc.\ H_2SO_4]{N_3H} \underset{\text{1°–Amine}}{R{-}NH_2} + CO_2 + N_2$$

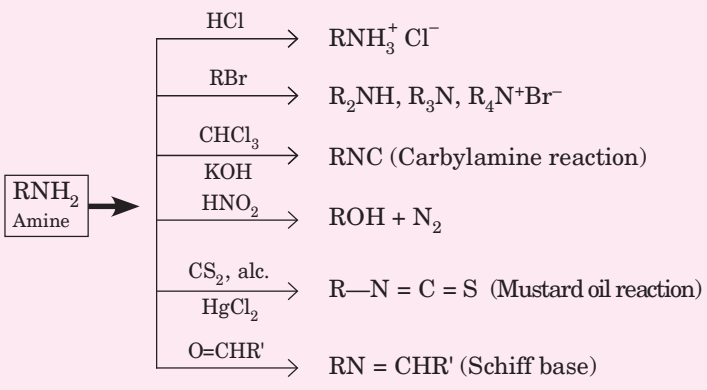
Properties of amines

- Because of the presence of a lone pair of electrons on the nitrogen atom of $-\ddot{N}H_2$ group, amines behave as **Lewis bases**.
- All aliphatic amines are more basic than ammonia. In aqueous solution, the order of basic character is :

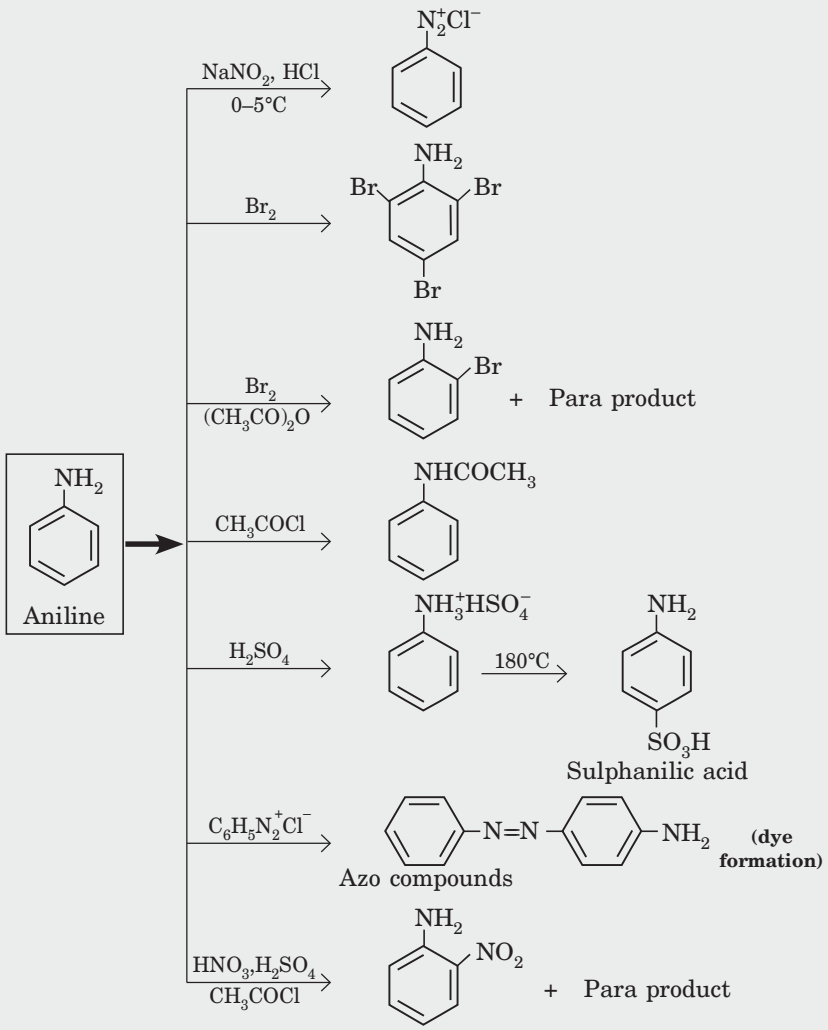
$$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N$$

- Aniline is less basic than ethylamine.

Reactions of Amines

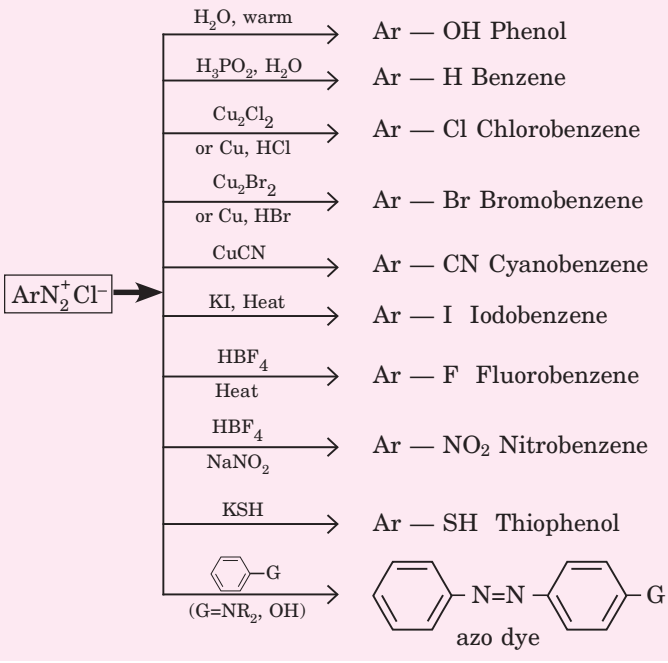


Reactions of Aniline



DIAZONIUM SALTS

Aromatic primary amines react with nitrous acid at 273–298 K (ice bath temperature), the product obtained is called diazonium salt $C_6H_5N_2^+X^-$. It contains the diazonium ion group $-N\equiv N^+$, attached to aryl group.

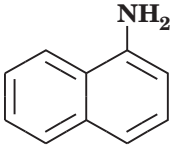
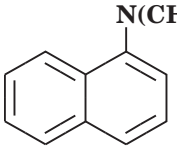


- Aryl diazonium salts are more stable than alkyl diazonium salts.

NCERT FILE Solved

NCERT In-text Questions

Q.1. Classify the following amines as primary, secondary and tertiary :

(*i*)  (*ii*)  (*iii*) $(C_2H_5)_2CHNH_2$ (*iv*) $(C_2H_5)_2NH$

Ans. (*i*) Primary (1°) (*ii*) Tertiary (3°) (*iii*) Primary (1°) (*iv*) Secondary (2°)

Q.2. (*i*) Write structures of different isomeric amines corresponding to the molecular formula, $C_4H_{11}N$.
(*ii*) Write IUPAC names of all the isomers.
(*iii*) What type of isomerism is exhibited by different pairs of amines ?

Ans. (*i*), (*ii*)

Primary amines

(*a*) $CH_3CH_2CH_2CH_2NH_2$ Butanamine

(*b*) $CH_3CH_2-\underset{\displaystyle NH_2}{\underset{|}{CH}}-CH_3$ Butan-2-amine

(*c*) $\overset{3}{C}H_3\overset{2}{C}H(\overset{1}{C}H_2-NH_2)-CH_3$ 2-Methylpropanamine

(*d*) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-NH_2$ 2-Methyl propan-2-amine

Secondary amines

(*e*) $CH_3CH_2CH_2NHCH_3$ N-methylpropanamine

(*f*) $CH_3CH(\underset{\displaystyle CH_3}{\underset{|}{\ }})-NH-CH_3$ N-Methylpropan-2-amine

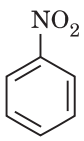
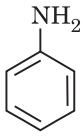
(*g*) $CH_3CH_2-NH-CH_2CH_3$ N-Ethylethanamine

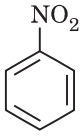
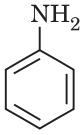
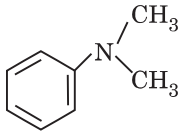
Tertiary amines

(*h*) $CH_3-N(\underset{\displaystyle CH_3}{\underset{|}{\ }})CH_2CH_3$ N, N-Dimethylethanamine

(*iii*) (*a*) – (*b*) and (*e*) – (*f*) are position isomers.
(*a*) – (*c*), (*b*) – (*d*) and (*a*) – (*d*) are chain isomers.
(*e*) – (*g*) and (*f*) and (*g*) are metamers.

Q.3. How will you convert
(*i*) Benzene into aniline ?
(*ii*) Benzene into N, N-dimethylaniline
(*iii*) Cl-$(CH_2)_6$-Cl into hexan-1,6-diamine ?

Ans. (*i*)  Benzene $\xrightarrow[\text{Conc. } H_2SO_4]{\text{Conc. } HNO_3}$  Nitrobenzene $\xrightarrow[\text{Reduction}]{\text{Fe, HCl}}$  Aniline

(*ii*)  Benzene $\xrightarrow[\text{Conc. } H_2SO_4]{\text{Conc. } HNO_3}$  $\xrightarrow[\text{Reduction}]{\text{Fe, HCl}}$  Aniline $\xrightarrow[\text{Heat}]{CH_3I \text{ (2 moles)}}$  N, N-Dimethylaniline

(*iii*) $Cl-(CH_2)_6-Cl$ + $4\,NH_3$(alc.) (excess) $\xrightarrow[-2\,NH_4Cl]{373\,K}$ $NH_2-(CH_2)_6-NH_2$

1,6-Dichlorohexane — Hexane-1,6-diamine

Q.4. rrange the following in increasing order of their basic strength :

(*i*) $C_2H_5NH_2$, $C_6H_5NH_2$, NH_3, $C_6H_5CH_2NH_2$ and $(C_2H_5)_2NH$ (*ii*) $C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$, $C_6H_5NH_2$

(*iii*) CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$, $C_6H_5NH_2$, $C_6H_5CH_2NH_2$

Ans. (*i*) ($_2H_5)_2NH > C_2H_5NH_2 > C_6H_5CH_2NH_2 > C_6H_5NH_2 > NH_3$

Due to +I effect of the two C_2H_5-groups in $(C_2H_5)_2$ NH as compared to one in $C_2H_5NH_2$, the lone pair on N is more available in $(C_2H_5)_2$ NH than $C_2H_5NH_2$ and therefore, $(C_2H_5)_2$ NH is more basic than C_2H_5 NH_2. Now aromatic amine, C_6H_5 NH_2 is less basic than both $(C_2H_5)_2$ NH and C_2H_5 NH_2 due to –I effect of C_6H_5-group. Due to the presence of C_6H_5-group, the electron density on the N atom becomes lower and hence less basic. Comparing $C_6H_5NH_2$ and $C_6H_5CH_2NH_3$, N is directly bonded to the benzene ring and hence the lone pair of electrons on the N atom is delocalised over the benzene ring. In contrast, N in $C_6H_5CH_2NH_2$ is not directly bonded to the benzene ring and hence its lone pair is not delocalised over the benzene ring. Therefore, the lone pair of electrons on N atom in $C_6H_5CH_2NH_2$ is more easily available for protonation than that on the N atom in $C_6H_5NH_2$. Hence $C_6H_5CH_2NH_2$ is more basic than $C_6H_5NH_2$. Hence, the correct order of basic character.

(*ii*) Due to increase in +I inductive effect of C_2H_5-group, the electron density on N-atom increases and therefore, the basic character is expected to increase as $C_2H_5NH_2 < (C_2H_5)_2NH < (C_2H_5)_3N$. In $C_6H_5NH_2$, the electron density on the N atom decreases due to the delocalisation of the lone pair of electrons over the benzene ring. Therefore, all the three ethyl amines are more basic than $C_6H_5NH_2$. Though $(C_2H_5)_3$ N is expected to be more basic than $(C_2H_5)_2$ NH, it is less basic because of steric hindrance to H-bonding for solvation of conjugate acid derived from $(C_2H_5)_3$ N. Therefore, $(C_2H_5)_3N$ is less basic than $(C_2H_5)_2NH$ but more basic than $C_2H_5NH_2$. So, the correct order of basic strength is :

$$(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > C_6H_5NH_2.$$

(*iii*) As explained in answer (*i*), $C_6H_5NH_2$ is less basic than $C_6H_5CH_2NH_2$ and all methyl amines are more basic than these amines due to +I effect of $–CH_3$ group [answer (*ii*)]. However, $(CH_3)_3$ N is less basic than $(CH_3)_2NH$ and CH_3NH_2 due to steric hindrance and less stabilization by H-bonding. Therefore, the correct order is :

$$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > C_6H_5CH_2NH_2 > C_6H_5NH_2$$

Q.5. omplete the following acid-base reactions and name the products :

(*a*) $CH_3CH_2CH_2NH_2 + HCl \longrightarrow$ (*b*) $(C_2H_5)_3N + HCl \longrightarrow$

Ans. (*a*) $CH_3CH_2CH_2NH_2 + HCl \longrightarrow CH_3CH_2CH_2NH^+{}_3Cl^-$

n-propylamine — *n*-propylammonium chloride

(*b*) $(C_2H_5)_3N + HCl \longrightarrow (C_2H_5)_3NH^+Cl^-$

Triethylammonium chloride

Q.6. Write reactions of the final alkylation product of aniline with excess of methyl iodide in the presence of sodium carbonate solution.

Ans.

$$C_6H_5\ddot{N}H_2 + CH_3I \longrightarrow [C_6H_5\overset{+}{N}H_2CH_3]I^-$$

Aniline — N-Methylanilinium iodide

$$2[C_6H_5NH_2CH_3]I^- + \ddot{N}a_2CO_3 \longrightarrow 2C_6H_5NHCH_3 + CO_2 + 2NaI$$

N-Methylaniline

$$C_6H_5NHCH_3 \xrightarrow[Na_2CO_3]{CH_3I} C_6H_5N(CH_3)_2 + CO_2 + 2NaI$$

N,N-Dimethyl aniline

$$C_6H_5\ddot{N}(CH_3)_2 + CH_3I \longrightarrow C_6H_5\overset{+}{N}(CH_3)_3I^-$$

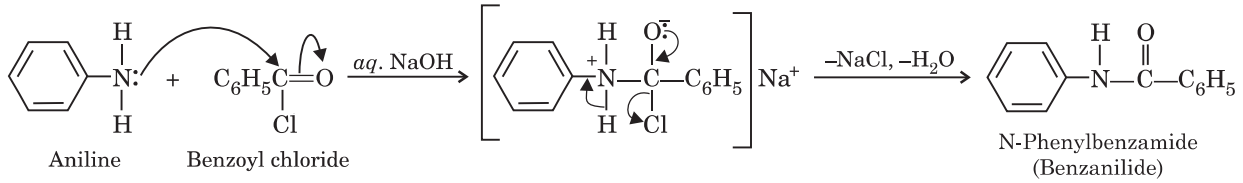
N,N,N-Trimethylanilinium iodide

$$2C_6H_5\overset{+}{N}(CH_3)_3I^- + Na_2CO_3 \longrightarrow [C_6H_5N^+(CH_3)_3]_2CO_3^{2-} + 2NaI$$

N,N,N-Trimethylanilinium carbonate

Q.7. Write chemical reaction of aniline with benzoyl chloride and write name of the product obtained.

Ans.



Aniline — Benzoyl chloride — N-Phenylbenzamide (Benzanilide)

Q.8. Write structures of different isomers corresponding to the molecular formula, C_3H_9N. Write IUPAC names of the isomers which will liberate nitrogen gas on treatment with nitrous acid.

Ans. Four structural isomers are possible

$CH_3CH_2CH_2NH_2$ — Propan-1-amine (1°)

$CH_3—\underset{\displaystyle NH_2}{\underset{|}{CH}}—CH_3$ — Propan-2-amine (1°)

$CH_3—NH—C_2H_5$ — N-Methylethanamine (2°)

$CH_3—\underset{\displaystyle CH_3}{\underset{|}{N}}—CH_3$ — N,N-Dimethylmethanamine (3°)

Only 1° amines react with HNO_2 to liberate N_2 gas

$$\underset{\text{Propan-1-amine}}{CH_3CH_2CH_2NH_2} + HNO_2 \longrightarrow \underset{\text{Propan-1-ol}}{CH_3CH_2CH_2OH} + H_2O + N_2$$

$$\underset{\text{Propan-2-amine}}{(CH_3)_2CH—NH_2} + HNO_2 \longrightarrow \underset{\text{Propan-2-ol}}{(CH_3)_2CHOH} + N_2 + H_2O$$

Q.9. onvert

***(i)* 3-Methylaniline into 3-nitrotoluene** ***(ii)* Aniline into 1,3,5-tribromobenzene.**

Ans. *(i)* 3-Methylaniline $\xrightarrow[273–278K]{NaNO_2, HCl}$ $\xrightarrow{HBF_4}$ (major product) $\xrightarrow[\Delta]{NaNO_2/Cu}$ 3-Nitrotoluene

(ii) Aniline $\xrightarrow{Br_2, H_2O}$ $\xrightarrow[273–278K]{NaNO_2,HCl}$ $\xrightarrow{H_3PO_2, Cu}$ 1,3,5-Tribromo benzene

NCERT Textbook Exercises

Q.1. Write IUPAC names of the following compounds and classify them into primary, secondary and tertiary amines.

(*i*) $(CH_3)_2CHNH_2$ (*ii*) $CH_3(CH_2)_2NH_2$ (*iii*) $CH_3NHCH(CH_3)_2$ (*iv*) $(CH_3)_3CNH_2$

(*v*) $C_6H_5NHCH_3$ (*vi*) $(CH_3CH_2)_2NCH_3$ (*vii*) *m*-$BrC_6H_4NH_2$

Ans. (*i*) Propan-2-amine (1°)
(*ii*) Propan-1-amine (1°)
(*iii*) N-Methylpropan-2-amine (2°)
(*iv*) 2-Methylpropan-2-amine
(*v*) N-Methylbenzenamine or N-Methylaniline
(*vi*) N-Ethyl-N-methylethanamine (3°)
(*vii*) 3-Bromobenzanamine or 3-Bromoaniline (1°)

Q.2. Give one chemical test to distinguish between the following pairs of compounds.

(*i*) Methylamine and dimethylamine **(*ii*) Secondary and tertiary amines**

(*iii*) Ethylamine and aniline **(*iv*) Aniline and benzylamine**

(*v*) Aniline and N-methylaniline

Ans. (*i*) These can be distinguished by carbylamine test. When heated with alcoholic solution of KOH and chloroform, methylamine gives foul smell of methyl isocyanide.

$$\underset{\text{Methylamine}}{CH_3NH_2} + HCl_3 + \underset{\text{(alc.)}}{KOH} \longrightarrow \underset{\substack{\text{Methyl isocyanide}\\ \text{(foul smell)}}}{CH_3NC} + KCl + H_2O$$

Dimethylamine does not give this test.

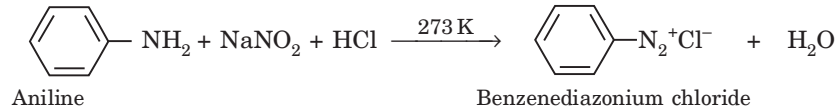
$$\underset{\text{Dimethylamine}}{(CH_3)_2NH} \xrightarrow[\Delta]{CHCl_3, KOH} \text{No reaction}$$

(*ii*) Secondary amines give Libermann nitrosoamine test while 3° amines do not. 2° amine on treatment with HNO_2 (prepared in situ by the action of HCl on $NaNO_2$) gives yellow coloured oily N-nitrosoamine.

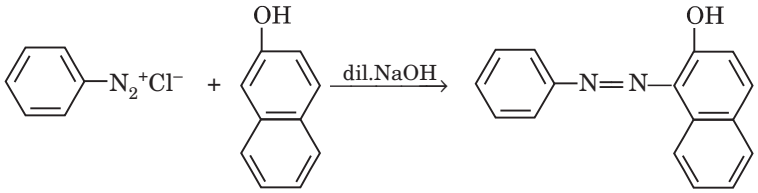
$$\underset{\text{Diethylamine}}{(CH_3CH_2)_2NH} + HO{-}N{=}O \longrightarrow \underset{\substack{\text{N-Nitrosodiethylamine}\\ \text{(Yellow colour)}}}{(CH_3CH_2)_2N{-}N{=}O} + H_2O$$

N-Nitrosodiethylamine on warming with a crystal of phenol and conc. H_2SO_4 gives a green solution which when made alkaline with aqueous NaOH turns deep blue and then red on dilution. Tertiary amines donot give this test.

(*iii*) These can be distinguished by azo dye test.
Dissolve the compound in conc. HCl and add ice-cold solution of HNO_2 ($NaNO_2$ + dil HCl) and then treat it with an alkaline solution of 2-naphthol. Appearance of brilliant orange or red dye indicates aniline.



Aniline — Benzenediazonium chloride



2-Naphthol — 1-Phenylazo-2-naphthol (Orange red dye)

Ethylamine does not form dye. It will give brisk effervescence due to the evolution of N_2 but solution remains clear.

(*iv*) These can be distinguished by azo dye test.
Aniline reacts with HNO_2 ($NaNO_2$ + dil. HCl) at 273–278K to form stable benzene diazonium chloride which on treatment with an alkaline solution of 2-naphthol gives an orange dye (as given in reaction (*iii*)).
Benzylamine does not give azo dye test.

(*v*) These can be distinguished by carbylamine test. Aniline being primary amines gives carbylamine test *i.e.*, when heated with an alcoholic solution of KOH and $CHCl_3$, it gives foul smell of phenyl isocyanide.

$$\underset{\text{Aniline}}{C_6H_5NH_2} + HCl_3 + \underset{\text{(alc.)}}{KOH} \xrightarrow{\Delta} \underset{\text{Phenylisocyanide}}{C_6H_5NC} + 3KCl + H_2O$$

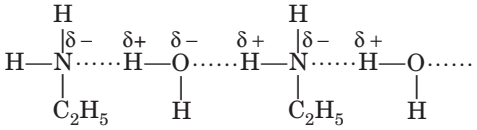
$$\underset{\text{N-Methylaniline}}{C_6H_5NH{-}CH_3} \xrightarrow[\Delta]{CHCl_3,\ KOH} \text{No reaction}$$

Q.3. Account for the following :

(*i*) pK_b of aniline is more than that of methylamine. ***(D.S.B. 2008)***
(*ii*) Ethylamine is soluble in water, whereas aniline is not.
(*iii*) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide.
(*iv*) Although amino group is *o*-and *p*-directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of *m*-nitroaniline.
(*v*) Aniline does not undergo Friedel Crafts reaction. ***(D.S.B. 2008)***
(*vi*) Diazonium salts of aromatic amines are more stable than those of aliphatic amines.
(*vii*) Gabriel phthalimide synthesis is preferred for synthesising primary amines.

Ans. (*i*) In aniline, the lone pair of electrons on N atom is delocalized over the benzene ring. As a result, electron density on the nitrogen decreases. On the other hand, in CH_3NH_2, +I effect of CH_3 group increases the electron density on N atom. Therefore, aniline is less basic than methylamine and hence pK_b of aniline is higher than that of methylamine.

(*ii*) Ethylamine dissolves in water due to intermolecular hydrogen bonding as shown below :



However, because of large hydrophobic part (*i.e.*, hydrocarbon part) of aniline, the extent of hydrogen bonding is less and therefore, aniline is insoluble in water.

(*iii*) Methylamine is more basic than water and therefore, accepts a proton from water forming OH^- ions.

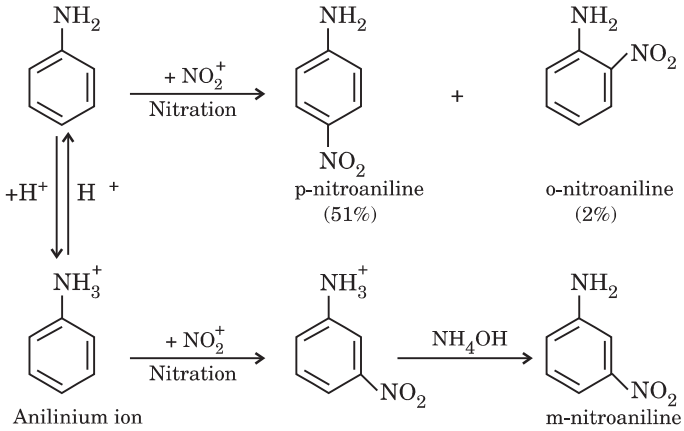
These OH^- ions combine with Fe^{3+} ions to form brown ppt. of hydrated ferric oxide.

$$FeCl_3 \longrightarrow Fe^{3+} + 3Cl^-$$

$$2Fe^{3+} + 6OH^- \longrightarrow 2Fe(OH)_3 \text{ or } Fe_2O_3.3H_2O$$

Hydrated ferric oxide (Brown ppt)

(*iv*) Under strongly acidic conditions of nitration (in the presence of a mixture of conc. $HNO_3 + H_2SO_4$), aniline gets protonated and is converted into anilinium ion having $-NH_3^+$ group. This group is deactivating group and is *m*-directing. So, the nitration of aniline gives *o*, *p*-nitroaniline (mainly *p*-product) while the nitration of anilinium ion gives *m*-nitroaniline.



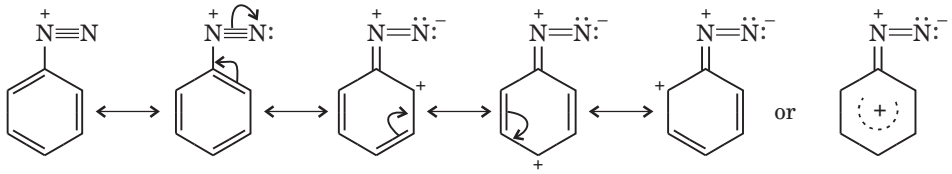
Thus, nitration of aniline gives a substantial amount of *m*-nitroaniline due to protonation of aniline.

(*v*) Aniline being a Lewis base reacts with Lewis acid such as $AlCl_3$ to form a salt.

$$\underset{\text{Lewis base}}{C_6H_5NH_2} + \underset{\text{Lewis acid}}{AlCl_3} \longrightarrow \underset{\text{Salt}}{C_6H_5NH_2^+AlCl_3^-}$$

As a result, N of aniline acquires +ve charge and hence it acts as a strong deactivating group for electrophilic substitution reaction. Hence aniline does not undergo Friedel Crafts reaction.

(*vi*) The diazonium salts of aromatic amines are more stable than those of aliphatic amines because of dispersal of positive charge on the benzene ring due to resonance :



This type of resonance stability is not possible in alkyl diazonium salts.

(*vii*) Gabriel phthalimide reaction gives pure 1° amines without any impurity of 2° or 3° amines. Therefore, it is preferred for the synthesis of 1° amines.

Q.4. Arrange the following :

(*i*) In decreasing order of the pK_b values : $C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$ ***(D.S.B. 2010)***

(*ii*) In decreasing order of basic strength : $C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_2H_5)_2NH$ and CH_3NH_2 ***(D.S.B. 2010)***

(*iii*) Increasing order of basic strength :

(*a*) Aniline, *p*-nitroaniline and *p*-toluidine

(*b*) $C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5CH_2NH_2$ ***(D.S.B. 2010)***

(*iv*) Decreasing order of basic strength in gas phase : $C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ and NH_3

(*v*) Increasing order of boiling point : C_2H_5OH, $(CH_3)_2NH$, $C_2H_5NH_2$

(*vi*) Increasing order of solubility in water : $C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_2H_5NH_2$

Ans. (*i*) Stronger the base lesser the pK_b value.

$C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$

Refer In-text Q.4.

(*ii*) $(C_2H_5)_2NH > CH_3NH_2 > C_6H_5NHCH_3 > C_6H_5NH_2$
Refer Intext Q. 4.

(*iii*) (*a*) *p*-nitroaniline < aniline < *p*-toluidine

(*b*) $C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$

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

In gas phase reactions, the stabilization of the conjugate acids due to hydrogen bonding is absent.

(*v*) Since the electronegativity of O is more than that of N, alcohols form stronger hydrogen bonds than amines. Therefore, the b.p. of C_2H_5OH (mol. mass = 46) is higher than those of $(CH_3)_2NH$ and $C_2H_5NH_2$ (each having mol mass = 45). Further, since the extent of hydrogen bonding depends upon the number of H-atoms on N atom, therefore, 1° amines with two H atoms on the N atom have higher b.p. than 2° amines (of comparable molecular mass) having only one H atom on N. Thus, the boiling point of $C_2H_5NH_2$ is more than that of $(CH_3)_2NH$. Thus, the b.p.s of given compounds increase as:

$$(CH_3)_2NH < C_2H_5NH_2 < C_2H_5OH$$

(*vi*) Solubility decreases with increase in molecular mass of amines due to increase in size of the hydrophobic hydrocarbon part and with the decrease in the number of H atoms on the N-atom which form hydrogen bonds. Among the given compounds, $C_6H_5NH_2$ has higher molecular mass (93) followed by $(C_2H_5)_2NH$ (73) while $C_2H_5NH_2$ has lowest molecular mass of 45. Thus, the solubility increases in the order :

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

Q.5. How will you convert

(*i*) Ethanoic acid into methanamine **(*ii*) Hexanenitrile into 1-aminopentane,**
(*iii*) Methanol to ethanoic acid, **(*iv*) Ethanamine into methanamine,**
(*v*) Ethanoic acid into propanoic acid, **(*vi*) Methanamine into ethanamine,**
(*vii*) Nitromethane into dimethylamine, **(*viii*) Propanoic acid into ethanoic acid ?**

Ans. (*i*) CH_3COOH (Ethanoic acid) $\xrightarrow[-SO_2,-HCl]{SOCl_2}$ CH_3COCl $\xrightarrow{NH_3(excess)}$ CH_3CONH_2 $\xrightarrow[\text{Hoffmann bromamide reaction}]{Br_2,KOH}$ CH_3NH_2 (Methanamine)

(*ii*) $CH_3(CH_2)_4CN$ (Hexanenitrile) $\xrightarrow[\text{Hydrolysis}]{H_3O^+}$ $CH_3(CH_2)_4COOH$ $\xrightarrow{SOCl_2}$ $CH_3(CH_2)_4COCl$ $\xrightarrow{NH_3(excess)}$ $CH_3(CH_2)_4CONH_2$

$CH_3(CH_2)_4CONH_2$ $\xrightarrow[\text{Hoffmann bromamide reaction}]{Br_2,KOH}$ $CH_3(CH_2)_4NH_2$ (1-Aminopentane)

(*iii*) CH_3OH (Methanol) $\xrightarrow{PCl_5}$ CH_3Cl $\xrightarrow{\text{alc. KCN}}$ CH_3CN $\xrightarrow[\text{Hydrolysis}]{H_3O^+}$ CH_3COOH (Ethanoic acid)

(*iv*) $CH_3CH_2NH_2$ (Ethanamine) $\xrightarrow{HONO}$ CH_3CH_2OH $\xrightarrow[\text{Oxidation}]{K_2Cr_2O_7,H^+}$ CH_3CHO $\xrightarrow{K_2Cr_2O_7,H^+}$ CH_3COOH

CH_3COOH $\xrightarrow{NH_3(excess)}$ H_3COONH_4 $\xrightarrow{\Delta}$ CH_3CONH_2 $\xrightarrow[\text{Hoffmann bromamide reaction}]{Br_2,KOH}$ CH_3NH_2 (Methanamine)

(*v*) CH_3COOH (Ethanoic acid) $\xrightarrow[\text{Reduction}]{LiAlH_4}$ CH_3CH_2OH $\xrightarrow[\text{or } PI_3]{P,I_2}$ CH_3CH_2I $\xrightarrow[-KI]{KCN}$ CH_3CH_2CN

CH_3CH_2CN $\xrightarrow[\text{Hydrolysis}]{H^+,H_2O}$ CH_3CH_2COOH (Propanoic acid)

(*vi*) CH_3NH_2 (Methanamine) $\xrightarrow{HONO}$ H_3OH $\xrightarrow{P,I_2}$ CH_3I $\xrightarrow{KCN}$ CH_3CN

CH_3CN $\xrightarrow[\text{Reduction}]{Na,C_2H_5OH}$ $CH_3CH_2NH_2$ (Ethanamine)

(*vii*) CH_3NO_2 (Nitromethane) $\xrightarrow[\text{Reduction}]{Sn,HCl}$ CH_3NH_2 $\xrightarrow[\Delta]{CHCl_3,KOH}$ CH_3NC $\xrightarrow[\text{Reduction}]{Na,C_2H_5OH}$ CH_3NHCH_3 (Dimethylamine)

(*viii*) CH_3CH_2COOH (Propanoic acid) $\xrightarrow{NH_3}$ $CH_3CH_2COONH_4$ $\xrightarrow{\Delta}$ $CH_3CH_2CONH_2$ $\xrightarrow[\text{Hoffmann bromamide reaction}]{Br_2,KOH}$ $CH_3CH_2NH_2$

$\xrightarrow{HONO}$ CH_3CH_2OH $\xrightarrow[\text{Oxidation}]{K_2Cr_2O_7,H^+}$ CH_3CHO (Ethanoic acid) $\xrightarrow[\text{Oxidation}]{K_2Cr_2O_7,H^+}$ CH_3COOH (Ethanoic acid)

Q.6. escribe the method for the identification of primary, secondary and tertiary amines. Also write chemical equations of the reactions involved.

Ans. Refer (Page 28–29).

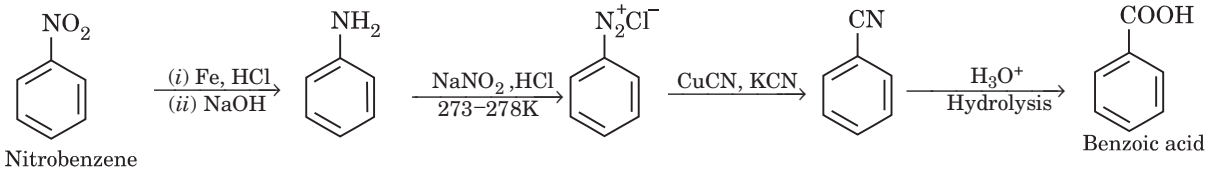
Q.7. Write short notes on the following :

(*i*) Carbylamine reaction **(*ii*) Diazotisation**
(*iii*) Hoffmann's bromamide reaction **(*iv*) Coupling reaction**
(*v*) Ammonolysis **(*vi*) Acetylation**
(*vii*) Gabriel phthalimide synthesis

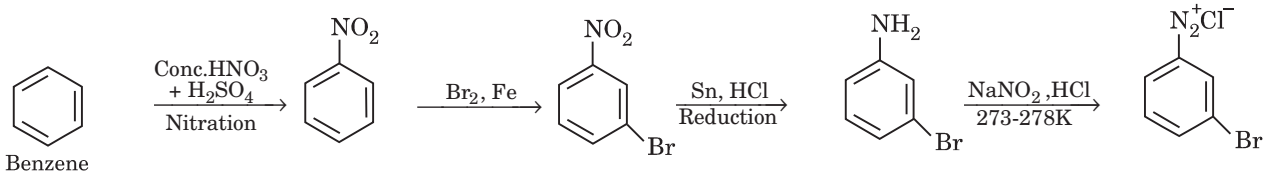
Ans. Refer Text (*i*) Page 28 (*ii*) Page 41 (*iii*) Page 13 (reaction 5) (*iv*) Page 35 (*v*) Page 10 (*vi*) Page 26 (*vii*) page 14.

Q.8. ccomplish the following conversions.

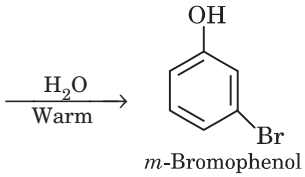
(*i*) Nitrobenzene to benzoic acid **(*ii*) Benzene to *m*-bromophenol**
(*iii*) Benzoic acid to aniline **(*iv*) Aniline to 2,4,6-tribromofluorobenzene**
(*v*) Benzyl chloride to 2-phenylethanamine **(*vi*) Chlorobenzene to *p*-chloroaniline**
(*vii*) Aniline to *p*-bromoaniline **(*viii*) Benzamide to toluene**
(*ix*) Aniline to benzyl alcohol

Ans. (*i*) 

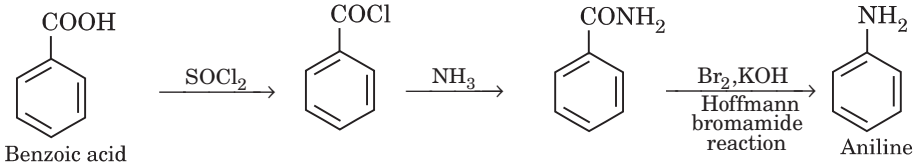
Nitrobenzene — Benzoic acid

(*ii*) 

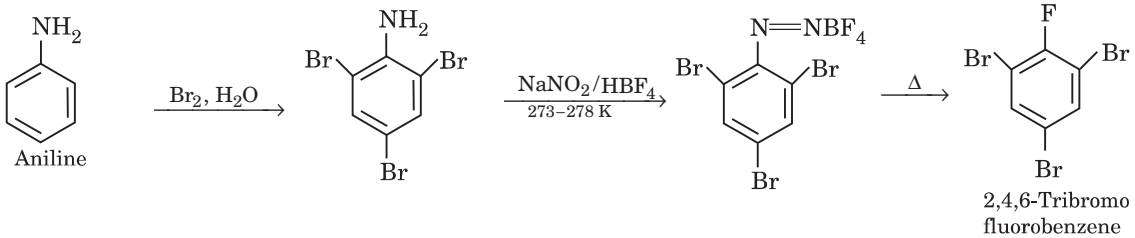
Benzene



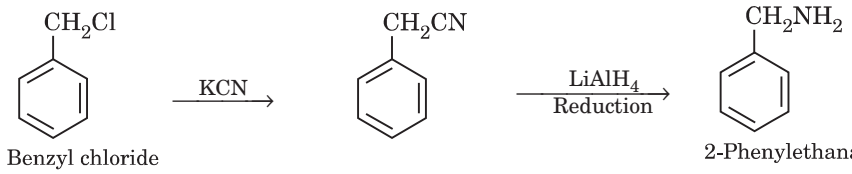
m-Bromophenol

(*iii*) 

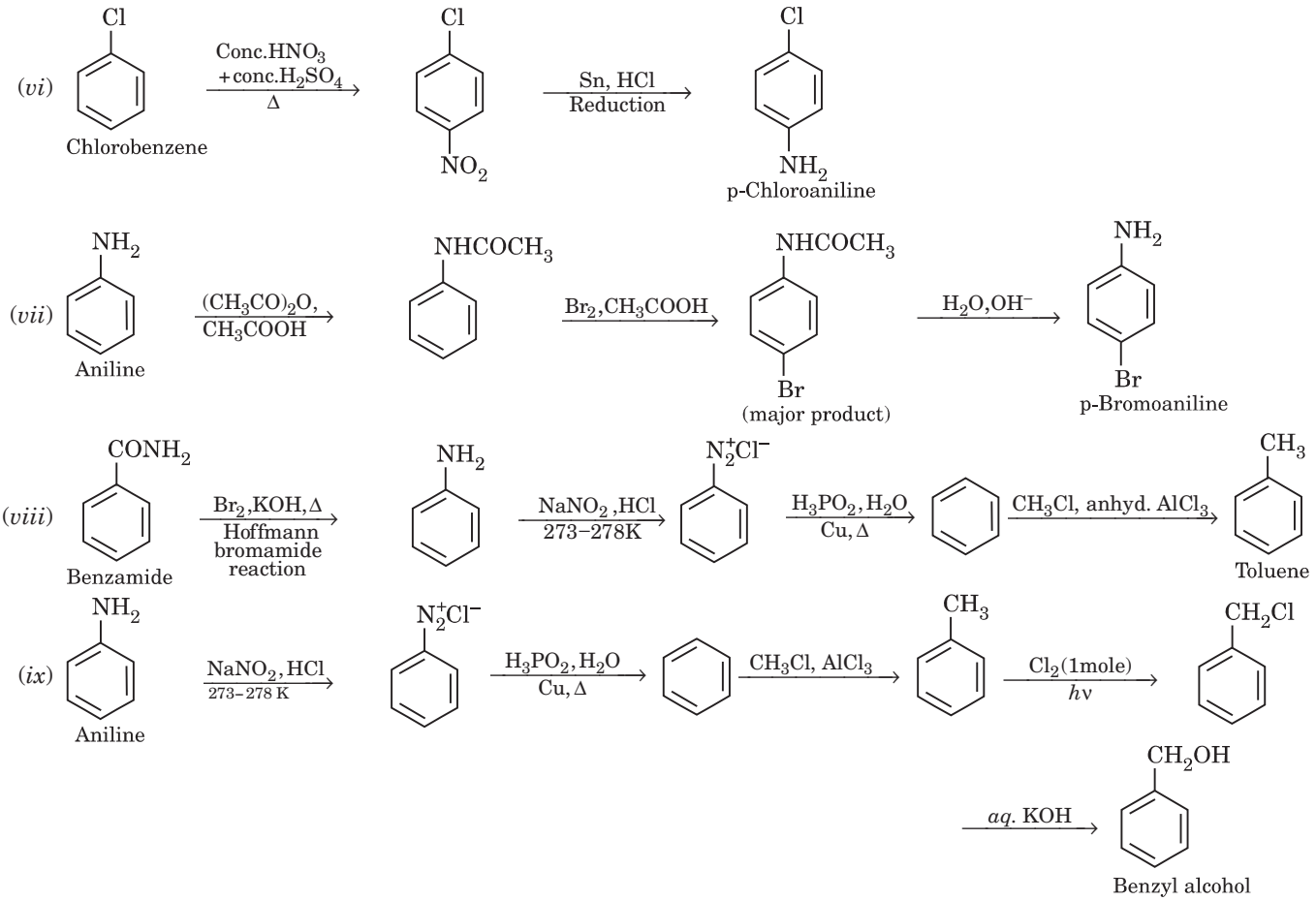
Benzoic acid — Aniline

(*iv*) 

Aniline — 2,4,6-Tribromo fluorobenzene

(*v*) 

Benzyl chloride — 2-Phenylethanamine



Q.9. ive the structures of A, B and C in the following reactions

(*i*) $CH_3CH_2I \xrightarrow{NaCN} A \xrightarrow[\text{Partial hydrolysis}]{OH^-} B \xrightarrow{NaOH + Br_2} C$

(*ii*) $C_6H_5N_2Cl \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow[\Delta]{NH_3} C$

(*iii*) $CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[0°C]{HNO_2} C$

(*iv*) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273\ K]{NaNO_2+HCl} B \xrightarrow[\Delta]{H_2O/H^+} C$

(*v*) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{NaOBr} B \xrightarrow{NaNO_2/HCl} C$

(*vi*) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273\ K]{HNO_2} B \xrightarrow{C_6H_5OH} C$

Ans. (*i*) $CH_3CH_2I \xrightarrow{NaCN} \underset{\text{Propane nitrile (A)}}{CH_3CH_2CN} \xrightarrow[\text{Partial hydrolysis}]{OH^-} \underset{\text{Propanamide (B)}}{CH_3CH_2-\overset{\overset{O}{\|}}{C}-NH_2} \xrightarrow[\text{Hoffmann bromamide reaction}]{NaOH+Br_2} \underset{\text{Ethanamine (C)}}{CH_3CH_2NH_2}$

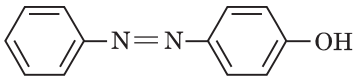
(*ii*) $C_6H_5N_2Cl \xrightarrow{CuCN} \underset{\text{Cyano benzene (A)}}{C_6H_5CN} \xrightarrow{H_2O/H^+} \underset{\text{Benzoic acid (B)}}{C_6H_5COOH} \xrightarrow[\Delta]{NH_3} \underset{\text{Benzamide (C)}}{C_6H_5CONH_2}$

(*iii*) $CH_3CH_2Br \xrightarrow{KCN} \underset{\text{Propane nitrile (A)}}{CH_3CH_2CN} \xrightarrow[\text{Reduction}]{LiAlH_4} \underset{\text{Propanamine (B)}}{CH_3CH_2CH_2NH_2} \xrightarrow{HNO_2,0°C} CH_3CH_2CH_2\overset{+}{N_2}Cl^-$

$\xrightarrow{H_2O} \underset{\text{Propanol (C)}}{CH_3CH_2CH_2OH}$

(*iv*) $C_6H_5NO_2 \xrightarrow[\text{Reduction}]{Fe/HCl} \underset{\text{Aniline (A)}}{C_6H_5NH_2} \xrightarrow[273\ K]{NaNO_2+HCl} \underset{\text{Benzene diazonium chloride (B)}}{C_6H_5N_2^+Cl^-} \xrightarrow{H^+, H_2O} \underset{\text{Phenol (C)}}{C_6H_5OH}$

(*v*) $CH_3COOH \xrightarrow[\Delta]{NH_3} \underset{\text{Ethanamide (A)}}{CH_3CONH_2} \xrightarrow[\text{Hoffmann bromamide reaction}]{NaOBr} \underset{\text{Methanamine (B)}}{CH_3NH_2} \xrightarrow{NaNO_2,\ HCl} \underset{\text{Methanol (C)}}{CH_3OH}$

(*vi*) $C_6H_5NO_2 \xrightarrow{Fe/HCl} \underset{\text{Aniline (A)}}{C_6H_5NH_2} \xrightarrow[273K]{HNO_2} \underset{\text{Benzene diazonium chloride (B)}}{C_6H_5N_2^+Cl^-} \xrightarrow[\text{Coupling reaction}]{C_6H_5OH}$  *p*-Hydroxyazobenzene (C)

Q.10. n aromatic compound 'A' on treatment with aqueous ammonia and heating forms compound 'B' which on heating with Br_2 and KOH forms a compound 'C' of molecular formula C_6H_7N. Write the structures and IUPAC names of compounds A, B and C.

Ans. (*i*) Since the compound C of molecular formula C_6H_7N is formed from B on treatment with Br_2 and KOH (Hoffmann bromamide reaction), therefore, the compound 'B' must be an amide and 'C' must be an amine. The only aromatic amine having molecular formula C_6H_7N is $C_6H_5NH_2$ (aniline).

(*ii*) Since 'C' is aniline, the amide from which is formed by must be benzamide ($C_6H_5CONH_2$).

$$\underset{\text{Aniline(C)}}{C_6H_5NH_2} \xleftarrow{Br_2,\ KOH} \underset{\text{Benzamide(B)}}{C_6H_5CONH_2}$$

Thus, B is benzamide.

(*iii*) Since B is formed from A with aqueous ammonia and heating, therefore, compound 'A' must be benzoic acid.

$$\underset{\text{Benzoic acid (A)}}{C_6H_5COOH} \xrightarrow[\text{Heat}]{aq.\ NH_3} \underset{\text{Benzamide (B)}}{C_6H_5CONH_2}$$

Thus, A = C_6H_5COOH, B = $C_6H_5CONH_2$, C = $C_6H_5NH_2$.

Q.11. Complete the following reactions :

(*i*) $C_6H_5NH_2 + CHCl_3 + \text{alc. KOH} \longrightarrow$ **(*ii*)** $C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow$

(*iii*) $C_6H_5NH_2 + H_2SO_4\text{(conc.)} \longrightarrow$ **(*iv*)** $C_6H_5N_2Cl + C_2H_5OH \longrightarrow$

(*v*) $C_6H_5NH_2 + Br_2(aq.) \longrightarrow$ **(*vi*)** $C_6H_5NH_2 + (CH_3CO)_2O \longrightarrow$

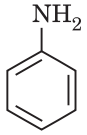
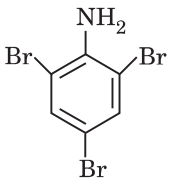
(*vii*) $C_6H_5N_2Cl \xrightarrow[(ii)\ NaNO_2/Cu,\Delta]{(i)\ HBF_4}$

Ans. (*i*) $C_6H_5NH_2 + CHCl_3 + \underset{\text{(alc)}}{3KOH} \longrightarrow \underset{\text{Phenyl isocyanide}}{C_6H_5NC} + 3KCl + 3H_2O$

(*ii*) $C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow \underset{\text{Benzene}}{C_6H_6} + N_2 + H_3PO_3 + HCl$

(*iii*) $C_6H_5NH_2 + H_2SO_4\text{(conc.)} \longrightarrow \underset{\text{Anilinium hydrogensulphate}}{C_6H_6\overset{+}{N}H_3HSO_4^-}$

(*iv*) $C_6H_5N_2Cl + C_2H_5OH \xrightarrow{\text{Reduction}} \underset{\text{Benzene}}{C_6H_6} + \underset{\text{Ethanal}}{CH_3CHO} + N_2 + HCl$

(*v*)  $+ Br_2(aq) \longrightarrow$  $+ 3HBr$

2,4,6-Tribromoaniline

(*vi*) $C_6H_5NH_2 + (CH_3CO)_2O \xrightarrow{CH_3COOH} \underset{\text{Acetanilide}}{C_6H_5CONHCH_3} + CH_3COOH$

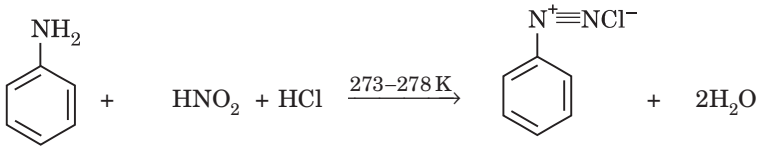
(*vii*) $C_6H_5N_2Cl \xrightarrow{(i)HBF_4} C_6H_5N_2^+BF_4^- \xrightarrow[\Delta]{(ii)NaNO_2,Cu} \underset{\text{Nitrobenzene}}{C_6H_5NO_2} + BF_3 + NaF$

Q.12. Why aromatic primary amines cannot be prepared by Gabriel phthalimide synthesis ?

Ans. Refer Text (Page 14).

Q.13. How do aromatic and aliphatic primary amines react with nitrous acid ?

Ans. Aromatic primary amines react with HNO_2 at 273–278 K to form aromatic diazonium salts.



Aniline — Benzenediazonium chloride

Aliphatic primary amines also react with HNO_2 at 273–278 K to form aliphatic diazonium salts. However, these are unstable even at low temperature and therefore, decompose readily to form alcohols (generally predominate) and N_2 is evolved.

$$\underset{\text{Ethylamine}}{CH_3CH_2NH_2} + HNO_2 + HCl \xrightarrow{273-278\,K} \underset{\text{Unstable}}{CH_3CH_2\overset{+}{N}\equiv NCl^-} \xrightarrow{H_2O} \underset{\text{Ethanol}}{CH_3CH_2OH} + N_2 + HCl$$

Q.14. Give plausible explanation for each of the following :

(*i*) Why are amines less acidic than alcohols of comparable molecular masses ?

(*ii*) Why are primary amines higher boiling than tertiary amines ?

(*iii*) Why are aliphatic amines stronger bases than aromatic amines ?

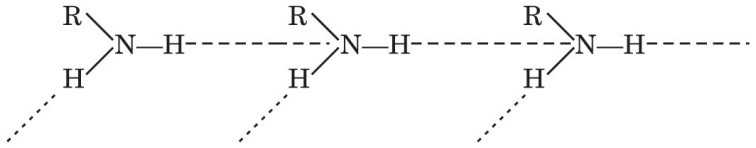
Ans. (*i*) Loss of proton from amines give amide ion whereas loss of a proton from alcohol gives an alkoxide ion.

$$\underset{\text{Amine}}{RNH_2} \longrightarrow \underset{\text{Amide ion}}{RNH^-} + H^+$$

$$\underset{\text{Alcohol}}{ROH} \longrightarrow \underset{\text{Alkoxide ion}}{RO^-} + H^+$$

Since O is more electronegative than N, therefore, RO^- can accommodate the –ve charge more easily than RNH^-. Consequently, RO^- is more stable than RNH^-. Thus, alcohols are more acidic than amines.

(*ii*) Primary amines (RNH_2) have two hydrogen atoms on the N atom and therefore, form intermolecular hydrogen bonding.



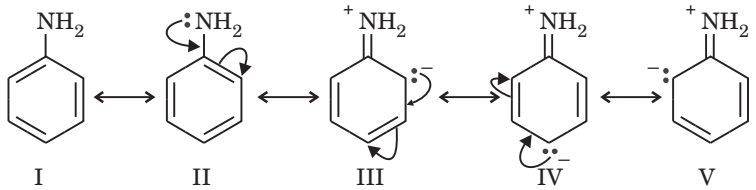
Tertiary amines (R_3N) donot have hydrogen atoms on the N atom and therefore, these donot form hydrogen bonds. As a result of hydrogen bonding in primary amines, they have higher boiling points than tertiary amines of comparable molecular mass. For example, b.p. of n-butylamine is 351 K while that of tert-butylamine is 319 K.

(*iii*) Both arylamines and alkylamines are basic in nature due to the presence of lone pair on N-atom. But arylamines are less basic than alkylamines. For example, aniline is less basic than ethylamine as shown by K_b values :

Ethylamine : $K_b = 4.7 \times 10^{-4}$

Aniline : $K_b = 4.2 \times 10^{-10}$

The less basic character of aniline can be explained on the basis of aromatic ring present in aniline. Aniline can have the following resonating structures :



I II III IV V

It is clear from the above resonating structures that three of these (III, IV and V) acquire some positive charge on N atom. As a result, the pair of electrons become less available for protonation. Hence, aniline is less basic than ethyl amine in which there is no such resonance.

NCERT Exemplar Problems

Subjective Questions

Note: *Objective Questions from Exemplar Problems are given in Competition File, page 107*

Short Answer Type Questions

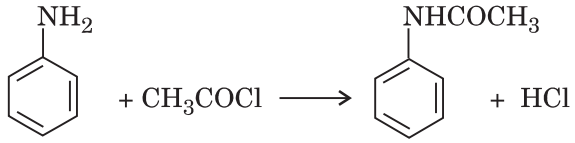
Q.1. What is the role of HNO_3 in the nitrating mixture used for nitration of benzene?

Ans. HNO_3 acts as a base in the nitrating mixture ($HNO_3 + H_2SO_4$) and provides the electrophile.

$$HNO_3 + H_2SO_4 \longrightarrow \underset{\text{Electrophile}}{NO_2^+} + HSO_4^- + H_2O$$

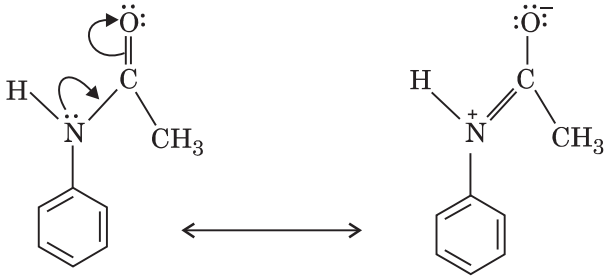
Q.2. Why is NH_2 group of aniline acetylated before carrying out nitration?

Ans. Aniline is very reactive. The direct nitration of aniline is unsatisfactory because of the susceptibility of the ring towards oxidation with nitric acid. However, to carry out nitration, the activation of benzene ring is reduced by first acetylating aniline with acetyl chloride.



Acetanilide

Explanation of reduced reactivity of NH_2 group in acetanilide. In acetanilide the oxygen of the group withdraws electrons from NH_2 group as shown below:



As a result, the electron pair on nitrogen gets displaced to the carboxyl group. Therefore, the unshared pair of electrons on nitrogen is less available for donation to the aromatic ring. Consequently, the electron density at ortho and para positions in the benzene ring gets reduced which in turn results in reduced reactivity towards electrophilic substitution of benzene.

Q.3. What is the product when $C_6H_5CH_2NH_2$ reacts with HNO_2?

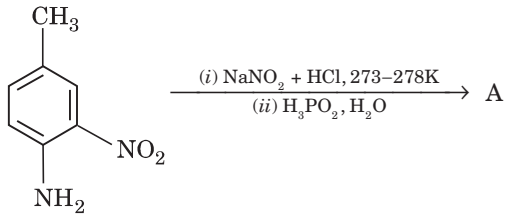
Ans. $C_6H_5CH_2NH_2 + HONO \longrightarrow C_6H_5CH_2OH + N_2 + H_2O$

Q.4. What is the best reagent to convert nitrile to primary amine?

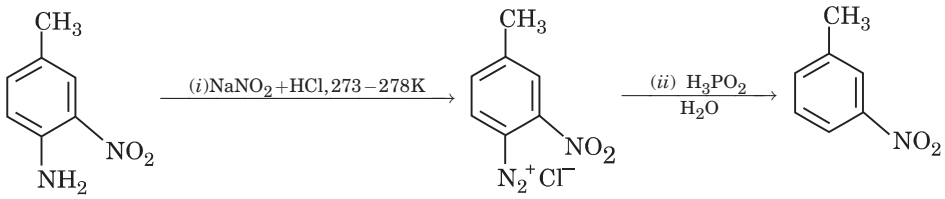
Ans. Reduction of nitriles with Na/alcohol or $LiAlH_4$ gives primary amine.

$$RCN + 4\,[H] \xrightarrow[LiAlH_4]{\text{Na/alcohol}} RCH_2NH_2$$

Q.5. Give the structure of 'A' in the following reaction.



Ans.



Q.6. What is Hinsberg reagent?

Ans. Benzene sulphonylchloride $C_6H_5SO_2Cl$.

Q.7. Why is benzene diazonium chloride not stored and is used immediately after its preparation?

Ans. Benzene diazonium chloride is very unstable and therefore, it is not stored.

Q.8. Why does acetylation of $—NH_2$ group of aniline reduce its activating effect?

Ans. Refer Q. No. 2.

Q.9. Explain why $MeNH_2$ is stronger base than MeOH?

Ans. Nitrogen is less electronegative than oxygen. Therefore, lone pair of electrons on nitrogen is readily available for donation. Hence, $MeNH_2$ is more basic than MeOH.

Q.10. What is the role of pyridine in the acylation reaction of amines?

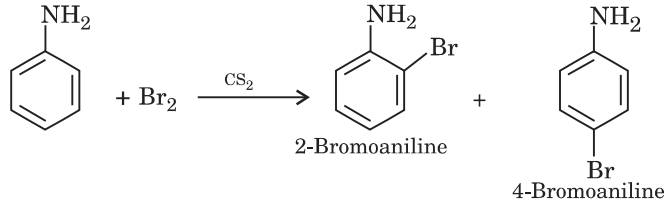
Ans. Pyridine and other bases are used to remove the side product(HCl) from the reaction mixture.

Q.11. Under what reaction conditions (acidic/basic), the coupling reaction of aryldiazonium chloride with aniline is carried out?

Ans. Coupling reaction is carried out in mild basic conditions.

Q.12. Predict the product of reaction of aniline with bromine in non-polar solvent such as CS_2.

Ans.



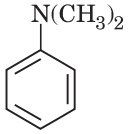
Q.13. Arrange the following compounds in increasing order of dipole moment.
$CH_3CH_2CH_3$, $CH_3CH_2NH_2$, CH_3CH_2OH.

Ans. $CH_3CH_2CH_3 < CH_3CH_2NH_2 < CH_3CH_2OH$.

Q.14. What is the structure and IUPAC name of the compound, allyl amine?

Ans. $CH_2 = CH–CH_2NH_2$: Prop-2-en-1-amine.

Q.15. Write down the IUPAC name of

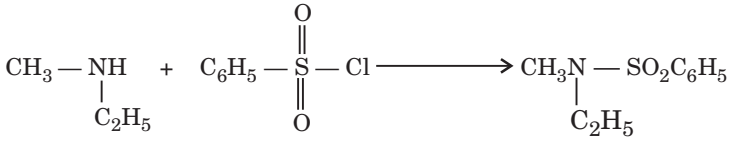


Ans. N,N–Dimethylbenzenamine.

Q.16. A compound Z with molecular formula C_3H_9N reacts with $C_6H_5SO_2Cl$ to give a solid, insoluble in alkali. Identify Z.

Ans. Z is an aliphatic amine which gives a solid insoluble in base. This means that reaction with $C_6H_5SO_2Cl$ must give a product without any replaceable hydrogen attached to nitrogen. Therefore, the amine must be a secondary amine. Hence, Z is ethylmethylamine.

Hence,



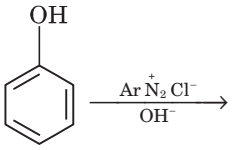
N-Ethyl-N-methyl
benzene sulphonamide

Q.17. A primary amine, RNH_2 can be reacted with $CH_3—X$ to get secondary amine, $R—NHCH_3$ but the only disadvantage is that 3° amine and quaternary ammonium salts are also obtained as side products. Can you suggest a method where RNH_2 forms only 2° amine?

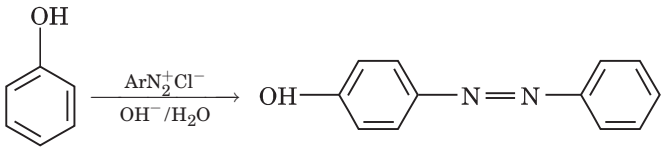
Ans. $\underset{1°}{RNH_2} \xrightarrow{KOH/CHCl_3} RNC \xrightarrow{H_2/Pd} \underset{2°}{RNHCH_3}$

Carbylamine reaction is shown by 1° amines only which results in the replacement of two hydrogen atoms attached to nitrogen atom of NH_2 group by one carbon atom. On catalytic reduction, the isocyanide forms a secondary amine with one methyl group.

Q.18. Complete the following reaction.



Ans.



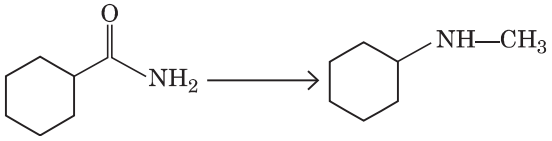
Q.19. Why is aniline soluble in aqueous HCl?

Ans. Aniline forms the salt anilinium chloride with HCl which is water soluble.

(A) Aniline (Colourless liquid,sparingly soluble in water)

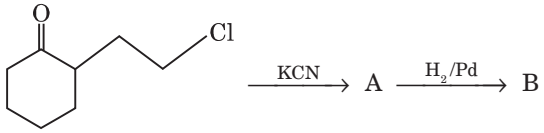
(B) Anilinium chloride (Water soluble salt)

Q.20. Suggest a route by which the following conversion can be accomplished.

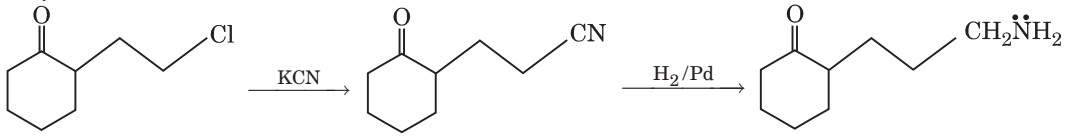


Ans.

Q.21. Identify A and B in the following reaction.



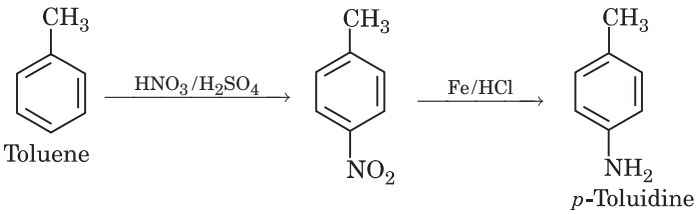
Ans.



Q.22. How will you carry out the following conversions?

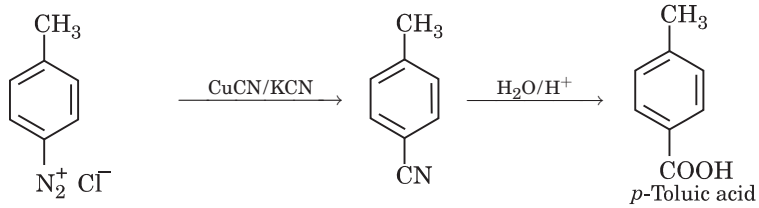
(*i*) toluene ⟶ *p*-toluidine (*ii*) *p*-toluidine diazonium chloride ⟶ *p*-toluic acid

Ans. (*i*)



Toluene — *p*-Toluidine

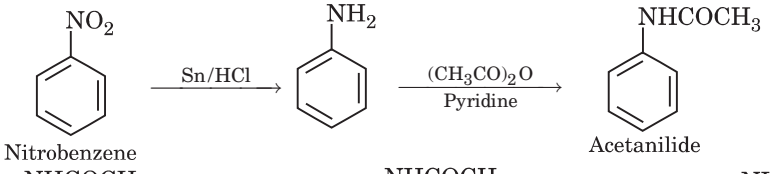
(*ii*)



p-Toluidine diazonium chloride — *p*-Toluic acid

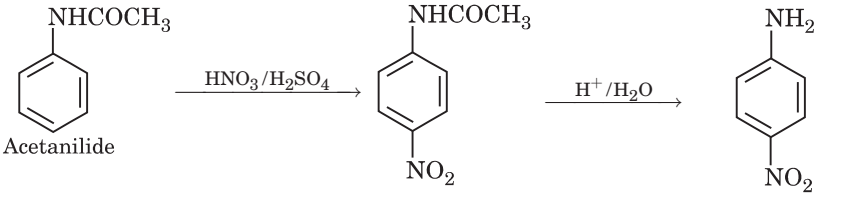
Q.23. Write following conversions:
(*i*) nitrobenzene ⟶ acetanilide
(*ii*) acetanilide ⟶ *p*-nitroaniline

Ans. (*i*)



Nitrobenzene Acetanilide

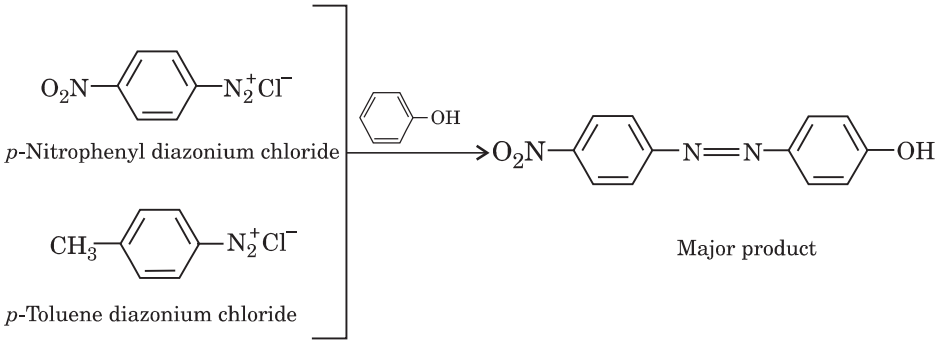
(*ii*)



Acetanilide p-Nitro aniline

Q.24. A solution contains 1 g mol. each of *p*-toluene diazonium chloride and *p*-nitrophenyl diazonium chloride. To this 1 g mol. of alkaline solution of phenol is added. Predict the major product. Explain your answer.

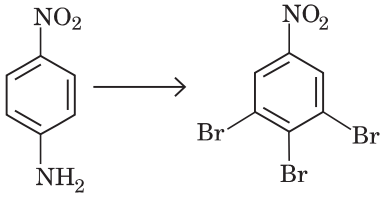
Ans. This reaction is an example of electrophilic aromatic substitution. In alkaline medium, phenol forms phenoxide ion which is more electron rich than phenol and hence more reactive for electrophilic attack. The electrophile in this reaction is aryldiazonium cation. *p*-Nitrophenyldiazonium cation is a stronger electrophile than *p*-toluene diazonium cation. Therefore, it couples preferentially with phenol.



p-Nitrophenyl diazonium chloride

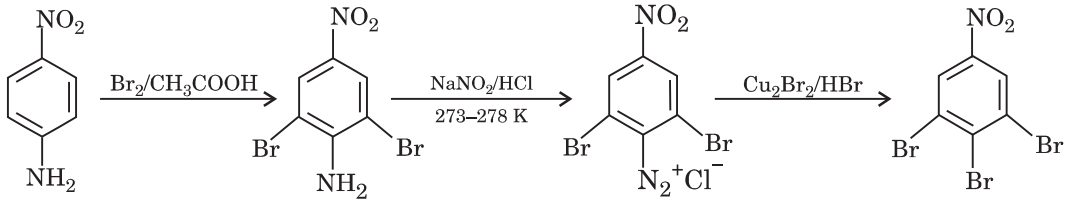
p-Toluene diazonium chloride Major product

Q.25. How will you bring out the following conversion?

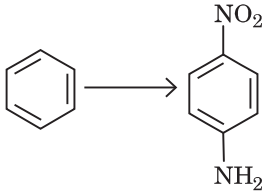


p-Nitroaniline 3, 4, 5-Tribromonitrobenzene

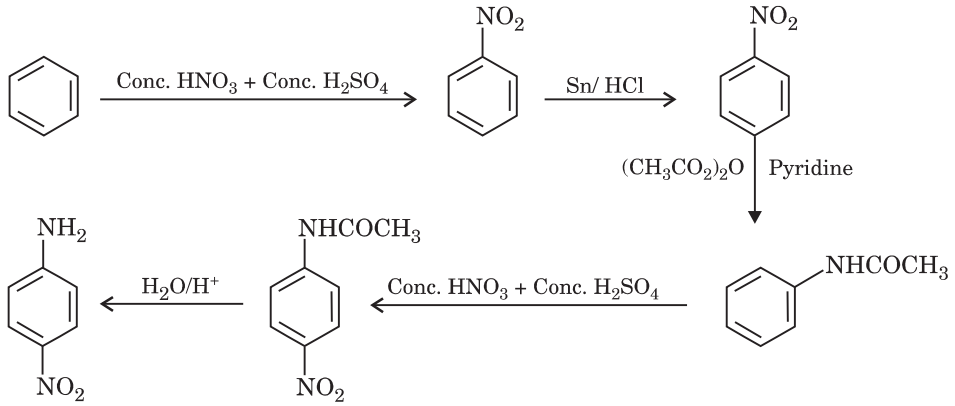
Ans.



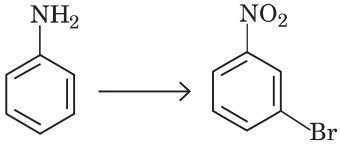
Q.26. How will you carry out the following conversion?



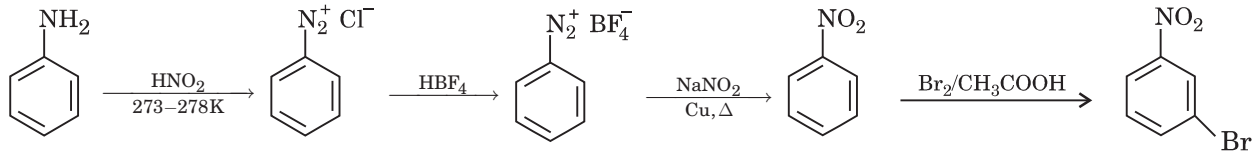
Ans.



Q.27. How will you carry out the following conversion?

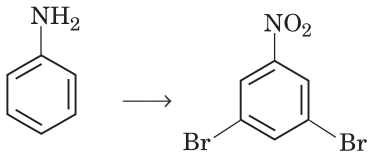


Ans.

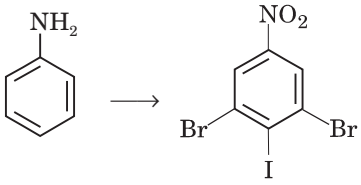


Q.28. How will you carry out the following conversions?

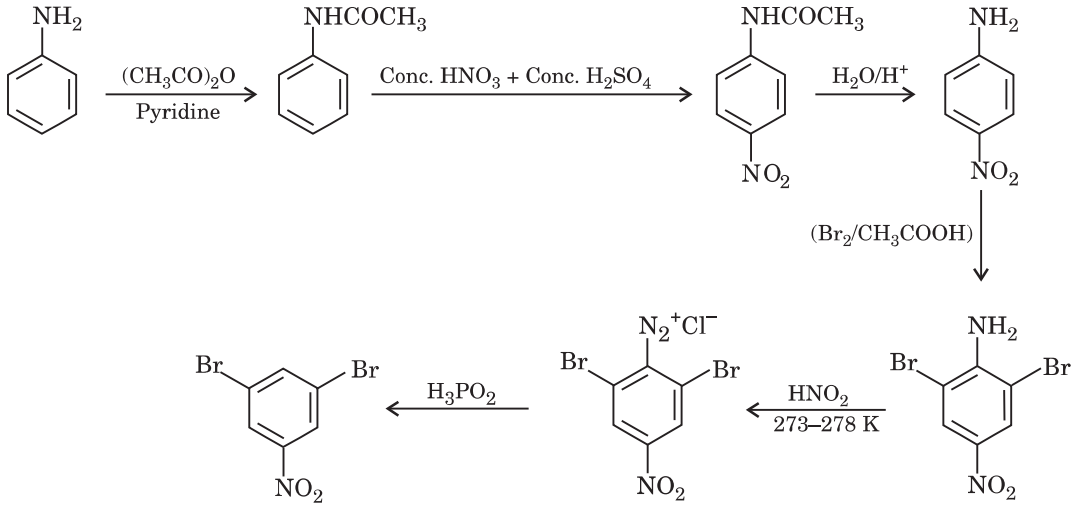
(*i*)



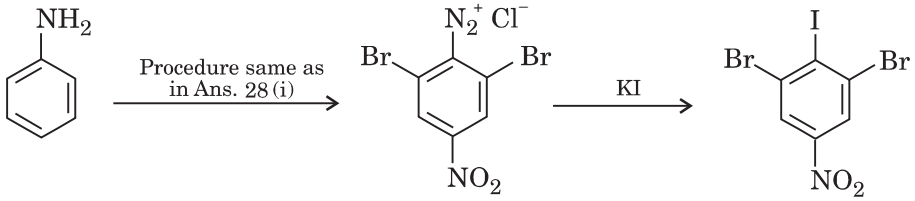
(*ii*)



Ans. (*i*)



(*ii*)



QUICK MEMORY TEST

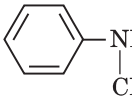
A. Say True or False

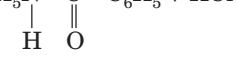
1. Amines act as Lewis bases.
2. In aqueous solution, trimethylamine is more basic than methylamine.
3. *p*-Bromoaniline is formed when aniline is treated with bromine water.
4. Azo dye test can be used to distinguish aromatic primary amines from aliphatic primary amines.
5. Catalytic reduction of carbylamines always gives primary amines.
6. N-Methylbenzamide on heating with aqueous solution of NaOH and Br_2 gives N-methylaniline.
7. Secondary amines evolve N_2 with nitrous acid.
8. Acetanilide is less basic than aniline.
9. Gabriel phthalimide synthesis is used for the preparation of aromatic primary amines.
10. Tertiary amines dissolve in nitrous acid to form corresponding salts.

B. Complete the missing links

1. Aniline on heating with fuming H_2SO_4 gives ..... .
2. The IUPAC name of lowest molecular mass tertiary amine is ..... .
3. In Schotten-Baumann reaction, aniline is heated with ..... .
4. Carbylamine test is used to test ..... amines.
5. Libermann nitroso reaction is used for the detection of ..... amines.
6. Hinsberg reagent is ..... .
7. Phenyl isocyanide on reduction with hydrogen and Raney nickel gives ..... .
8. Secondary amines react with aldehydes and ketones containing α-hydrogen to form ..... .
9. Reaction of acetamide with NaOH and Br_2 gives .....
10. In Hoffmann bromamide reaction, the carbonyl group is lost as ..... .

11. $CH_3CH_2CONH_2 + 4H \xrightarrow[\text{ether}]{LiAlH_4}$ ..... + ...

12.  + $H_2SO_4 \longrightarrow$ ..... .

13. $C_2H_5NH_2$ + ... $\xrightarrow{\text{aq. NaOH}}$  + HCl .

14. $R_2NH + Cl-\underset{\underset{O}{\|}}{C}-Cl \longrightarrow$ ..... + ...

15.  $-N_2Cl + CH_3CH_2OH \longrightarrow$ ..... + ... + ... + ...

C. Choose the correct alternative

1. Isocyanide test is used for the detection of *primary/secondary* amines.
2. Amino group is *ortho-para/meta* director.
3. *Primary/tertiary* amines donot react with Hinsberg's reagent.
4. Out of aniline and benzylamine, *aniline/benzylamine* gives azo dye test.
5. On treating benzene diazonium chloride with hypophosphorous acid, the product is *phenol/benzene*.
6. pK_b of aniline is *less/more* than *p*-$C_6H_4(NH_2)NH_2$.
7. K_b of *p*-methylaniline is *more/less* than aniline.
8. Aniline is *less/more* basic than ethylamine.
9. Electron withdrawing group on aniline makes it *less/more* basic.
10. Gabriel phthalimide synthesis is used for the preparation of *primary aromatic/primary aliphatic* amines.

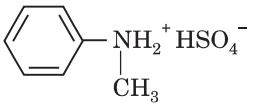
Answers QUICK MEMOR TEST

A. Say True or False

1. True 2. False
3. **False :** 2, 4, 6-Tribromoaniline is formed.
4. True
5. **False :** Give secondary amines.
6. **False :** Secondary amides donot undergo Hoffmann bromamide reaction.
7. False 8. True 9. False 10. True

B. Complete the missing links

1. Sulphanilic acid
2. N, N-Dimethylmethanamine
3. benzoyl chloride
4. primary
5. secondary
6. benzene sulphonyl chloride
7. N-methylaniline
8. enamines
9. methylamine
10. carbonate ion

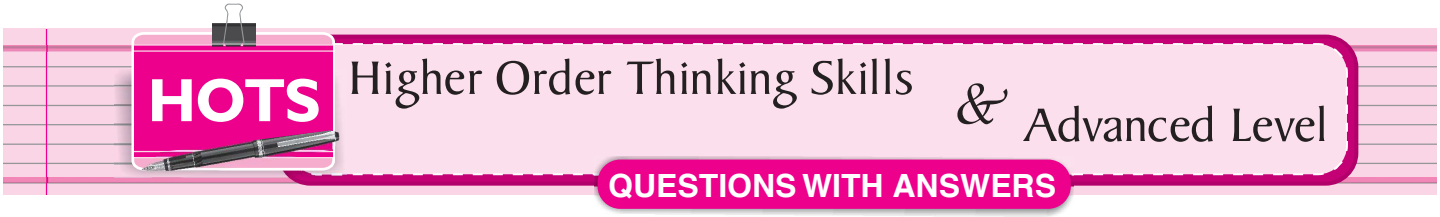
11. $CH_3CH_2CH_2NH_2 + H_2O$ **12** 

13. C_6H_5COCl **14.** $R_2N-\underset{\underset{O}{\|}}{C}-NR_2 + 2HCl$

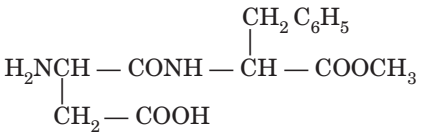
15.  $+ CH_3CHO + N_2 + HCl$

C. Choose the correct alternative

1. primary	**2.** ortho-para	**3.** tertiary
4. aniline	**5.** benzene	**6.** more
7. more	**8.** less	**9.** less
10. primary aliphatic		



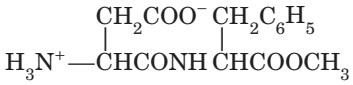
Q.1. Aspartame, an artificial sweetener, is a peptide and has the following structure :

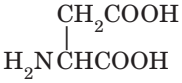
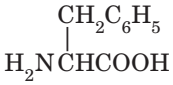


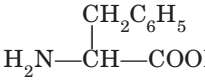
(*i*) Identify the four functional groups.
(*ii*) Write the zwitter ionic structure.
(*iii*) Write the structures of the amino acids obtained from the hydrolysis of aspartame.
(*iv*) Which of the two amino acids is more hydrophobic ? ***(I.I.T. 2001)***

Ans. (*i*) The four functional groups are :

(*a*) $-NH_2$ (amino group) (*b*) —CONH (peptide or amide group)
(*c*) —COOH (carboxylic group) (*d*) $COOCH_3$ (ester group)

(*ii*) 

(*iii*)  and 

(*iv*)  will be more hydrophobic due to bulky alkyl groups.

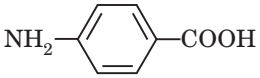
Q.2. *tert*-Butylamine cannot be prepared by action of ammonia on *tert*-butyl bromide. Why ? Explain.

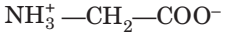
Ans. *tert*-Butylamine is a 3° alkyl halide. On treatment with a base like NH_3, it prefers to undergo elimination reaction rather than substitution. Therefore, the product is isobutylene instead of *tert*-butylamine.

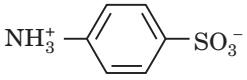
Isobutylene (elimination) *tert*-Butylbromide *tert*-Butylamine

Q.3. Explain : 2-aminoethanoic acid exists as a dipolar ion as does *p*-amino sulphonic acid but *p*-amino benzoic acid does not.

Ans. The aliphatic $-NH_2$ group is sufficiently basic to accept an H^+ from COOH group. The COOH group is not strong enough to donate H^+ to the weakly basic $ArNH_2$ but SO_3H group sufficiently strong enough to donate H^+ to weakly basic $ArNH_2$.

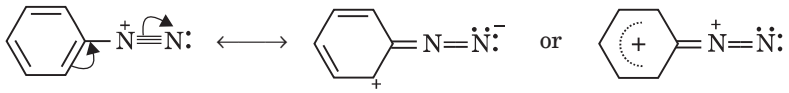

p-amino benzoic acid


p-amino ethanoic aicd


p-amino sulphonic acid

Q.4. Why are aryldiazonium ion more stable than alkyldiazonium ion ?

Ans. The stability of aryldiazonium ion is due to resonance by electron release from *o*- and *p*-positions of the ring.



This type of resonance stability is not possible in alkyldiazonium ion.

Q.5. *p*-methoxyaniline is a stronger base than aniline but *p*-nitroaniline is a weaker base than aniline. Explain.

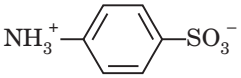
Ans. Methoxy group ($-OCH_3$) is electron releasing group and increases the electron density on N atom. Therefore, it has greater electron donating tendency than aniline and thus is a stronger base than aniline. On the other hand, nitro group is electron withdrawing group and therefore, decreases the electron density on nitrogen atom. As a result, *p*-nitroaniline is a weaker base than aniline.

Q.6. Can we prepare aniline by Gabriel phthalimide reaction ?

Ans. Aniline cannot be prepared by Gabriel phthalimide reaction because it requires the treatment of potassium phthalimide with C_6H_5Cl or C_6H_5Br. Since aryl halides donot undergo nucleophlic substitution reactions under ordinary conditions, therefore, the reaction does not occur. Hence, aniline cannot be prepared by this method.

Q.7. Sulphanilic acid is insoluble in water and organic solvents. Explain.

Ans. Sulphanilic acid is ionic in nature and therefore, it is insoluble in organic solvents. Its insolubility in water is typical of dipolar salts. Not all such salts dissolve in water.



Q.8. Why is an amide more acidic than amine ?

Ans. The amide has the following resonating structures :

Due to the delocalisation of lone pair of electrons on N over C=O group, amino group acquires a positive charge which makes N—H bond weak. Moreover, the anion formed after removal of a proton is also stabilized by resonance as :

However, no such stabilization is possible in amines.

Q.9. Which is more basic $PhNH_2$ or Ph_2NH ?

Ans. Aromatic amines are less basic than alkylamines because the electron density of the lone pair of electrons is delocalized into the ring, mainly at ortho and para positions. Increase in number of phenyl groups bonded to N increases delocalization and hence decreases basicity. Therefore, $PhNH_2$ isomer is more basic than Ph_2NH.

Q.10. An optically inactive compound (A) having molecular formula $C_4H_{11}N$ on treatment with HNO_2 gave an alcohol (B). (B) on heating at 440 K gave an alkene (C). (C) on treatment with HBr gave an optically active compound (D)having the molecular formula C_4H_9Br. Identify A, B, C and D and write down their structural formulae. Also write equations involved.

Ans. Since compound (A) is optically inactive and contains nitrogen which gives alcohol with HNO_2, it is primary amine. The reactions may be given as :

$$\underset{\substack{\text{(A)}\\\text{1-Aminobutane}}}{CH_3CH_2CH_2CH_2NH_2} \xrightarrow{HNO_2} \underset{\substack{\text{B)}\\\text{Butan-1-ol}}}{CH_3CH_2CH_2CH_2OH} + N_2 + H_2O$$

$$\underset{\text{(B)}}{CH_3CH_2CH_2CH_2OH} \xrightarrow[-H_2O]{H_2SO_4,\ 440\ K} \underset{\substack{\text{(C)}\\\text{But-1-ene}}}{CH_3CH_2CH=CH_2}$$

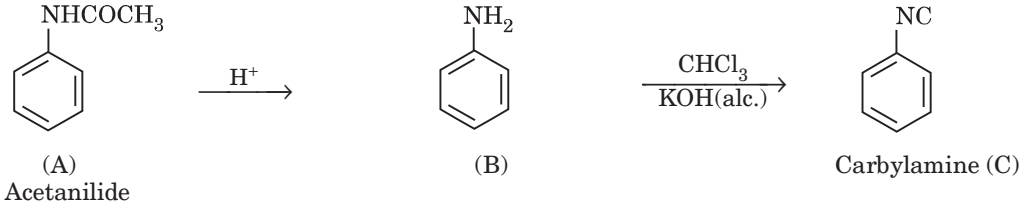
$$\underset{\text{(C)}}{CH_3CH_2CH=CH_2} \xrightarrow{HBr} \underset{\substack{\text{(D)}\\\text{2-Bromobutane (optically active)}}}{CH_3CH_2\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3}$$

Q.11. A colourless substance (A) is sparingly soluble in water and gives (B) on heating with mineral acids. Compound (B) on reaction with $CHCl_3$ and alcoholic potash produces an obnoxious smell of carbylamine due to the formation of (C). Compound (A) on reaction with chlorosulphonic acid gives (D) which on treatment with ammonia gives (E). Compound (E) on hydrolysis gives sulphanilamide; a well known drug. Give structures of (A) to (E) with proper reasoning.

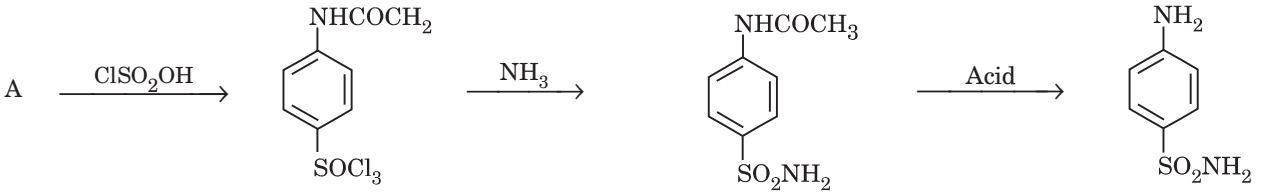
Ans. The reaction of B with chloroform and alcoholic KOH gives carbylamine. This indicates that B is a primary aromatic amine. Since sulphanilamide is the final product, it means that B is aniline.

Now, B is formed by the acidic hydrolysis of A, which is colourless and sparingly soluble in water, therefore, A is acetanilide.

The reactions may be explained as :



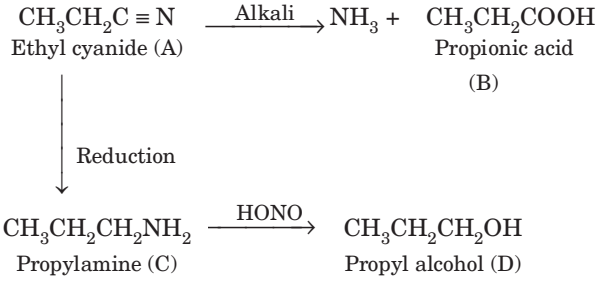
(A) Acetanilide (B) Carbylamine (C)



(D) (E) Sulphanilamide

Q.12. An organic compound A (C_3H_5N) on boiling with alkali gives ammonia and sodium salt of an acid B ($C_3H_6O_2$). A on reduction gives C(C_3H_9N) which with nitrous acid gives D (C_3H_8O). Give the structural formulae of A, B, C and D.

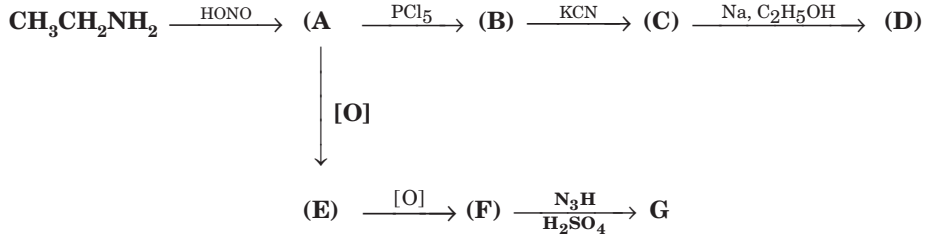
Ans. The chemical reactions are :



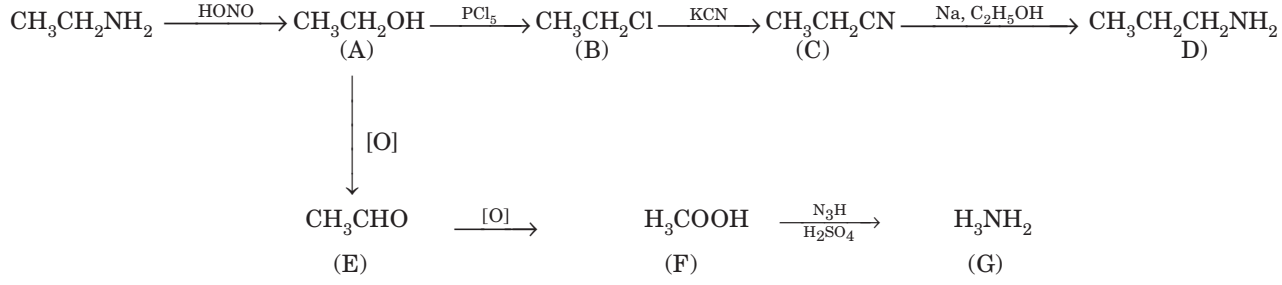
Ethyl cyanide (A) Propionic acid (B)

Propylamine (C) Propyl alcohol (D)

Q.13 Identify (A) to (G) in the following reaction scheme :



Ans.



Q.14. $C_5H_{13}N_2 \xrightarrow[-N_2]{aq.\ NaNO_2,HCl}$ **Y + Some other product**

(X) Tertiary alcohol

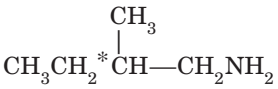
Optically active

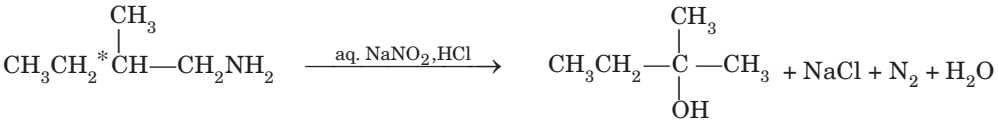
(*a*) Identify (X) and (Y)

(*b*) Is (Y) optically active ?

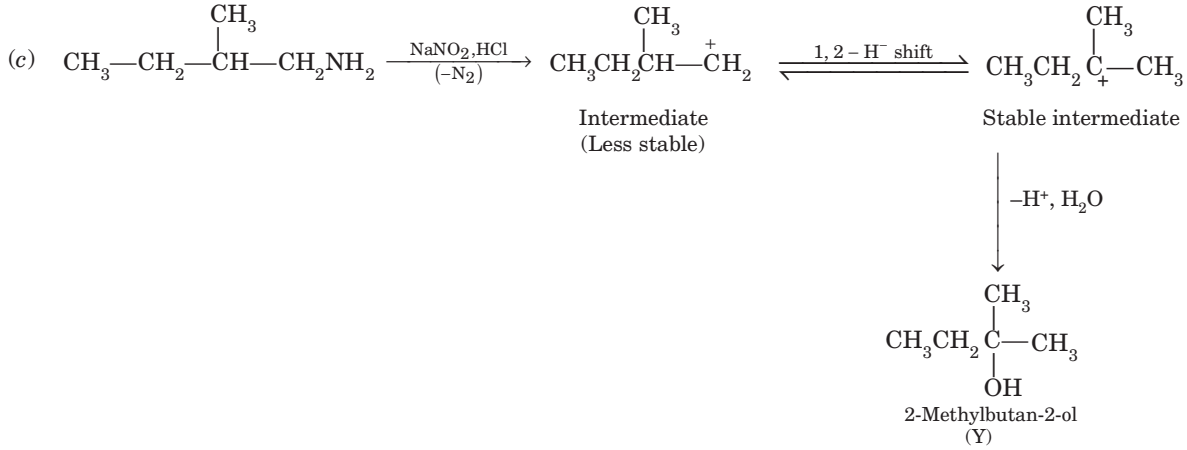
(c) Give structures of intermediates (if any) in the formation of (X) to (Y)

Ans. (*a*) Since compound (X) on treatment with $NaNO_2$/HCl evolves N_2 gas, it must be a primary amine. Further, since it is optically active, it must contain a chiral carbon. The $-NH_2$ cannot be directly attached to a chiral carbon because such amines readily undergo, racemization due to nitrogen inversion. Therefore, the structure of (X) is :



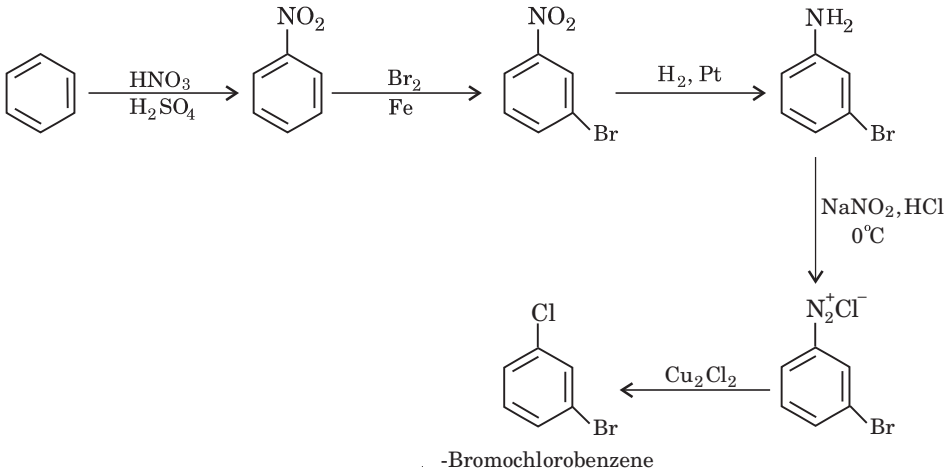


(*b*) No, Y is not optically active.

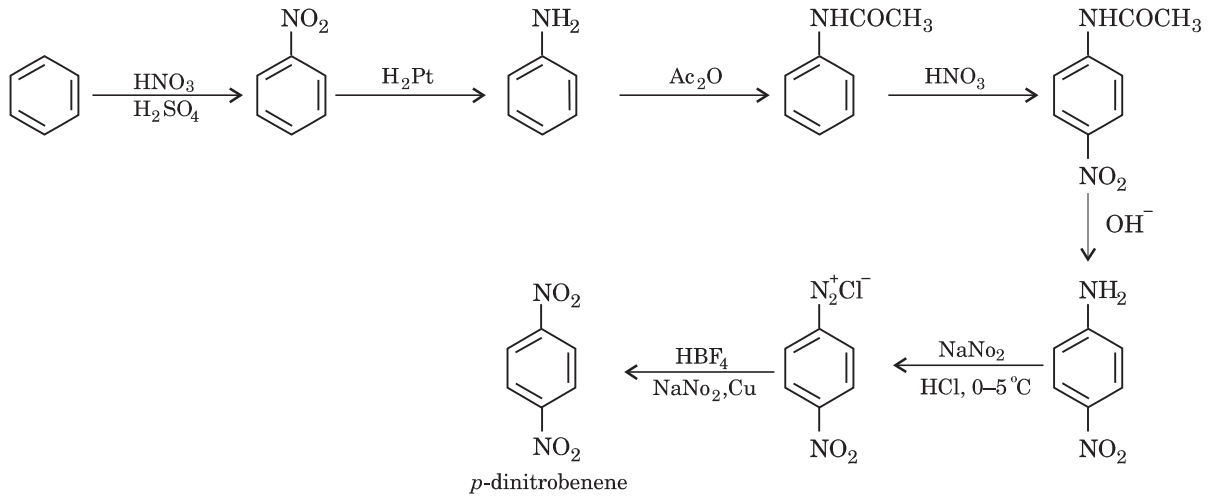


Q.15. Starting with benzene and using suitable reagents, outline the synthesis of
(*i*) *m*-bromochlorobenzene (*ii*) *p*-dinitrobenzene (*iii*) *m*-bromoiodobenzene

Ans. (*i*)

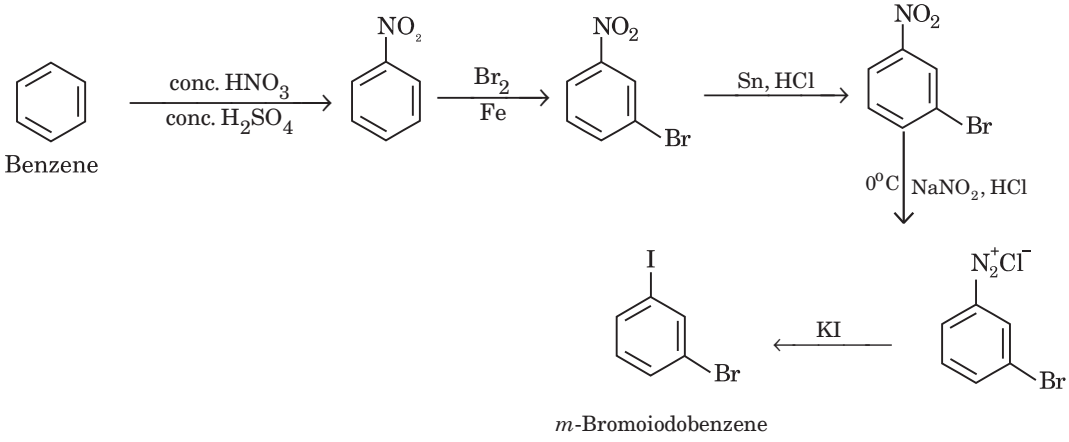


(*ii*)



p-dinitrobenene

(*iii*)

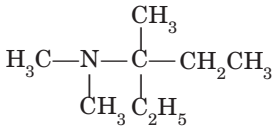


m-Bromoiodobenzene

Revision Exercises

Very Short Answer Questions *carrying 1 mark*

1. Write the IUPAC name of the following :



2. Write the structural formulae of all the amines with molecular formula C_2H_7N.

3. What is the name of the reaction when benzene diazonium chloride is treated with cuprous chloride ?

4. How is iodobenzene obtained from benzene diazonium chloride? (*Meghalaya S.B. 2016*)

5. Write a chemical reaction to prepare an azo dye from benzene diazonium chloride. (*Uttarakhand S.B. 2013*)

6. Complete the reaction :

$ArN_2Cl + H_3PO_2 + H_2O \longrightarrow$

7. What happens when aniline is treated with Br_2 water ? (*Meghalaya S.B. 2016*)

8. Write the reaction of aniline with conc. H_2SO_4. (*Jammu S.B. 2016*)

9. pK_b of aniline is more than that of methylamine. Why? (*Assam S.B. 2013*)

10. How will you convert aniline to phenylisocyanide? (*Assam S.B. 2013*)

11. Arrange the following in the increasing order of basicity: aniline, *p*-nitroaniline, *p*-toluidine. (*Hr. S.B. 2013*)

12. What is carbylamine test for 1° amines? (*Hr. S.B. 2017*)

13. Arrange the following in the increasing order of their basic strength in aqueous solutions :

CH_3NH_2, $(CH_3)_3N$, $(CH_3)_2NH$ (*D.S.B. 2013*)

14. The strongest base among the following compounds is

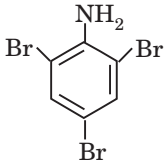
NH_3, H_3CNH_2, $(H_3C)_2$ NH, $H_5C_6NH_2$ (*Manipur S.B 2014*)

15. Complete the reaction :

$CH_3–CH_2C \equiv N \xrightarrow{Na(Hg)/C_2H_5OH} ?$ (*Meghalaya S.B. 2015*)

16. What happens when benzene diazonium chloride solution is added slowly to boiling dil. mineral acid?
(*Meghalaya S.B. 2015*)

17. Write the IUPAC name of



(*D.S.B. 2016*)

18. How is benzamide converted into benzylamine?
(*Pb. S.B. 2018*)

19. Write down diazotisation reaction. (*Pb. S.B. 2017*)

20. Complete the following reaction:

$$Ar\text{–}NH_2 \xrightarrow[0\text{–}5^\circ C]{NaNO_2, HCl} A \xrightarrow{CuCN} B$$

(*Mizoram. S.B. 2018*)

21. Write down Hinsberg's test for primary amines.
(*Pb. S.B. 2017*)

22. Write IUPAC name of the following compound:
$CH_3NHCH(CH_3)_2$ (*D.S.B. 2017*)

23. Write IUPAC name of the following compound:
$(CH_3CH_2)_2NCH_3$ (*D.S.B. 2017, Hr. S.B. 2018*)

24. Write in the increasing order of basicity of the following:
$C_2H_5NH_2$, $C_6H_5NH_2$, $(C_2H_5)_2NH$ and $C_6H_5CH_2NH_2$
(*Hr.S.B. 2018*)

CBSE QUESTIONS

25. Why do amines react as nucleophiles?
(*A.I.S.B. 2006, C.B.S.E. Sample paper 2011*)

26. Arrange the following compounds in the increasing order of their solubility in water :
$C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_2H_5NH_2$
(*A.I.S.B. 2011, D.S.B. 2014*)

27. Give a chemical test to distinguish between ethylamine and aniline. (*A.I.S.B. 2011*)

28. Arrange the following in an increasing order of their basic strength :
$C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_6H_5)_2NH$ and CH_3NH_2
(*A.I.S.B. 2011, Hr. S.B. 2013*)

29. Write the structure of *n*-methylethanamine.
(*A.I.S.B. 2013*)

30. The conversion of primary aromatic amines into diazonium salts is known as ..... *A.I.S.B. 2014*)

31. Write the IUPAC name of the compound:

$$CH_3\text{—}NH\text{—}CH_2\text{—}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{—}CH_3$$

(*A.I.S.B. 2016*)

MCQs. from State Boards' Examinations

32. When a primary amine reacts with chloroform in ethanolic KOH, then the product is
(*a*) isocyanide (*b*) aldehyde
(*c*) cyanide (*d*) alcohol
(*Jharkhand S.B. 2013*)

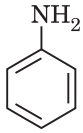
33. Which of the following does not react with Hinsberg reagent?
(*a*) $C_2H_5NH_2$ (*b*) $(C_2H_5)_2NH$
(*c*) $(C_2H_5)_3N$ (*d*) CH_3NH_2
(*Hr. S.B. 2013*)

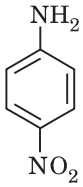
34. $C_6H_5N_2Cl + CuCN \longrightarrow C_6H_5CN + N_2 + CuCl$ is
(*a*) Balz-Schiemann (*b*) Gattermann reaction
(*c*) Simonini reaction (*d*) Sandmeyer reaction
(*Hr. S.B. 2013*)

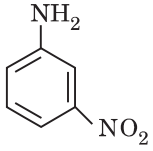
35. Which of the following is most basic?
(*a*) Benzylamine (*b*) Aniline
(*c*) Acetanilide (*d*) *p*-nitroaniline
(*Hr. S.B. 2013, 2016*)

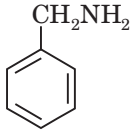
36. Among the following which one is strongest base?
(*a*) Ammonia (*b*) Methylamine
(*c*) Ethylamine (*d*) None of these
(*Uttarakhand S.B. 2013*)

37. Which of the following compound is the most basic?

(*a*) 

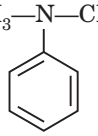
(*b*) 

(*c*) 

(*d*) 

(*West Bengal S.B. 2018*)

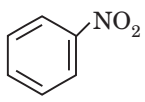
38. The IUPAC name of $CH_3\text{—}N\text{—}CH_2CH_3$ is

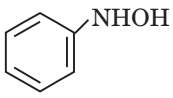


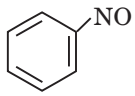
(*a*) N-Ethyl- N-methylbenzenamine
(*b*) N-Methyl- N-ethylbenzenamine
(*c*) N, N-Ethyl methyl benzenamine
(*d*) N, N-Methyl ethyl benzenamine
(*Mizoram S.B. 2014*)

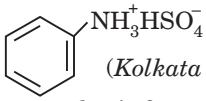
39. Gabriel phthalimide reaction is used for the preparation of
(*a*) 1° amine (*b*) 2° amine
(*c*) 3° amine (*d*) all of these
(*Uttarakhand S.B. 2015*)

40. Which of the following compound will be formed when aniline reacts with H_2SO_4?

(*a*) 

(*b*) 

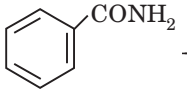
(*c*) 

(*d*) 

(*Kolkata S.B. 2016*)

41. Which one of the following is most basic ?
(*a*) $C_2H_5NH_2$ (*b*) NH_3
(*c*) $CH_3CH_2NH_2$ (*d*) CH_3NH_2
(*H.P.S.B. 2016*)

42. $C_2H_5NH_2 + HNO_2 \rightarrow A$, A is :
(*a*) C_2H_5OH (*b*) C_2H_5NHOH
(*c*) C_2H_6 (*d*) $C_2H_5NO_2$(*Hr.S.B. 2016*)

43.  $\xrightarrow[\Delta]{H_3O^+}$ P, P is :

(*a*) Benzoic acid (*b*) Aniline
(*c*) Benzonitrile (*d*) Benzylamine (*Hr. S.B. 2016*)

44. $CH_3C \equiv N \xrightarrow{N_2/Ni}$ P, P will be?

a) CH_3CH_2NC (*b*) $CH_3CH_2NH_2$
(*c*) CH_3NHCH_3 (*d*) CH_3NH_2
(*Hr.S.B. 2018*)

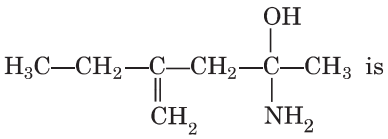
45. Which of the following compound gives dye test?

(*a*) Aniline (*b*) Methylamine
(*c*) Diphenylamine (*d*) Ethylamine
(*Meghalaya S.B. 2018*)

46. Gabriel phthalimide reaction is used for the preparation of

a) primary aromatic amines
b) secondary amines
(*c*) aliphatic primary amines
(*d*) tertiary amines
(*Meghalaya S.B. 2018*)

47 The IUPAC name of the compound



(*a*) 2- mino- 4- ethyl -2 - hydroxypent - 4 - ene
b) 2-Amino - 4 - ethylpent - 4 - en - 2 - ol
(*c*) 4-Ethyl - 2 - hydroxypent - 4 -en - 2 - amine
d) 2-Amino - 4 - methylhexan - 2 -ol
(*Mizoram S.B. 2018*)

Short Answer Questions *carrying 2 or 3 marks*

1. Explain the following :

(*i*) Tertiary amines do not undergo acylation.

(*ii*) CH_3NH_2 is stronger base than ammonia.

(*iii*) It is difficult to prepare pure amines by ammonolysis of alkyl halides.

2. An amine (A) C_3H_9N reacts with nitrous acid at 0 to 5°C to give an oily layer separated from reaction mixture. Write the structure of A and its reaction with

(*i*) acetyl chloride

(*ii*) methyl magnesium bromide.

3. (*a*) Why have primary amines higher boiling point than tertiary amines?

(*b*) How can you find out wheather a given amine is a primary amine? Write the chemical reaction involved in the test you perform.
(*H.P.S.B. 2008, Meghalaya S.B. 2016*)

4. In the following cases rearrange the compounds as directed:

(*i*) In an increasing order of basic strength :
$_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_2H_5)_2NH$ and CH_3NH_2

(*ii*) In a decreasing order of basic strength :
Aniline, *p*-nitroaniline and *p*-toluidine

(*iii*) In an increasing order of pK_b values :
$C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$
D.S.B. 2010)

5. Complete the following chemical equations :

(*i*) $C_6H_5N_2Cl + C_6H_5NH_2 \xrightarrow{OH^-}$

(*ii*) $C_6H_5N_2Cl + CH_3CH_2OH \longrightarrow$

(*iii*) $RNH_2 + CHCl_3 + KOH \longrightarrow$
(*D.S.B. 2010*)

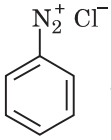
6. (*a*) Explain why an alkylamine is more basic than ammonia?

(*b*) How would you convert :

(*i*) Aniline to nitrobenzene

(*ii*) Aniline to iodobenzene (*D.S.B. 2011*)

7. (*a*) Complete the following reaction:

 $+ H_2O \xrightarrow{>278K}$?

(*b*) Explain ethylamine is more basic than ammonia.

(*c*) What is carbylamine reaction? (*H.P.S.B. 2018*)

8. (*a*) Write chemical test to distinguish between CH_3NH_2 and $(CH_3)_2NH$.

(*b*) Fill in the blanks :

(*i*) $CH_3CH_2I \xrightarrow{NaCN}$? $\xrightarrow[\text{hydrolysis}]{OH^-, \text{partial}}$?

(*ii*) $C_6H_5N_2Cl \xrightarrow{CuCN}$? $\xrightarrow[H^+]{H_2O}$? (*Hr. S.B. 2012*)

9. Write chemical equations for the following conversions :

(*i*) Nitrobenzene to benzoic acid.

ii) Benzyl chloride to 2-phenyl ethanamine

iii) Aniline to benzoic acid. (*D.S.B. 2012*)

10. What happens when

(*i*) Aniline reacts with Br_2 water.

(*ii*) Benzene diazonium chloride is reacted with HCl in the presence of copper.

(*iii*) Acetamide is reacted with $LiAlH_4$ in the presence of ether. (*Jharkhand S.B. 2013*)

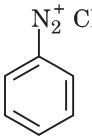
11. (*a*) Complete the following reactions :

(*i*) $C_2H_5NH_2 + CHCl_3 + KOH$ (alc.) $\xrightarrow{Warm}$

(*ii*) $C_6H_5N_2^+Cl^- \xrightarrow{Cu_2Cl_2, HCl}$

(*b*) Write coupling reaction. (*H.P. S.B. 2013*)

12. (*a*) Complete the following reaction:

 $\xrightarrow[HCl]{Cu_2Cl_2}$?

(*b*) Convert aniline into benzoic acid.

c) What is Balz-Schiemann reaction? (*H.P.S.B. 2018*)

13. How will you achieve the synthesis of only 4-bromoaniline from aniline without the production of the trisubstituted aniline. (*Meghalaya S.B. 2013*)

Or

a) Why have primary amines higher boiling points than tertiary amines?

(*b*) Write the products obtained in the nitration of aniline.

c) What is carbylamine reaction? (*Meghalaya S.B. 2013*)

14. (*a*) Identify A, B, C and D :

(*i*) $CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B$

(*ii*) $C_6H_5NO_2 \xrightarrow{Fe + HCl} C \xrightarrow[0°C]{NaNO_2, HCl} D$

b) Write one chemical test to distinguish between ethylamine and aniline. *(Assam S.B. 2013)*

15. Give the structures of A, B and C in the following reactions:

(*i*) $C_6H_5N_2^+Cl^- \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow[\Delta]{NH_3} C$

(*ii*) $C_6H_5NO_2 \xrightarrow{Sn, HCl} A \xrightarrow{NaNO_2, HCl} B \xrightarrow[\Delta]{H_2O/H^+} C$

(D.S.B. 2013)

16. Write Hinsberg's test to distinguish primary, secondary and tertiary amines. *(Uttarakhand S.B. 2014)*

17. Discuss the effect of electron donating and electron withdrawing group on basicity of aromatic amines.

Or

Write short notes on the following:

(*i*) Carbylamine reaction,

(*ii*) Gabriel-phthalimide synthesis. *(Hr. S.B. 2014)*

18. How will you convert the following:

(*i*) Nitrobenzene into aniline

(*ii*) Ethanoic acid into methanamine

(*iii*) Aniline into N-phenylethanamide.

(Write the chemical equations involved) *(D.S.B. 2014)*

19. Give the structures of A, B and C in the following reactions:

(*i*) $CH_3Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[273\ K]{HNO_2} C$

(*ii*) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{Br_2+KOH} B \xrightarrow{CHCl_3+NaOH} C$

(D.S.B. 2014)

20. Give chemical equations for the following reactions:

(*i*) Gatterman Reaction

(*ii*) Carbylamine reaction

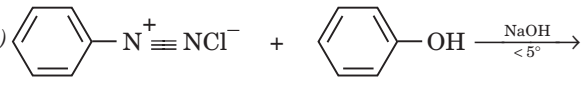
(*iii*) Ammonolysis

(Hr. S.B. 2018)

21. *(a)* What is Hoffmann's bromamide reaction? Write the reaction involved in it.

(b) Secondary amine is stronger base than tertiary amine. Give reason.

(c) Complete the following reactions:

(*i*)  $\xrightarrow[<5°]{NaOH}$

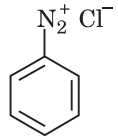
(*ii*) $C_2H_5NH_2 + CH_3COCl \longrightarrow$ *(Nagaland SB 2015)*

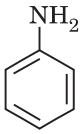
22. Write the following name reactions with chemical equations.

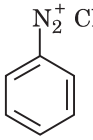
(*i*) Ammonolysis (*ii*) Hoffmann bromamide reaction

(*iii*) Coupling reaction *(Uttarakhand S.B. 2015)*

23. Complete the following reactions:

(*i*)  $\xrightarrow{CuCN}$?

(*ii*)  $\xrightarrow[pyridine]{(CH_3CO)_2O}$?

(*iii*)  $\xrightarrow{OH^-}$? *(Hr. S.B. 2015)*

24. *(a)* Give chemical tests to distinguish between primary, secondary and tertiary amines?

(b) Give reasons for the following:

(*i*) $C_2H_5NH_2$ is a stronger base as compared to aniline.

(*ii*) Aniline does not show Friedel Crafts reaction.

(Hr. S.B. 2015)

25. *(a)* How will you convert aniline to benzene?

(b) Write the following reactions:

(*i*) Balz Schiemann reaction

(*ii*) Carbylamine reaction

(*iii*) Diazotisation *(Pb. S.B. 2015)*

26. *(a)* Account for the correct order of decreasing basicity of ethylamine, 2-aminoethanol and 3-amino propan-1-ol

(b) How will you convert aniline into chlorobenzene?

(c) Write a short note on carbylamine test.

Or

(a) Write coupling reaction.

(b) Give a chemical test to distinguish between aniline and N-methylaniline.

(c) How will you convert benzoic acid to aniline?

(H.P.S.B. 2016)

27. *(a)* Tertiary amines do not undergo acylation. Explain?

(b) Write a short note on Hoffmann's degradation reaction.

(c) How will you convert aniline into benzene diazonium chloride?

Or

(a) Write diazotisation reaction.

(b) Aromatic amines cannot be prepared by Gabriel phthalimide synthesis. Explain.

(c) How will you convert methylamine into ethylamine?

(d) Complete the following:

$CH_3OH \xrightarrow{P,I_2} ? \xrightarrow{KCN} ? \xrightarrow[Na]{4H/alc.} ?$

(H.P.S.B. 2016)

28. *(a)* Give a chemical test to distinguish between the following pair of compounds:

Methylamine and ethylamine

(b) How will you convert benzene to aniline ?

(c) Write a short note on Gabriel phthalimide synthesis.

Or

(a) Write a short note on ammonolysis reaction.

(b) Aniline does not undergo Friedel Crafts alkylation. Explain.

(c) Arrange the following compounds in order of their basic strength in aqueous solution:

NH_3, $C_6H_5NH_2$, CH_3NH_2, $(CH_3)_3N$

(d) Complete the following reaction:

$$CH_3OH \xrightarrow{PBr_3} A \xrightarrow{KCN(alc.)} B \xrightarrow{LiAlH_4} C$$

(H.P.S.B. 2016)

29. (a) Account for the following observations:

(i) Aniline does not undergo Friedel Crafts reactions.

(ii) pK_b for aniline is more than that for methylamine.

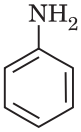
(b) Give a chemical test to distinguish between methylamine and dimethylamine. *(Hr. S.B. 2016)*

30. (a) Why is secondary amine more basic than the tertiary amine?

(b) How can 1°, 2° and 3° amine be distinguished by Hinsberg test?

(c) Complete the reaction:

(i) $CH_3CONH_2 + 4[H] \xrightarrow{LiAlH_4/ether} ?$

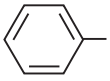
(ii)  $\xrightarrow{HNO_3 + H_2SO_4}$

(Nagaland S.B. 2018)

31. (i) Arrange the following compounds in an increasing order of basic strength in their aqueous solutions:

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

(ii) Identify the products in the following reaction:

 $\xrightarrow[273-278\ K]{NaNO_2/HCl} A \xrightarrow[Heat]{CHCl_3/KOH} B$

(Tripura S.B. 2016)

32. Identify A, B, C and D in the following conversions:

$$A \xrightarrow[273-278\ K]{NaNO_2/HCl} CH_3OH \xrightarrow{PCl_3} B \xrightarrow{KCN} C \xrightarrow{LiAlH_4} D$$

(Assam S.B. 2016)

33. Complete the following reactions :

(i) $C_6H_5NH_2 + CHCl_3 + KOH \longrightarrow$

(ii) $C_6H_5N_2Cl + C_2H_5OH \longrightarrow$

(iii) $C_2H_5NH_2 + HNO_2 \longrightarrow$ *(Jharkhand S.B. 2016)*

34. Write the structures of A, B and C in the following :

(i) $C_6H_5CONH_2 \xrightarrow{Br_2/aq.KOH} A \xrightarrow[0-5°C]{NaNO_2/HCl} B \xrightarrow{KI} C$

(ii) $CH_3Cl \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[\Delta]{CHCl_3 + alc\ KOH} C$

(D.S.B. 2016)

35. (i) Arrange the following in decreasing order of their basic strength:

$C_6H_5NH_2$, $C_2H_5NH_2$, $(C_2H_5)_2NH$, NH_3

(ii) Identify the organic product in the following reaction. Give its IUPAC name.

$C_2H_5NH_2 \xrightarrow{NaNO_2+HCl} ?$ *(Assam S.B. 2017)*

36. (i) Arrange the following amines in order of increasing their basic strength:

Aniline, *p*-nitroaniline, *p*-toluidine

(ii) How do aliphatic primary amines react with nitrous acid? Give equation. *(Meghalaya S.B. 2017)*

37. (i) Write the major product of the following reaction:

$C_6H_5N_2^+Cl^- + H_3PO_2 + H_2O \rightarrow ?$

(ii) Write the products formed when aniline undergoes direct nitration. *(Meghalaya S.B. 2017)*

38. Give the chemical equations for each of the following reactions:

(i) Hoffmann bromamide reaction.

(ii) Carbylamine reaction. *(Manipur S.B. 2017)*

39. What are diazonium salts?

How is nitrobenzene converted to benzenediazonium chloride? *(Manipur S.B. 2017)*

40. (a) Write a note on Hoffmann bromamide reaction giving suitable chemical reaction.

(b) Tertiary amines are stronger bases than primary amines. Why? *(Mizoram S.B. 2017)*

41. (a) What happens when aniline reacts with bromine water at room temperature?

(b) Give a chemical test for primary amines.

(c) Write the diazotisation reaction of aniline.

(Assam S.B. 2018)

42. (a) Aliphatic amines are stronger base than aromatic amines. Explain.

(b) Toluene is more easily nitrated than benzene. Explain

(c) Discuss the deactivating *m*-directing nature of nitro group. *(Hr.S.B. 2017)*

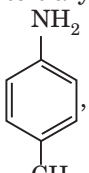
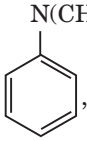
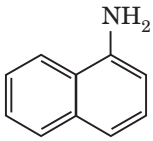
43. (a) Why are aliphatic amines stronger base than the aromatic amines?

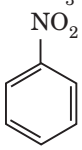
(b) What is carbylamine reaction? Give the reaction.

(c) Give one test to distinguish primary, secondary and tertiary amines from each other

(Nagaland S.B. 2017)

44. (a) Classify the following amines as primary, secondary and tertiary.

 ,  , $(C_2H_5)_2NH$, 

(b)  $\xrightarrow{Sn, HCl} B \xrightarrow{Br_2/H_2O} C$

Identify the products B and C and write their formulae. *(Kerala S.B. 2017)*

45. Identify the compounds X, Y and Z in the following reactions:

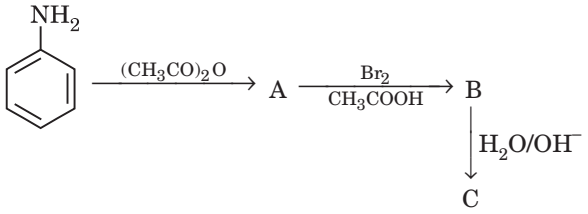
$$C_6H_5NH_2 \xrightarrow[273-278K]{NaNO_2} X \xrightarrow{CuBr/HBr} Y \xrightarrow[anhy.AlCl_3]{(CH_3CO)_2O} Z$$

(Major product)

(Manipur S.B. 2017)

46 *(a)* Explain, with the help of chemical equations, how the following compounds would be obtained from benzene diazonium chloride:
(*i*) Iodobenzene
ii) 4-Aminoazobenzene

(*b*) Complete the following reaction:



(*c*) What will happen if aniline is treated with aqueous bromine? *(Meghalaya S.B. 2018)*

47. *(a)* Explain carbylamine reaction with equation.
(*b*) How does nitrobenzene is reduced to aniline? Give equation.
(*c*) Write the IUPAC name of $C_6H_5—\underset{\displaystyle CH_3}{\overset{\displaystyle |}{N}}—CH_3$

(Karnataka S.B. 2018)

48. *(a)* Name the test used to identify primary amines using $CHCl_3$ and ethanoic KOH.
(*b*) How can you convert methyl iodide to ethanamine?
(Kerala S.B. 2018)

CBSE QUESTIONS

49. Account for the following observations:
(*a*) pK_b of aniline is more than that of methylamine.
(*b*) Methylamine solution in water reacts with ferric chloride solution to give a precipitate of ferric hydroxide.
(*c*) Aniline does not undergo Friedel-Crafts reaction.
(A.I.S.B. 2008, D.S.B. 2008)

50. Write one chemical reaction each to illustrate the following:
(*i*) Hoffmann's bromamide reaction
(*ii*) Gabriel phthalimide synthesis.
(A.I.S.B. 2008)

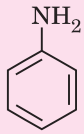
51. *(a)* Arrange the following compounds in an increasing order of basic strengths in their aqueous solutions :
NH_3, CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$.
(*b*) Complete the following reaction equations :
(*i*) $RCONH_2 \xrightarrow[H_2O]{LAH}$
(*ii*) $C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow$
(*iii*) $C_6H_5NH_2 + Br_2(aq) \longrightarrow$
(A.I.S.B. 2009)

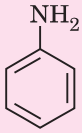
52. Give the chemical tests to distinguish between the following pairs of compounds :
(*i*) Ethylamine and aniline
(*ii*) Aniline and benzylamine
(A.I.S.B. 2010)

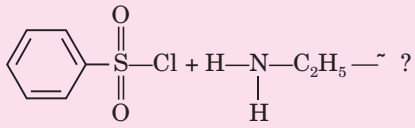
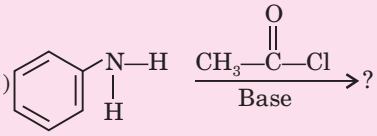
53. Give chemical tests to distinguish between the following pairs of compounds :
(*i*) Methylamine and Dimethylamine
(*ii*) Aniline and N-Methylaniline
(A.I.S.B. 2010)

54. Describe the following giving the relevant chemical equation in each case :
(*i*) Carbylamine reaction
(*ii*) Hoffmann bromamide reaction.
(A.I.S.B. 2012, Hr. S.B. 2018)

55. Give the structures of the products A, B and C in the following reactions:
(*i*) $CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[0°C]{HNO_2} C$
(*ii*) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{NaOH + Br_2} B \xrightarrow{CHCl_3 + alc\ KOH} C$
(A.I.S.B. 2013)

56. Complete the following reactions :
(*i*) $CH_3CH_2NH_2 + CHCl_3 + alc.\ KOH \longrightarrow$
(*ii*) $C_6H_5N_2^+Cl^- \xrightarrow[(Room\ Temp.)]{H_2O}$
(*iii*)  $+ HCl\ (aq) \longrightarrow$ *(A.I.S.B. 2013)*

57. Write the main products of the following reactions :
(*i*) $C_6H_5N_2^+Cl^- \xrightarrow{H_3PO_2 + H_2O} ?$
(*ii*)  $\xrightarrow{Br_2(aq)} ?$
(*iii*) $CH_3—\underset{\displaystyle O}{\overset{\displaystyle ||}{C}}—NH_2 \xrightarrow{Br_2 + NaOH} ?$ *(A.I.S.B. 2013)*

58. Write the main products of the following reactions :
(*i*) $CH_3CH_2NH_2 \xrightarrow[0°C]{HNO_2} ?$
(*ii*) 
(*iii*) 

(A.I.S.B. 2013)

59. Write the structures of A, B and C in the following :
(*i*) $C_6H_5COO^-NH_4^+ \xrightarrow{\Delta} A \xrightarrow{Br_2/KOH} B \xrightarrow[pyridine]{CH_3COCl} C$
(*ii*) $C_6H_5N^+BF_4^- \xrightarrow[453–473\ K]{Heat} A \xrightarrow{Sn/HCl} B \xrightarrow[\Delta]{CHCl_3 + alc.KOH} C$
(A.I.S.B. 2016)

60. Give reasons:

(i) Acetylation of aniline reduces its activation effect.

(ii) CH_3NH_2 is more basic than $C_6H_5NH_2$.

(iii) Although $-NH_2$ is *o/p* directing group, yet aniline on nitration gives a significant amount of *m*-nitroaniline.

(D.S.B. 2017, A.I.S.B. 2017)

61. Write the structures of compounds A, B and C in the following reactions:

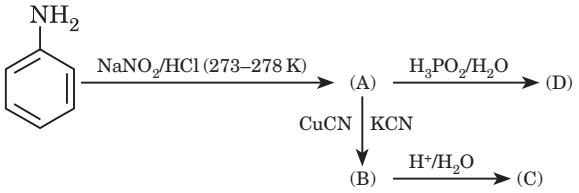
(a) $CH_3-COOH \xrightarrow{NH_3/\triangle} A \xrightarrow{Br_2/KOH(aq)} B \xrightarrow{CHCl_3 + alc.\ KOH} C$

(b) $C_6H_5N_2^+BF_4^- \xrightarrow[\triangle]{NaNO_2/Cu} A \xrightarrow{Fe/HCl} B \xrightarrow{CH_3COCl/pyridine} C$ *A.I.S.B. 2017)*

Long Answer Questions *carrying 5 marks*

1. *(a)* Explain why aniline does not undergo Friedel-Crafts reaction?

(b) Identify the compounds (A) and (B) in the following sequence of reactions:



(c) Why are aliphatic amines more basic than aromatic amines?

(d) Why aromatic primary amines cannot be prepared by Gabriel phthalimide synthesis?

(e) Complete the following reaction:

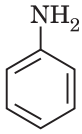
$$_6H_5NH_2 + C_6H_5OH \xrightarrow{NaNO_2\,/\,HCl\,(273-278\ K)}$$

(Meghalaya S.B. 2014)

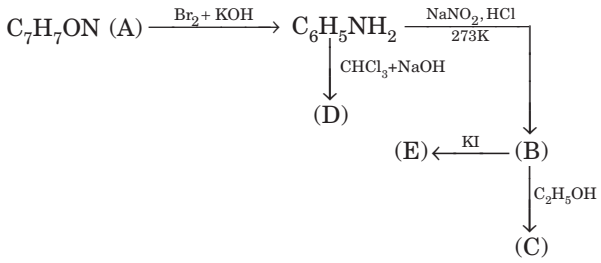
2. *(a)* Why are alkylamines stronger base than arylamines?

(b) $RCONH_2 + Br_2 + 4KOH \longrightarrow ?$

(c) What is diazotisation reaction?

(d)  $+ CH_3COCl \xrightarrow{Pyridine} ?$ *(H.P.S.B. 2018)*

3. An aromatic compound 'A' of molecular formula C_7H_7ON undergoes a series of reactions as shown below. Write the structures of A, B, C, D and E in the following reactions:



Or

(a) Write the structures of main products formed when aniline reacts with the following reagents:

(i) Br_2 water

(ii) HCl

(iii) $(CH_3\ CO)_2$/pyridine

(b) Arrange the following in the increasing order of their boiling point:

$_2H_5NH_2$, C_2H_5OH, $(CH_3)_3N$

(c) Give a simple chemical test to distinguish between the following pair of compounds:

$(CH_3)_2NH$ and $(CH_3)_3N$ *(D.S.B. 2015)*

4. *(a)* Illustrate the following reactions giving suitable example in each case:

(i) Hoffmann bromamide degradation reaction

(ii) Diazotisation

(iii) Gabriel phthalimide synthesis

(b) Distinguish between the following pairs of compounds

(i) Aniline and N-methylaniline

(ii) $(CH_3)_2NH$ and $(CH_3)_3N$

Or

(a) Write the structures of main products formed when benzene diazonium chloride ($C_6H_5N_2^+Cl^-$) reacts with following reagents:

(i) CuCN/KCN

(ii) H_2O

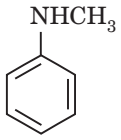
(iii) CH_3CH_2 OH

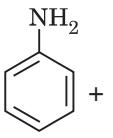
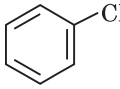
(b) Arrange the following:

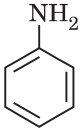
(i) $C_2H_5NH_2$, C_2H_5OH, $(CH_3)_3N$: in increasing order of their boiling point.

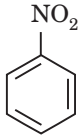
(ii) Aniline, *p*-nitroaniline, *p*-methylaniline in the increasing order of their basic strength. *(A.I.S.B. 2015)*

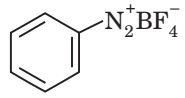
5. Write the organic products in the following reactions:

(i)  $\xrightarrow[Aqueous\ NaNO_2]{dil.HCl}$

(ii)  $+$  $\longrightarrow$

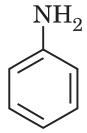
(iii)  $+ CHCl_3 \xrightarrow[Heat]{Ethanolic\ KOH}$

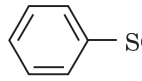
(iv)  $\xrightarrow[(b)\ Aqueous\ NaOH]{(a)\ Sn/HCl(conc.)}$

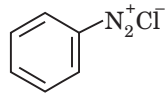
(v)  $\xrightarrow[\text{Cu powder, Heat}]{\text{Aqueous } NaNO_2}$

(vi) $RCN \xrightarrow[\text{Dry ether, Heat}]{LiAlH_4}$ *(Kolkata S.B. 2016)*

6. *(a)* Write the structures of the main products of the following reactions:

(i)  $\xrightarrow[\text{Pyridine}]{(CH_3CO)_2O}$

(ii)  $\xrightarrow{(CH_3)_2NH}$

(iii)  $\xrightarrow{CH_3CH_2OH}$

(b) Give a simple chemical test to distinguish between aniline and N, N-dimethylaniline.

(c) Arrange the following in the increasing order of their pK_b values:
$C_6H_5NH_2$, $C_2H_5NH_2$, $C_6H_5NHCH_3$

(A.I.S.B. 2018)

Or

(a) Write the reactions involved in the following:

(i) Hoffmann bromamide degradation reaction

(ii) Diazotisation

(iii) Gabriel phthalimide synthesis

(b) Give reasons:

(i) $(CH_3)_2$ NH is more basic than $(CH_3)_3N$ in an aqueous solution.

(ii) Aromatic diazonium salts are more stable than aliphatic diazonium salts. *(A.I.S.B. 2018)*

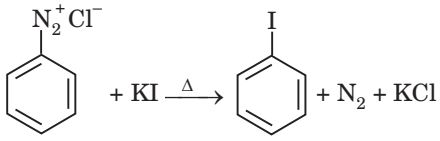
Hints & Answers *for* Revision Exercises

Very Short Answer Questions

1. N, N-Dimethyl-3-methyl-3-pentanamine

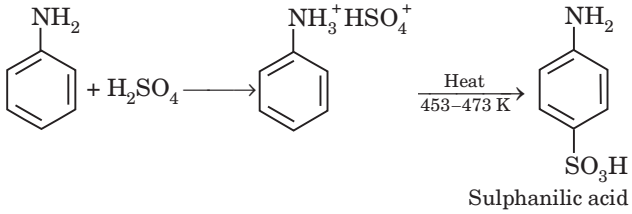
2. $CH_3CH_2NH_2$ and CH_3NHCH_3

3. Sandmeyer reaction.

4. 
Iodobenzene

6. $ArN_2Cl + H_3PO_2 + H_2O \longrightarrow ArH + H_3PO_3 + HCl + N_2$

7. 2,4,6- Tribromoaniline (white ppt).

8. 
Sulphanilic acid

9. Aniline is less basic than methylamine and therefore, its pK_b is more.

10. $C_6H_5NH_2 + CHCl_3 + 3KOH\ (alc.) \xrightarrow{\text{Warm}} C_6H_5NC + 3KCl + 3H_2O$

11. *p*-nitroaniline < aniline < *p*-toluidine

13. $(CH_3)_3N < CH_3NH_2 < (CH_3)_2$ NH

14. $(H_3C)_2NH$

15. $CH_3CH_2C \equiv N \xrightarrow{Na\,(Hg)/C_2H_5OH} CH_3CH_2CH_2NH_2$

16. Phenol is formed.

17. 2,4,6-Tribromoaniline.

18. $\underset{\text{Benzamide}}{C_6H_5CONH_2} \xrightarrow[\text{Ether}]{LiAlH_4} \underset{\text{Banzylamine}}{C_6H_5CH_2NH_2}$

20. $Ar\text{-}NH_2 \xrightarrow[0-5\,^\circ C]{NaNO_2, HCl} \underset{(A)}{ArN_2^+Cl^-} \xrightarrow{CuCN} \underset{(B)}{Ar\text{–}CN}$

22. N-Methylpropan-2-amine

23. N-Ethyl-N-methylethanamine

24. $C_6H_5NH_2 < C_6H_5CH_2NH_2 < C_2H_5NH_2 < (C_2H_5)_2NH$

26. $C_6H_5NH_2 < (C_2H_5)_2$ NH $< C_2H_5NH_2$

27. Aniline gives azo dye test while ethylamine does not give azo dye test.

28. $(C_6H_5)_2$ NH $< C_6H_5NH_2 < C_6H_5N\,(CH_3)_2 < CH_3NH_2$

29. $CH_3CH_2NHCH_3$

30. Diazotization

31. N-Methyl-2-methyl propanamine.

32. *(a)*	**33.** *(c)*	**34.** *(d)*	**35.** *(a)*
36. *(c)*	**37.** *(d)*	**38.** *(a)*	**39.** *(a)*
40. *(d)*	**41.** *(c)*	**42.** *(a)*	**43.** *(a)*
44. *(b)*	**45.** *(a)*	**46.** *(c)*	**47.** *(b)*

Competition File

Additional Useful Information and Objective Questions

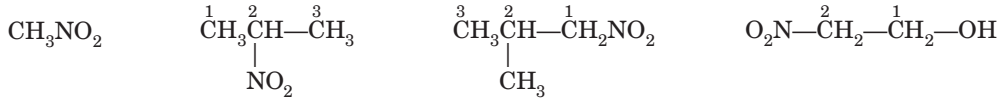
ADDITIONAL USEFUL INFORMATION

➤ NITRO COMPOUNDS

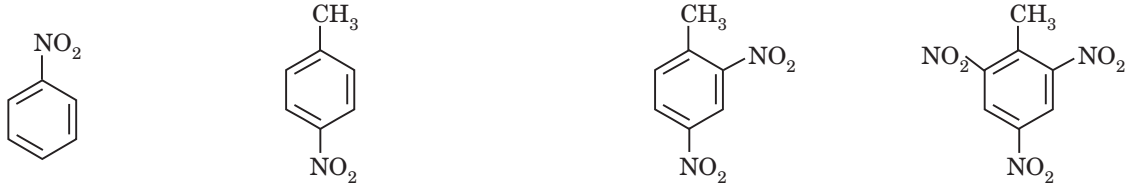
These compounds contain the functional group – NO_2. These may be aliphatic or aromatic according as the nitro group is attached to an alkyl or an aryl group.

$R–NO_2$ (Aliphatic nitro compound) $C_6H_5—NO_2$ (Aromatic nitro compound) or $Ar—NO_2$

According to IUPAC system, these are named by prefixing **nitro** to the name of parent alkane or arene. The positions of the nitro group and other substituents if any on the parent chain or arene are indicated. For example,



Nitromethane; 2-Nitro propane; 2-Methyl-1-nitropropane; 2 Nitroethanol



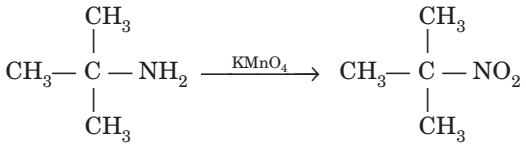
Nitrobenzene; 4-Nitrotoluene (1-Methyl-4-nitrobenzene); 2, 4-Dinitrotoluene (1-Methyl-2, 4-dinitrobenzene); 2, 4, 6-Trinitrotoluene (TNT)

Methods of Preparation of Nitro Compounds

- **From alkyl halides** by reacting alkyl halide with alcoholic solution of silver nitrite.

$$C_2H_5I + AgNO_2(alc) \longrightarrow \underset{\text{Nitroethane}}{C_2H_5NO_2} + AgI$$

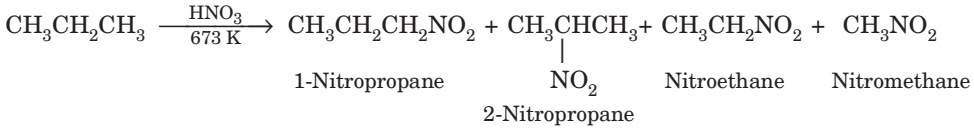
- **From tertiary alkyl amines** by reacting a primary amine containing a tertiary alkyl group with $KMnO_4$ (oxidation).



2-Methylpropan-2-amine; 2-Methyl-2-nitropropane

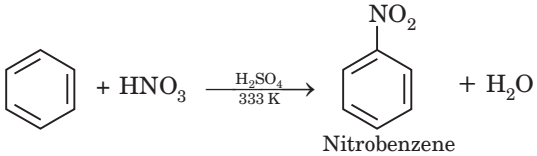
- **From hydrocarbons.** With fuming HNO_3, aliphatic alkanes give a mixture of nitroalkanes resulting by cleavage of carbon-carbon bonds.

$$CH_3CH_3 \xrightarrow[673\ K]{\text{fuming } HNO_3} CH_3CH_2NO_2 + CH_3NO_2$$



1-Nitropropane; 2-Nitropropane; Nitroethane; Nitromethane

Aromatic nitro compounds are prepared by nitration of benzene.



Nitrobenzene

Properties of Nitro Compounds

Nitroalkanes are colourless (when pure), pleasant smelling liquids. Both nitroalkanes and nitroarenes are highly polar compounds (dipole moment 3-4D) and therefore, have strong dipole- dipole interactions. As a result, nitroalkanes have much higher boiling points than hydrocarbons of comparable molecular masses.

1. **Hydrolysis.** Primary nitroalkanes when treated with boiling HCl or 85% H_2SO_4 undergo hydrolysis to form a carboxylic acid and the corresponding salt of hydroxylamine.

Competition File

$$RCH_2NO_2 \xrightarrow[\Delta]{HCl/H_2O} R{-}\overset{\overset{O}{\|}}{C}{-}NHOH \xrightarrow{HCl/H_2O} RCOOH + \underset{\text{Hydroxylamine hydrochloride}}{NH_2OH.HCl}$$

$$CH_3CH_2NO_2 \xrightarrow[\Delta]{H_2SO_4/H_2O} CH_3{-}\overset{\overset{O}{\|}}{C}{-}NHOH \xrightarrow[\Delta]{H_2SO_4/H_2O} CH_3COOH + \underset{\text{Hydroxylamine hydrogen sulphate}}{\overset{+}{N}H_3OH.HSO_4^-}$$

Secondary nitro compounds upon hydrolysis with boiling HCl give a ketone and nitrous oxide.

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH{-}NO_2 \xrightarrow{\text{Boiling HCl}} \underset{\text{Acetone}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C{=}O} + \underset{\text{Nitrous oxide}}{N_2O} + H_2O$$

Tertiary nitroalkanes, however, do not undergo hydrolysis with hydrochloric acid.

2. **Reduction.** The nitroalkanes are reduced as:

$$RNO_2 \xrightarrow[-H_2O]{+2H} \underset{\text{Nitroso}}{R{-}N{=}O} \xrightarrow{+2H} \underset{\text{N-Alkyl hydroxylamine}}{R{-}NHOH} \xrightarrow[-H_2O]{+2H} \underset{\text{Amine}}{RNH_2}$$

The final product depends upon the pH of the reaction medium and nature of the reducing agent. Some common examples are:

(i) in acidic medium.

$$CH_3CH_2NO_2 + 6H \xrightarrow[Fe/HCl]{Sn/HCl} CH_3CH_2NH_2 + 2H_2O$$

$$C_6H_5NO_2 + 6H \xrightarrow[Fe/HCl]{Sn/HCl} C_6H_5NH_2 + 2H_2O$$

(ii) in neutral medium

$$CH_3NO_2 + 4H \xrightarrow[\Delta]{Zn/NH_4Cl,H_2O} \underset{\text{N-Methylhydroxylamine}}{CH_3NHOH} + ZnO$$

(iii) in alkaline medium

$$2C_6H_5NO_2 \xrightarrow[\Delta]{Zn/CH_3OH - NaOH} \underset{\text{Azobenzene}}{C_6H_5{-}N = NC_6H_5}$$

$$2C_6H_5NO_2 \xrightarrow[\Delta]{Zn/NaOH} \underset{\text{Hydrazobenzene}}{C_6H_5NH{-}NH{-}C_6H_5}$$

(iv) catalytic reduction

$$CH_3CH_2NO_2 + 3H_2 \xrightarrow[Pt\text{ or }Pd]{Raney\ Ni} CH_3CH_2NH_2 + 2H_2O$$

$$C_6H_5NO_2 + 3H_2 \xrightarrow{Pt,Pd/C} C_6H_5NH_2 + 2H_2O$$

(v) ith $LiAlH_4$

$$CH_3CH_2NO_2 \xrightarrow{LiAlH_4,\ dry\ ether} CH_3CH_2NH_2$$

Reduction of nitroarenes give azo compounds

$$2C_6H_5NO_2 \xrightarrow[dry\ ether]{Li\ AlH_4} \underset{\text{Azobenzene}}{C_6H_5N{=}NC_6H_5}$$

3. **Action with nitrous acid.** Primary nitroalkanes react with nitrous acid (HONO) to form blue coloured nitroso- nitroalkanes which dissolve in aqueous NaOH to give red solutions.

$$CH_3CH_2NO_2 + HONO \longrightarrow \underset{\text{Nitrolic acid (Dissolves in NaOH to give blood red colouration)}}{\begin{matrix}CH_3C{=}NOH\\|\\NO_2\end{matrix}}$$

Competition File

Secondary nitroalkanes give blue coloured nitroso derivative

$(CH_3)_2CHNO_2 + HONO \longrightarrow (CH_3)_2\underset{\underset{NO}{|}}{C}-NO_2$

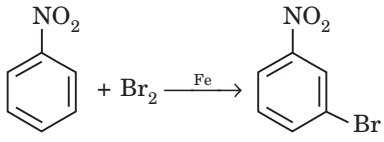
Nitroso derivative (blue)

Tertiary nitroalkanes do not react wth nitrous acid because these do not have α-H atoms.

4. **Action with aldehydes and ketones.** Due to the presence of α-hydrogen atom, primary and secondary nitroalkanes undergo condensation with aldehydes or ketones in the presence of alcoholic KOH. This reaction is quite similar to aldol condensation and proceeds via formation of carbanion.

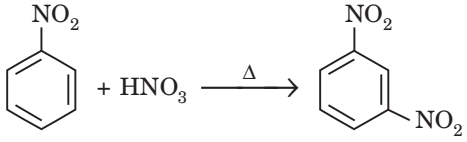
$$\underset{\text{Benzaldehyde}}{C_6H_5-\overset{\overset{H}{|}}{C}=O} + CH_3NO_2 \xrightarrow{\text{alc.KOH}} C_6H_5-\overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C}}-CH_2-NO_2 \xrightarrow[-H_2O]{\text{Heat}} C_6H_5-CH=CHNO_2$$

5. **Electrophilic substitution reactions.** Since $-NO_2$ group is strongly deactivating and ***m*- directing**, therefore, *m*-derivatives are formed.

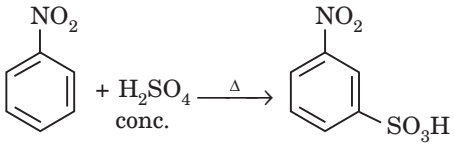


m-Bromonitrobenzene

;



m-Dinitrobenzene



m-Nitrobenzenesulphonic acid

➤ CYANIDES AND ISOCYANIDES

When the alkyl or aryl group is attached to the carbon of CN group, the compounds are called **cyanides** and when the alkyl or aryl group is attached to the nitrogen atom of CN group, the compounds are called **isocyanides.**

R—CN	R—NC
Cyanides	Isocyanides

According to IUPAC system, cyanides are called **alkane nitriles** and isocyanides are called **alkyl carbylamines**.

CH_3CN	CH_3CH_2CN	C_6H_5CN
Ethanenitrile	Propanenitrile	Benzonitrile
CH_3NC	CH_3CH_2NC	C_6H_5NC
Methyl carbylamine	Ethyl carbylamine	Phenyl carbylamine

Preparation

- **From alkyl halides** by reacting alkyl halide with KCN or AgCN

$CH_3CH_2Br + KCN \longrightarrow \underset{\text{Propanenitrile}}{CH_3CH_2CN} + KBr$

$C_6H_5Br + AgCN(alc.) \longrightarrow \underset{\text{Ethyl carbylamine}}{CH_3CH_2NC} + A\ Br$

- **From amides**

$CH_3CONH_2 \xrightarrow{P_2O_5} CH_3CN + H_2O$

$C_6H_5CONH_2 \xrightarrow{P_2O_5} C_6H_5CN + H_2O$

Properties

1. **Hydrolysis.** Alkyl cyanides can be hydrolysed under acidic and basic conditions to give amides, which further get hydrolysed giving carboxylic acids.

$$CH_3CN + H_2O \xrightarrow[\text{or } OH^-]{H^+} \underset{\text{Amide}}{CH_3CONH_2} \xrightarrow[\text{or } OH^-]{H^+} \underset{\text{Carboxylic acid}}{CH_3COOH}$$

Isocyanides are hydrolysed to primary amines.

$$CH_3NC \xrightarrow{H_2O,\ H^+} CH_3NH_2 + HCOOH$$

Competition File

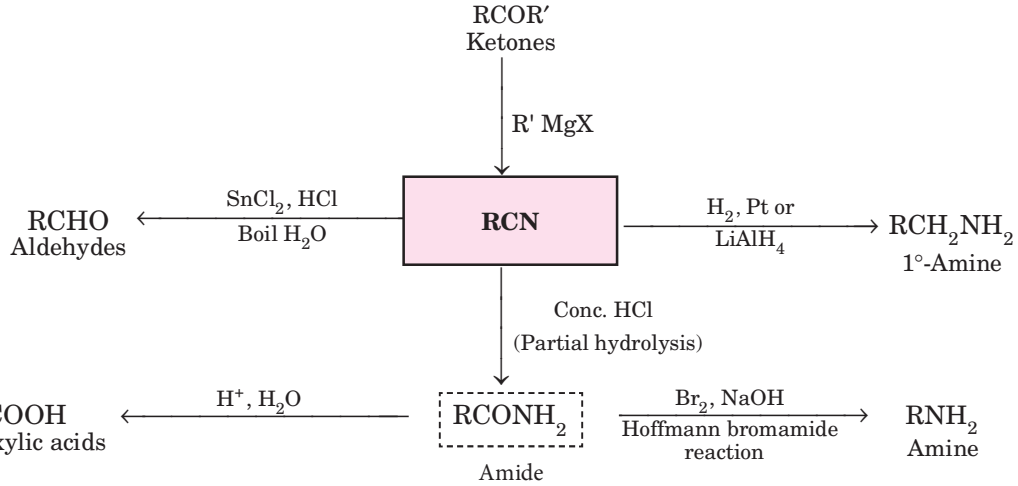
2. Reduction. Alkyl cyanides are reduced to primary amines either by H_2 in the presence of Ni or Pt or by $LiAlH_4$.

$$CH_3CN + 2H_2 \xrightarrow[\text{or } LiAlH_4]{\text{Pt or Ni}} \underset{\text{Ethyl amine (1°)}}{CH_3CH_2NH_2}$$

Isocyanides are reduced to secondary amines.

$$CH_3NC + 2H_2 \xrightarrow{\text{Ni or Pt}} \underset{\text{Dimethylamine (2°)}}{CH_3NHCH_3}$$

▶ The alkyl nitriles or cyanides are useful intermediates in organic synthesis because these can be easily converted into *amines, aldehydes, ketones, esters, amides, carboxylic acids,* etc. They provide a synthetic route for **stepping up the series**.



▶ Acetonitrile (CH_3CN) is used as a **solvent of choice for many organic reactions.** Its extensive use as solvent is because:

(*i*) It is not reactive in mild acidic and basic conditions.
(*ii*) It has high polarity and is capable of dissolving a variety of reactants.
(*iii*) It has moderate boiling point and therefore, can be easily removed.
(*iv*) It is miscible with water and a number of organic solvents.

OBJECTIVE TYPE QUESTIONS

Multiple Choice Questions *M. C. Q.*

A Topicwise MULTIPLE CHOICE QUESTIONS *with only one correct answer*

Select the Correct Answer :

Amines

A1. Out of the following compounds, which is the most basic in aqueous solution?
(*a*) CH_3NH_2 (*b*) $(CH_3)_2NH$
(*c*) $(CH_3)_3N$ (*d*) $C_6H_5NH_2$.

A2. Which of the following amines gives carbylamine reaction ?
(*a*) $C_2H_5NH_2$ (*b*) $(C_2H_5)_2NH$
(*c*) $(C_2H_5)_3N$ (*d*) $CH_3NHC_2H_5$.

A3. Aniline undergoes condensation to form Schiff base on reacting with
(*a*) acetyl chloride (*b*) ammonia
(*c*) acetone (*d*) benzaldehyde.

A4. An isocyanide on reduction with hydrogen in the presence of Pt gives
(*a*) amide (*b*) primary amine
(*c*) secondary amine (*d*) alcohol.

A5. Aniline on oxidation with $Na_2Cr_2O_7$ and H_2SO_4 gives
(*a*) benzoic acid (*b*) *m*-amino benzoic acid
(*c*) Schiff's base (*d*) *p*-benzoquinone.

A6. Ethylamine reacts with nitrous acid to form
(*a*) C_2H_5OH (*b*) C_2H_5OH, N_2, H_2O
(*c*) $C_2H_5N_2^+Cl^-$ (*d*) C_2H_5NHOH, NH_3.

Answers

A1. (*b*) **A2.** (*a*) **A3.** (*d*) **A4.** (*c*) **A5.** (*d*) **A6.** (*b*)

Competition File

A7. Hinsberg's reagent is
(*a*) benzene sulphonyl chloride
(*b*) benzene sulphonic acid
(*c*) phenyl isocyanide
(*d*) benzene sulphonamide.

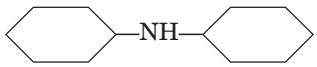
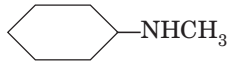
A8. Which of the following reactions is given by only primary amines ?
(*a*) Reaction with HONO
(*b*) Reaction with chloroform and alcoholic KOH
(*c*) Reaction with acetyl chloride
(*d*) Reaction with Grignard reagent.

A9. Amino (—NH_2) group is susceptible to oxidation by HNO_3, therefore, nitration is done in the presence of :
(*a*) dil H_2SO_4 (*b*) CS_2 at 0°C
(*c*) CH_3COCl (*d*) Water.

A10. Aniline reacts with $NaNO_2$ and HCl at room temperature to give
(*a*) nitroaniline (*b*) phenol
(*c*) diazonium chloride (*d*) chloroaniline.

A11. Silver chloride is soluble in methylamine due to the formation of
(*a*) Ag $H_3NH_2)Cl$ (*b*) Ag + CH_3Cl + NH_4Cl
(*c*) [Ag $(CH_3NH_2)_2$]Cl (*d*) AgOH.

A12. Diethylamine reacts with nitrous acid to give
(*a*) $(C_2H_5)_2NH^+NO_2^-$ (*b*) $(C_2H_5)_2NNO$
(*c*) C_2H_5OH (*d*) N_2 and alcohol.

A13. Maximum pK_b value is of
(*a*) $(CH_3)_2$ NH
(*b*) $(CH_3CH_2)_2$ NH
(*c*) 
(*d*) 

A14. Gabriel phthalimide reaction is used for the preparation of
(*a*) primary aromatic amines
(*b*) secondary amines
(*c*) primary aliphatic amines
(*d*) tertiary amines.

A15. Reaction of ethylamine with chloroform in alcoholic KOH gives
(*a*) C_2H_5CN (*b*) C_2H_5NC
(*c*) CH_3CN (*d*) CH_3NC.

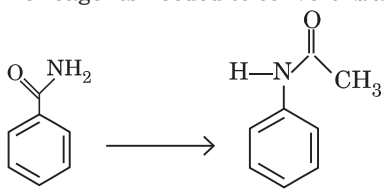
A16. Reaction of acetamide with bromine water and KOH gives
(*a*) CH_3COOH (*b*) $CH_3CH_2NH_2$
(*c*) CH_3COONH_4 (*d*) CH_3NH_2.

A17. Hoffmann degradation of *m*-bromobenzamide gives
(*a*) aniline (*b*) *m*-bromoaniline
(*c*) bromobenzene (*d*) *m*-bromoethyl benzene.

A18. Which of the following is Hoffmann mustard oil reaction ?
(*a*) Reaction of aromatic amine with iodoform
(*b*) Reaction of primary amine with $CHCl_3$
(*c*) Reaction of primary amine with CS_2 and $HgCl_2$
(*d*) Reaction of secondary amine with nitrous acid.

A19. On heating aniline with CS_2 in the presence of $HgCl_2$ the product is :
(*a*) Phenyl cyanide
(*b*) Phenyl isocyanide
(*c*) Phenyl isothiocyanate
(*d*) *p*-Aminobenzene sulphonic acid

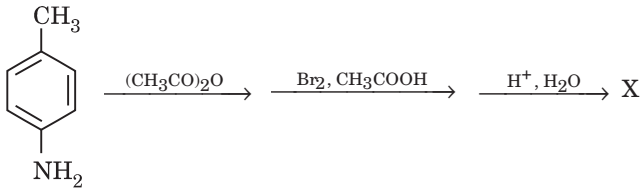
A20. The reagents needed to convert is/are



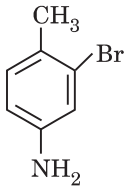
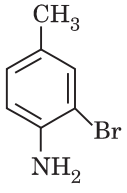
(*a*) KOH, Br_2; $LiAlH_4$
(*b*) KOH, Br_2; CH_3COCl
(*c*) HONO, Cu_2Cl_2, $(CH_3CO)_2O$
(*d*) KOH, Br_2; Ni, H_2, CH_3COCl

A21. A positive carbylamine test is given by
(*a*) N, N-dimethylaniline
(*b*) 2, dimethylaniline
(*c*) N-methyl-*o*-methylaniline
(*d*) *p*-methyl benzylamine

A22. In the reaction



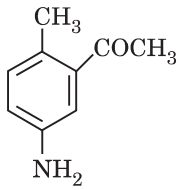
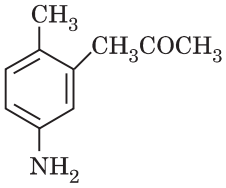
X is :

(*a*) 
(*b*) 

Answers

A7.(*a*) **A8.** (*b*) **A9.** (*c*) **A10.** (*c*) **A11.** (*c*) **A12.** (*b*) **A13.** (*c*) **A1** (*c*) **A15.** (*b*) **A16.** (*d*)
A17.(*b*) **A18.** (*c*) **A19** (*c*) **A20.** (*b*) **A21.** (*d*)

Competition File

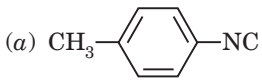
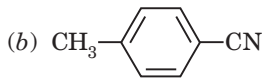
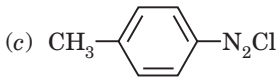
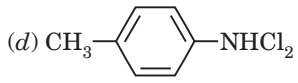
(*c*)  (*d*) 

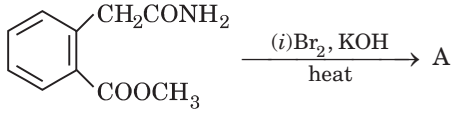
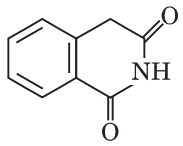
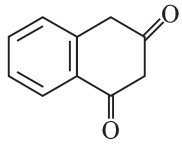
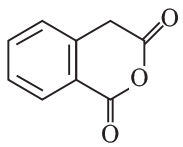
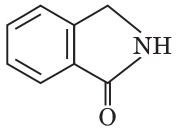
A23. The compound $C_5H_{13}N$ is optically active and reacts with HONO to give $C_5H_{11}OH$. The compound is
(*a*) N-methylbutanamine (*b*) 2-Aminopentane
(*c*) 1-Aminopentane (*d*) N,N'-Dimethylpropanamine

A24. In the reaction of *p*-chlorotoluene with KNH_2 in liquid NH_3, the major product is
(*a*) *o*-toluidine (*b*) *m*-toluidine
(*c*) *p*-toluidine (*d*) *p*-chloroaniline

A25. *p*-chloroaniline and anilinium hydrochloride cannot be distinguished by
(*a*) Sandmeyer's reaction (*b*) $NaHCO_3$
(*c*) $AgNO_3$ (*d*) Carbylamine test.

A26. $CH_3CH_2Cl \xrightarrow{NaCN} X \xrightarrow{Ni/H_2} Y \xrightarrow[\text{anhydride}]{\text{Acetic}} Z$
Z in the above sequence is
(*a*) $CH_3CH_2CH_2NHCOCH_3$
(*b*) $CH_3CH_2CH_2NH_2$
(*c*) $CH_3CH_2CH_2CONHCH_3$
(*d*) $CH_3CH_2CH_2CONHCOCH_3$

A27. The reaction of chloroform with alcoholic KOH and *p*-toluidine forms
(*a*)  (*b*) 
(*c*)  (*d*) 

A28. In the following reaction, the product A is

(*a*)  (*b*) 
(*c*)  (*d*) 

A29. Which of the following compound will dissolve in an alkali solution after it undergoes reaction with Hinsberg's reagent?
(*a*) CH_3NH_2 (*b*) $(CH_3)_2NH$
(*c*) $C_6H_5NHC_6H_5$ (*d*) $(CH_3)_3N$

A30. Secondary amines can be prepared by
(*a*) reduction of nitriles
(*b*) Hoffmann bromamide reaction
(*c*) reduction of amides
(*d*) reduction of isonitriles

Diazonium Salts

A31. Which of the following statement is incorrect?
(*a*) Diazonium salts are crystalline solids
(*b*) They are unstable and explode in dry state
(*c*) Aromatic diazonium salts are less stable than aliphatic diazonium salts
(*d*) These are readily soluble in water

A32. In Balz–Schiemann reaction, benzene diazonium chloride reacts with
(*a*) KI (*b*) CuCN/KCN
(*c*) HBF_4 (*d*) HBF_4 and $NaNO_2$,Cu

A33. The indicator methyl orange is prepared by coupling diazonium salt of sulphanilic acid with
(*a*) aniline
(*b*) N, N-dimethylaniline
(*c*) *p*-methylaniline
(*d*) naphthol.

A34. Benzene diazonium chloride on reaction with phenol in weakly basic medium gives
(*a*) diphenyl ether (*b*) *p*-hydroxyazobenzene
(*c*) chlorobenzene (*d*) benzene

A35. Benzene diazonium chloride reacts with nitrous acid in the presence of Cu_2O to give
(*a*) C_6H_5CN (*b*) C_6H_5OH
(*c*) $C_6H_5NO_2$ (*d*) C_6H_6

A36. Which of the following reaction represents Sandmeyer's reaction?
(*a*) $C_6H_5N_2^+Cl^- \xrightarrow{CuCN/KCN} C_6H_5CN + N_2$
(*b*) $C_6H_5N_2^+Cl^- \xrightarrow{Cu,\ HCl} C_6H_5Cl + N_2$
(*c*) $C_6H_5N_2^+Cl^- \xrightarrow[HCl]{Cu_2Cl_2} C_6H_5Cl + N_2$
(*d*) $C_6H_5N_2^+Cl^- \xrightarrow{HBF_4} C_6H_5F + N_2$

Answers

A2 (*b*) **A23.** (*b*) **A24.** (*b*) **A25** (*d*) **A26.** (*a*) **A27.** (*a*) **A28.** (*d*) **A29.** (*a*) **A30.** (*d*) **A31.** (*c*)
A32. (*c*) **A33.** (*b*) **A34** (*b*) **A35.** (*c*) **A36.** (*c*)

Competition File

A37. Aniline when diazotized in cold and then treated with dimethyl aniline gives a coloured product. Its structure would be

(*a*) CH_3—C$_6$H$_4$—N=N—C$_6$H$_4$—NH_2

(*b*) $(CH_3)_2N$—C$_6$H$_4$—N=N—C$_6$H$_5$

(*c*) $(CH_3)_2N$—C$_6$H$_4$—NH—C$_6$H$_5$

(*d*) CH_3NH—C$_6$H$_4$—N=N—C$_6$H$_4$—$NHCH_3$

A38. Which of the following diazonium salt is most stable?

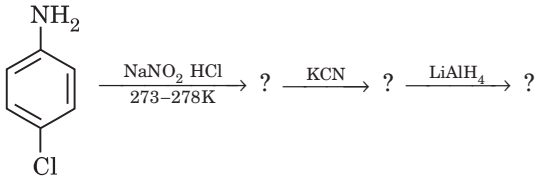
(*a*) *p*-Nitrobenzenediazonium chloride

(*b*) 2,4 Dintrobenzenediazonium chloride

(*c*) 2,4,6-Trinitrobenzenediazonium chloride

(*d*) *p*-Methoxybenzenediazonium chloride

A39. The final product in the following reaction is



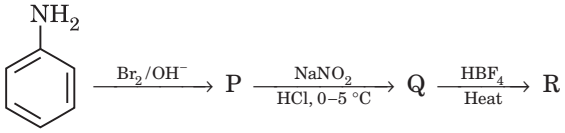
(*a*) *p*-chlorobenzylamine

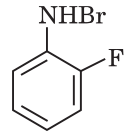
(*b*) *p*-chlorophenol

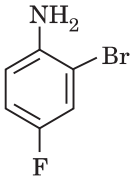
(*c*) *p*-chlorobenzyl alcohol

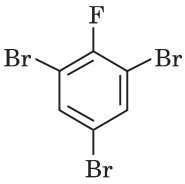
(*d*) *p*-chloro benzamide

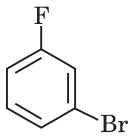
A40. The product R in the following reaction is



(*a*) 

(*b*) 

(*c*) 

(*d*) 

Answers

A37 (*b*) **A38.** (*d*) **A39.** (*a*) **A40** (*c*)

B MULTIPLE CHOICE QUESTIONS *from competitive examinations*

AIPMT & Other State Boards' Medical Entrance

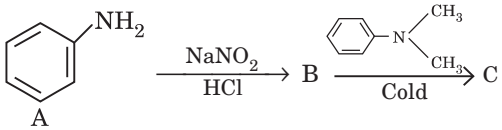
B1. Which one of the following on reduction with lithium aluminium hydride yields a secondary amine ?

(*a*) Methyl isocyanide (*b*) Acetamide

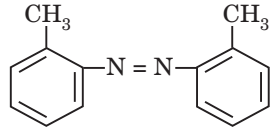
(*c*) Methyl cyanide (*d*) Nitroethane.

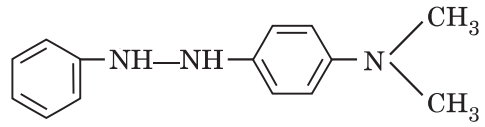
(C SE Med. 2007)

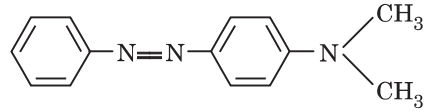
B2. In a reaction of aniline a coloured product C was obtained.

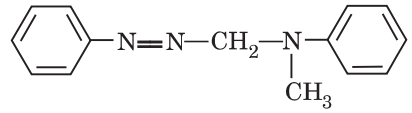


The structure of C would be :

(*a*) 

(*b*) 

(*c*) 

(*d*) 

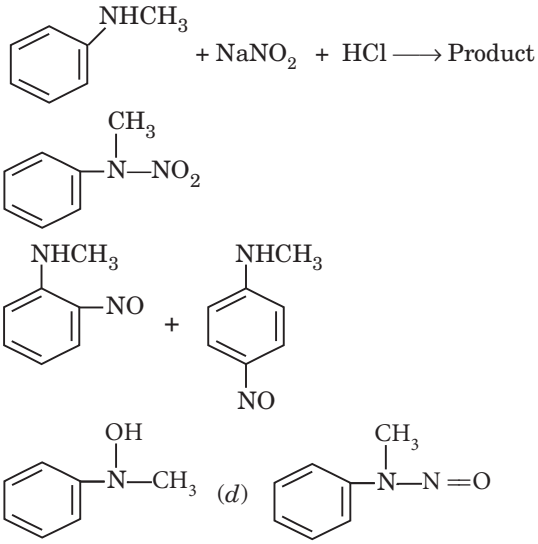
(C.B.S.E. P.M.T. 2008)

Answers

B1. (*a*) **B2.** (*c*)

Competition File

B3. Predict the product



(C.B.S.E. PMT 2009)

B4. Nitrobenzene can be prepared from benzene by using a mixture of conc. HNO_3 and H_2SO_4. In the mixture, HNO_3 acts as a/an

(*a*) acid (*b*) base
(*c*) catalyst (*d*) reducing agent

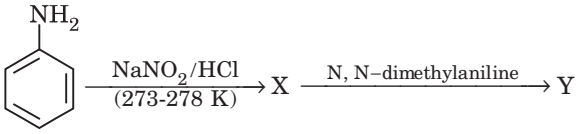
(C.B.S.E. PMT 2009)

B5. Acetamide is treated with the following reagents separately. Which one of these would yield methyl amine ?

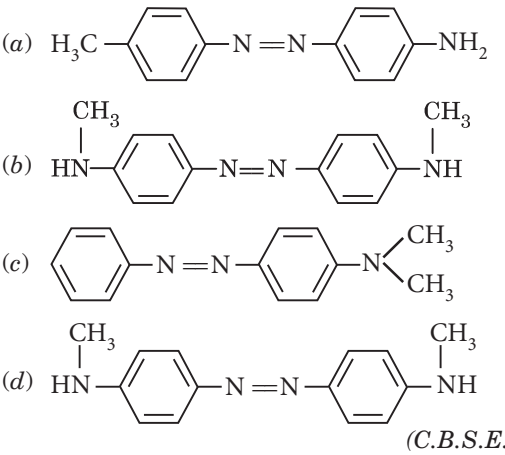
(*a*) Hot conc. H_2SO_4 (*b*) PCl_5
(*c*) NaOH – Br_2 (*d*) Sodalime

(C.B.S.E. PMT 2010)

B6. Aniline in a set of the following reactions yielded a coloured product 'Y'.



The structure of 'Y' would be :



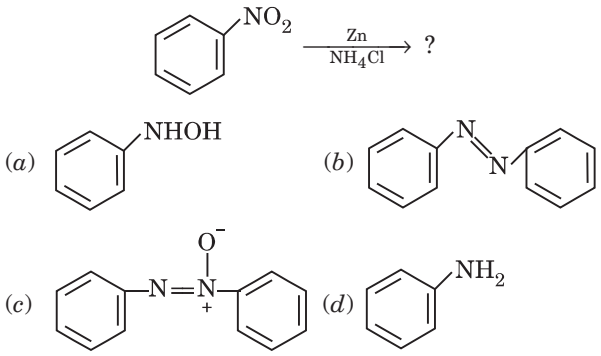
(C.B.S.E. PMT 2010)

B7. Which of the following statements about primary amines is 'false' ?

(*a*) Aryl amines react with nitrous acid to produce phenols
(*b*) Alkyl amines are stronger bases than ammonia
(*c*) Alkyl amines are stronger bases than aryl amines
(*d*) Alkyl amines react with nitrous acid to prduce alcohols.

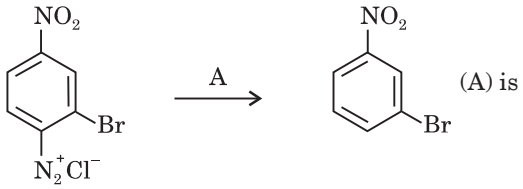
(C.B.S.E. PMT 2010)

B8. What is the product obtained in the following reaction ?



(AIPMT 2011)

B9. In the reaction :



(*a*) H_3PO_2 and H_2O (*b*) H^+ / H_2O
(*c*) $HgSO_4 / H_2SO_4$ (*d*) Cu_2Cl_2

(NEET 2013)

B10. Nitrobenzene on reaction with conc. HNO_3/H_2SO_4 at 80–100°C forms which one of the following product ?

(*a*) 1, 4-Dinitrobenzene
(*b*) 1, 2, 4-Trinitrobenzene
(*c*) 1, 2-Dinitrobenzene
(*d*) 1,3 Dinitrobenzene

(NEET 2013)

B11. Which of the following will be most stable diazonium salt $RN_2^+X^-$?

(*a*) $CH_3N_2^+X^-$ (*b*) $C_6H_5N_2^+X^-$
(*c*) $CH_3CH_2N_2^+X^-$ (*d*) $C_6H_5CH_2N_2^+X^-$

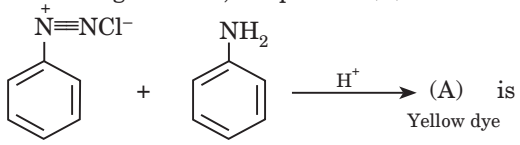
(AIPMT 2014, Karnataka CET 2018)

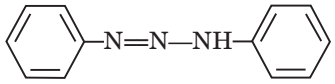
Answers

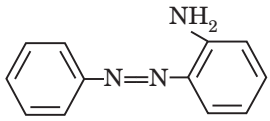
B3. (*d*) **B4.** (*b*) **B5.** (*c*) **B6.** (*c*) **B7.** (*a*) **B8.** (*a*) **B9.** (*a*) **B10.** (*d*) **B11.** (*b*)

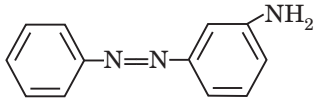
Competition File

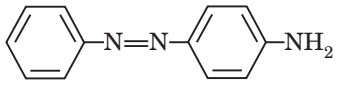
B12. In the following reaction, the product (A)



(*a*) 

(*b*) 

(*c*) 

(*d*) 

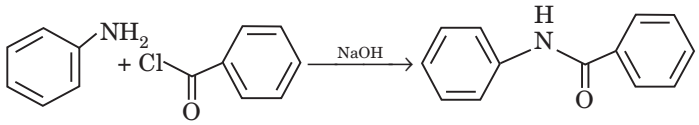
AIPMT 2014)

B13. The number of structural isomers possible from the molecular formula C_3H_9N is:

(*a*) 2 (*b*) 3

(*c*) 4 (*d*) 5 *(AIPMT 2015)*

B14. The following reaction :



is known by the name:

(*a*) Acetylation reaction

(*b*) Schotten-Baumann reaction

(*c*) Friedel-Craft's reaction

(*d*) Perkin's reaction *(AIPMT 2015)*

B15. Method by which aniline cannot be prepared is :

(*a*) reduction of nitrobenzene with H_2/Pd in ethanol.

(*b*) potassium salt of phthalimide treated with chlorobenzene followed by hydrolysis with aqueous NaOH solution.

(*c*) hydrolysis of phenylisocyanide with acidic solution.

(*d*) degradation of benzamide with bromine in alkaline solution. *(AIPMT 2015)*

B16. The electrolytic reduction of nitrobenzene in strongly acidic medium produces

(*a*) azobenzene (*b*) aniline

(*c*) p-aminophenol (*d*) azoxybenzene.

(AIPMT 2015)

B17. The correct statement regarding the basicity of arylamines is :

(*a*) arylamines are generally more basic than alkylamines because of aryl group

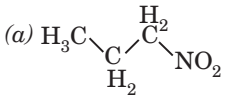
(*b*) arylamines are generally more basic than alkylamines because the nitrogen atom in arylamines is *sp*-hybridised

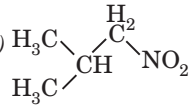
(*c*) arylamines are generally less basic than alkylamines because the nitrogen lone-pair electrons are delocalised by interaction with the aromatic ring π-electron system.

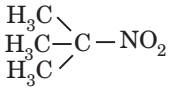
(*d*) arylamines are generally more basic than alkylamines because the nitrogen lone-pair electrons are not delocalised by interaction with the aromatic ring π-electron system.

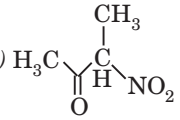
(NEET 2016)

B18. Which one of the following nitro-compound does not react with nitrous acid?

(*a*) 

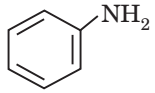
(*b*) 

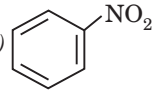
(*c*) 

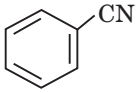
(*d*) 

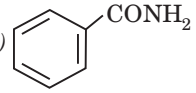
(NEET 2016)

B19. A given nitrogen–containing aromatic compound 'A' reacts with Sn/HCl, followed by HNO_2 to give an unstable compound 'B'. 'B', on treatment with phenol, forms a beautiful coloured compound 'C' with the molecular formula $C_{12}H_{10}N_2O$. The structure of compound 'A' is

(*a*) 

(*b*) 

(*c*) 

(*d*) 

(NEET 2016)

B20. Which of the following reactions is appropriate for converting acetamide to methanamine?

(*a*) Hoffmann bromamide reaction

(*b*) Stephen's reaction

(*c*) Gabriel phthalimide synthesis

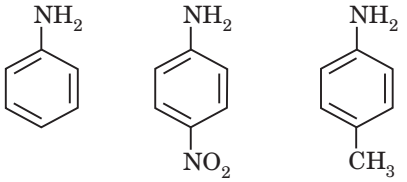
(*d*) Carbylamine reaction *(NEET 2017)*

Answers

B12.(*d*) **B13.** (*c*) **B14.** (*b*) **B15.** (*b*) **B16.** (*c*) **B17.** (*c*) **B18.** (*c*) **B19.** (*b*) **B20.** (*a*)

Competition File

B21. The correct increasing order of basic strength for the following compounds is



(I) (II) (III)

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

(NEET 2017)

B22. Nitration of aniline in strongly acidic medium also gives *m*-nitroaniline because

(*a*) inspite of substituents, nitro group always goes to only *m*-position

(*b*) in electrophilic substitution reactions, amino group is *meta* directive

(*c*) in absence of substituents, nitro group always goes to *m*-position

(*d*) in acidic (strong) medium, aniline is present as anilinium ion. *(NEET 2018)*

B23. Aniline is treated with $NaNO_2$/HCl at 0°C to give compound X which on treatment with cuprous cyanide gives another compound Y. When compound Y is treated with H_2/Ni compound Z is obtained. The compound Z is

(*a*) Benzyl alcohol (*b*) Benzylamine
(c) N-ethylaniline (d) Phenol
(*e*) Phenyl hydroxylamine *(Kerala PMT 2010)*

B24. The strongest base in aqueous solution among the following amines is

(*a*) N, N-diethylethanamine (*b*) N-ethylethanamine
(*c*) N-methylmethanamine (*d*) ethanamine
(*e*) phenylmethanamine *(Kerala P.M.T. 2011)*

B25. Aniline is treated with bromine water to give an organic compound 'X' which when treated with $NaNO_2$ and HCl at 0°C gives a water soluble compound 'Y'. Compound 'Y' on treatment with Cu_2Cl_2 and HCl gives compound 'Z'. Compound 'Z' is

(*a*) *o*-bromochlorobenzene

(*b*) *p*-bromochlorobenzene

(*c*) 2, 4, 6 tribromophenol

(*d*) 2, 4, 6 tribromochlorobenzene

(*e*) 2, 4-dibromophenol *(Kerala P.M.T. 2011)*

B26. Anilinium hydrogensulphate on heating with sulphuric acid at 453-473 K produces

(*a*) benzene sulphonic acid
(*b*) anthranilic acid
(*c*) aniline
(*d*) *m*-aminobenzene sulphonic acid
(*e*) sulphanilic acid *(Kerala P.M.T. 2011)*

B27. Secondary amines could be prepared by

(*a*) reduction of nitriles
(*b*) Hoffmann bromamide reaction
(*c*) reduction of amides
(*d*) reduction of isonitriles
(*e*) reduction of nitro compounds

(Kerala P.M.T 2012)

B28. Which one of the following amines cannot be prepared by Gabriel phthalimide synthesis?

(*a*) Ethylamine (*b*) Isopropylamine
(*c*) *n*–Propylamine (*d*) Ethylmethylamine
(*e*) Allylamine *(Kerala PMT 2015)*

B29. Which one of the following amines forms a non–acidic and alkali insoluble product with *p*–toluenesulphonyl chloride?

(*a*) Tertiary butylamine (*b*) *n*–Butylamine
(*c*) Isobutylamine (*d*) Diethylamine
(*e*) N, N-Dimethylethylamine *(Kerala PMT 2015)*

B30. Which of the following compound is most basic ?

(*a*) Aniline (*b*) Cyclohexylamine
(*c*) *o*-Nitroaniline (*d*) o-Toluidine
(*e*) *p*-Methoxyaniline *(Kerala PMT 2015)*

JEE (Main) & Other State Boards' Engineering Entrance

B31. Fluorobenzene can be synthesised in the laboratory

(*a*) from aniline by diazotisation followed by heating the diazonium salt with HBF_4

(*b*) by direct fluorination of benzene with F_2 gas

(*c*) by reacting bromobenzene with NaF solution

(*d*) by heating phenol with HF and KF

(I.E.E.E. 2006)

B32. In the chemical reaction,

$CH_3CH_2NH_2 + CHCl_3 + 3KOH \longrightarrow (A) + (B) + 3H_2O$

The compounds (A) and (B) are respectively :

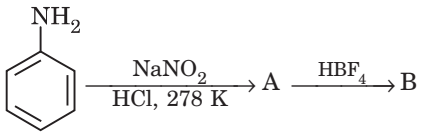
(*a*) $CH_3CH_2CONH_2$ and 3KCl
(*b*) C_2H_5NC and K_2CO_3
(*c*) C_2H_5NC and 3KCl
(*d*) C_2H_5CN and 3KCl. *(A.I.E.E.E. 2007)*

Answers

B21.(*c*) **B22.** (*d*) **B23.** (*b*) **B24.** (*b*) **B25.** (*d*) **B26.** (*e*) **B27.** (*d*) **B28.** (*d*) **B29.** (*d*) **B30.** (*b*)
B31. (*a*) **B32.** (*c*)

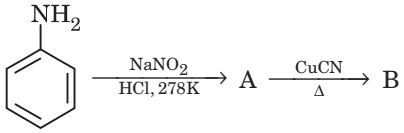
Competition File

B33. In the chemical reactions



The compound 'A' and 'B' respectively are :
(*a*) benzene diazonium chloride and fluorobenzene
(*b*) nitrobenzene and chlorobenzene
(*c*) nitrobenzene and fluorobenzene
(*d*) phenol and benzene *(AIEEE 2010)*

B34. In the chemical reactions :



the compounds A and B respectively are :
(*a*) benzenediazonium chloride and benzonitrile
(*b*) Nitrobenzene and chlorobenzene
(*c*) Phenol and bromobenzene
(*d*) Fluorobenzene and phenol *(A I.E.E.E. 2011)*

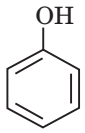
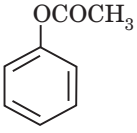
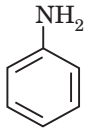
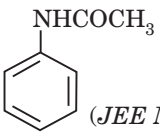
B35. A compound with molecular mass 180 is acylated with CH_3COCl to get a compound with molecular mass 390. The number of amino groups present per molecule of the former compound is
(*a*) 6 (*b*) 2
(*c*) 5 (*d*) 4 *(JEE Main 2013)*

B36. Considering the basic strength of amines in aqueous solution, which one has the smallest pK_b value?
(*a*) $C_6H_5NH_2$ (*b*) $(CH_3)_2NH$
(*c*) CH_3NH_2 (*d*) $(CH_3)_3N$
(JEE Main 2014)

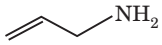
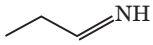
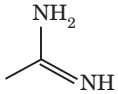
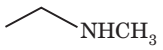
B37. On heating an aliphatic primary amine with chloroform and ethanolic potassium hydroxide, the organic compound formed is
(*a*) an alkyl isocyanide (*b*) an alkanol
(*c*) an alkanediol (*d*) an alkyl cyanide.
(JEE Main 2014)

B38. In the Hoffmann bromamide degradation reaction, the number of moles of NaOH and Br_2 used per mole of amine produced are
(*a*) one mole of NaOH and one mole of Br_2
(*b*) four moles of NaOH and two moles of Br_2
(*c*) two moles of NaOH and two moles of Br_2
(*d*) four moles of NaOH and one mole of Br_2.
(JEE Main 2016)

B39. Which of the following compound will give significant amount of meta product during mono-nitration reaction?

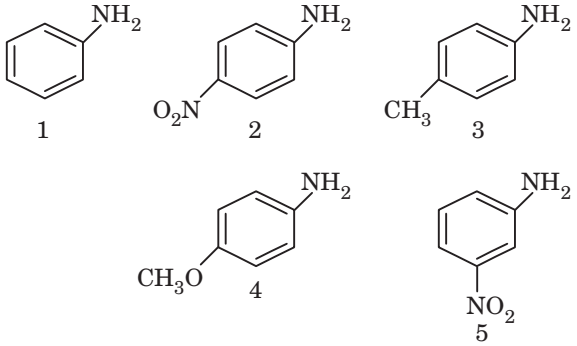
(*a*) 
(*b*) 
(*c*) 
(*d*) 
(JEE Main 2017)

B40. The increasing order of basicity of the following compounds is:

(*A*) 
(*B*) 
(*C*) 
(*D*) 

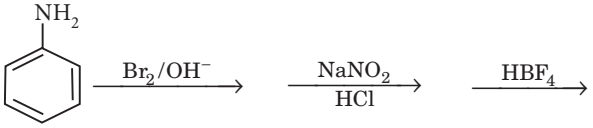
(*a*) (A) < B) < (C) < (D) (*b*) (B) < (A) < (C) < (D)
(*c*) (B) < (A) < (D) < (C) (*d*) (D) < (B) < (A) < (C)
(JEE Main 2018)

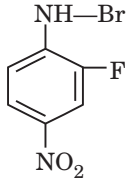
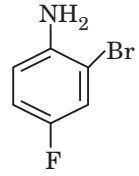
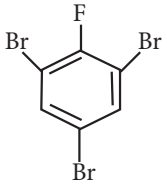
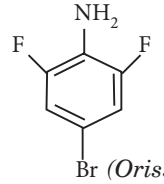
B41. The correct order of increasing basic nature of the following bases is



(*a*) 2 < 5 < 1 (*b*) 5 < 2 < 1 < 3 < 4
(*c*) 2 < 5 < 1 < 4 < 3 (*d*) 5 < 2 < 1 < 4 < 3
(*e*) 2 < 5 < 4 < 3 < 1 *(Kerala P.E.T. 2008)*

B42. The final product in the following sequence of reaction is



(*a*) 
(*b*) 
(*c*) 
(*d*) 
(Orissa J.E.E. 2009)

Answers

B33.(*a*) **B34** (*a*) **B35.** (*c*) **B36.** (*b*) **B37.** (*a*) **B38.** (*d*) **B39.** (*c*) **B40.** (*c*) **B41.** (*a*) **B42.** (*c*)

Competition File

B43. Choose the amide which on reduction with $LiAlH_4$ yields a secondary amine

(*a*) Ethanamide

(*b*) N-Methyl ethanamide

(*c*) N, N-dimethyl ethanamide

(*d*) Phenyl methanamide

(*e*) Butanamide *(Kerala C.E.T. 2009)*

B44. Which one of the following is the correct order of increasing basic strength of nitrogen compounds in aqueous soultion?

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

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

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

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

(*e*) $C_2H_5NH_2 < C_6H_5NH_2 < NH_3 < (C_2H_5)_2NH < C_6H_5CH_2NH_2$ *(Kerala P.E.T. 2012)*

B45. Benzylamine is a stronger base than aniline because:

(*a*) The lone pair of electrons on the nitrogen atom in benzylamine is delocalised.

(*b*) The lone pair of electrons on the nitrogen atom in aniline is delocalised.

(*c*) The lone pair of electrons on the nitrogen atom in aniline is not involved in resonance.

(*d*) Benzylamine has a higher molecular mass than aniline *(Karnataka C.E.T 2012)*

B46. Which one of the following gives amine on heating with amide?

(*a*) Br_2 in aqueous KOH

(*b*) Br_2 in alcoholic KOH

(*c*) Cl_2 in sodium

(*d*) Sodium in ether. *(Karnataka CET 2013)*

B47. Positive carbylamine test is shown by

(*a*) N, N-dimethylaniline (*b*) triethylamine

(*c*) N-methylaniline (*d*) *p*-methylbenzylamine

(*e*) dimethylamine *(Kerala PET 2013)*

B48. The best reagent for converting 2-phenylpropanamide into 2-phenylpropanamine is

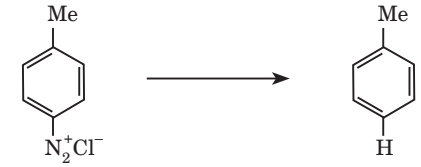
(*a*) Br_2 in aqueous NaOH

(*b*) excess of H_2

(*c*) iodine in the presence of red phosphorus

(*d*) $LiAlH_4$ in ether *(AMU Engg. 2013)*

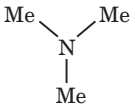
B49. The reagent with which the following reaction is best accomplished is

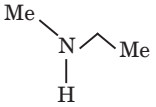


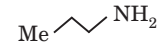
(*a*) H_3PO_2 (*b*) H_3PO_3

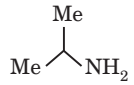
(*c*) H_3PO_4 (*d*) $NaHSO_3$ *(WB JEE 2014)*

B50. An amine C_3H_9N reacts with benzene sulphonyl chloride to form a white precipitate which is insoluble in aq. NaOH. The amine is

(*a*) 

(*b*) 

(*c*) 

(*d*) 

(WB JEE 2014)

B51. An aromatic compound A (C_7H_9N) on reacting with $NaNO_2$/HCl at 0°C forms benzyl alcohol and nitrogen gas. The number of isomers possible for the compound A is

(*a*) 5 (*b*) 7

(*c*) 3 (*d*) 6 *(Karnataka CET 2014)*

B52. One of the following amides will not undergo Hoffmann bromamide reaction

(*a*) $CH_3CONHCH_3$ (*b*) $CH_3CH_2CONH_2$

(*c*) CH_3CONH_2 (*d*) $C_6H_5CONH_2$

(Karnataka CET 2015)

B53. In the given series of reactions:

2-Bromopropane $\xrightarrow[\text{heat}]{\text{alc. AgCN}}$ X $\xrightarrow{LiAlH_4}$ Y

The IUPAC name of product Y is

(*a*) N-isopropylmethanamine

(*b*) N-methylpropan-2-amine

(*c*) N-methylpropanamine

(*d*) Butan-2-amine. *(Karnataka CET 2015)*

B54. Diethyl amine when treated with nitrous acid yields

(*a*) Diethyl ammonium nitrite

(*b*) Ethyl alcohol

(*c*) N-nitroso diethyl amine

(*d*) Triethyl ammonium nitrite *(MH- CET 2015)*

B55. The correct order of basicity of the following compounds is

1. 

2. 

3. 

4. 

(*a*) 1 < 2 < 3 < 4 (*b*) 1 < 2 < 4 < 3

(*c*) 2 < 1 < 3 < 4 (*d*) 4 < 3 < 2 < 1

(WB- JEE 2016)

Answers

B43. (*b*) **B44** (*b*) **B45.** (*b*) **B46.** (*a*) **B47.** (*d*) **B48.** (*d*) **B49.** (*a*) **B50.** (*b*) **B51.** (*a*) **B52.** (*a*)
B53. (*b*) **B54.** (*c*) **B55.** (*c*)

Competition File

B56. Which one of the following can be prepared by Gabriel phthalimide synthesis ?
(*a*) Aniline (*b*) *o*-Toluidine
(*c*) Benzylamine (*d*) N-Methylethanamine
(*e*) 4-Bromoaniline (*Kerala PET 2016*)

B57. 4-Nitrotoluene is treated with bromine to get compound 'P'. 'P' is reduced with Sn and HCl to get compound 'Q'. 'Q' is diazotised and the product is treated with phosphinic acid to get compound 'R'. 'R' is oxidized with alkaline $KMnO_4$ to get compound 'S'. Compound 'S' is
(*a*) 2-bromo-4-hydroxybenzoic acid
(*b*) benzoic acid
(*c*) 4-bromobenzoic acid
(*d*) 3-bromobenzoic acid
(*e*) 2-bromobenzoic acid (*Kerala PET 2016*)

B58. In the following sequence of reactions:

$$A \xrightarrow{\text{Reduction}} B \xrightarrow{HNO_2} CH_3CH_2OH$$

The compound A is
(*a*) propane nitrile (*b*) ethane nitrile
(*c*) nitromethane (*d*) methyl isocyanate.
(*Karnataka C.E.T. 2016*)

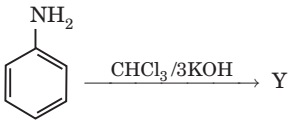
B59. An organic compound A on reduction gives compound B, which on reaction with trichloromethane and caustic potash forms C. The compound 'C' on catalytic reduction gives N-methyl benzenamine, the compound 'A' is
(*a*) nitrobenzene (*b*) nitromethane
(*c*) methanamine (*d*) benzenamine.
(*Karnataka C.E.T. 2016*)

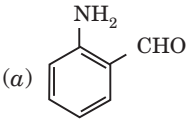
B60. The compound that would produce a nauseating smell/odour with a hot mixture of chloroform and ethanolic potassium hydroxide is
(*a*) $PhCONH_2$ (*b*) $PhNHCH_3$
(*c*) $PhNH_2$ (*d*) PhOH (*WB JEE 2017*)

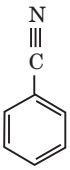
B61. Among Me_3N, C_5H_5N and MeCN (Me = methyl group), the electronegativity of N is in the order
(*a*) $MeCN > C_5H_5N > Me_3N$
(*b*) $C_5H_5N > Me_3N > MeCN$
(*c*) $Me_3N > MeCN > C_5H_5N$
(*d*) electronegativity is same in all. (*WB JEE 2017*)

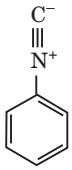
B62. The yield of acetanilide in the reaction (100% conversion) of 2 moles of aniline with 1 mole of acetic anhydride is
(*a*) 270 g (*b*) 135 g
(*c*) 67.5 g *d*) 177 g (*WB JEE 2017*)

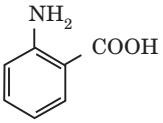
B63. The product Y for the below reaction is

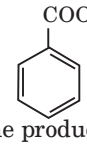


(*a*) 

(*b*) 

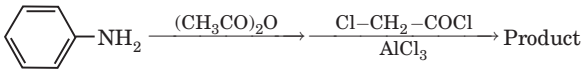
(*c*) 

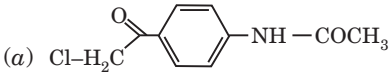
(*d*) 

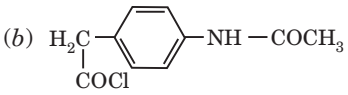
(*e*) 

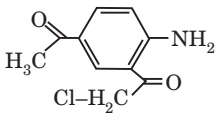
(*Kerala P.E.T. 2017*)

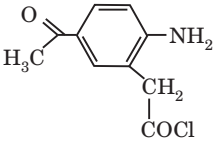
B64. The product formed in the following reaction is

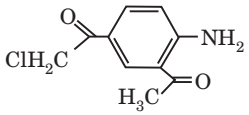


(*a*) 

(*b*) 

(*c*) 

(*d*) 

(*e*) 

(*Kerala P.E.T. 2017*)

B65. What product will form when N, N-dimethylaniline reacts with $NaNO_2$ and dilute HCl at low temperature?
(*a*) *p*-Nitroso-N, N-dimethylaniline
(*b*) Methyl-*n*-hexylamine
(*c*) *m*-Benzenediazonium chloride
(*d*) N-Nitroso-N-methylaniline
(*J.K. CET 2018*)

B66. Which of the following shows the correct reaction for nitrobenzene reduction?
(*a*) Nitrobenzene reacts with Zn dust and NH_4Cl to produce aniline.
(*b*) Nitrobenzene reacts with $LiAlH_4$ to produce phenyl hydroxylamine.
(*c*) Nitrobenzene reacts with Fe and HCl to produce nitrosobenzene.
(*d*) Nitrobenzene reacts with Zn dust and NH_4Cl to produce phenyl hydroxylamine.
(*J.K. CET 2018*)

Answers

B56.(*c*) **B57.** (*e*) **B58.** (*b*) **B59.** (*a*) **B60.** (*c*) **B61.** (*a*) **B62.** (*b*) **B63.** (*c*) **B64.** (*a*) **B65.** (*a*) **B66.** (*d*)

Competition File

B67. Identify the correct basicity order in the nitroanilines? (Symbols and notations carry their usual meaning)

(*a*) *o*-Nitroanilines < *p*-nitroanilines < *m*-nitroanilines

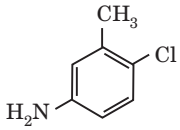
(*b*) *m*-Nitroanilines < *p*-nitroanilines < *o*-nitroanilines

(*c*) *p*-Nitroanilines < *o*-nitroanilines < *m*-nitroanilines

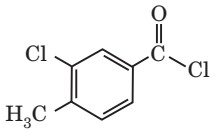
(*d*) *o*-Nitroanilines < *m*-nitroanilines < *p*-nitroanilines

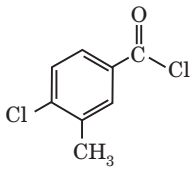
(*J.K. CET 2018*)

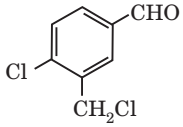
B68. Identify 'M' in the following sequence of reactions:

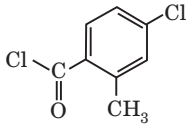
$C_8H_6Cl_2O \xrightarrow{NH_3} C_8H_8ClNO \xrightarrow[NaOH]{Br_2}$ 

(M)

(*a*) 

(*b*) 

(*c*) 

(*d*) 

(*WB JEE 2018*)

B69. If aniline is treated with conc. H_2SO_4 and heated at 200 °C, the product is

(*a*) anilinium sulphate

(*b*) benzenesulphonic acid

(*c*) *m*-aminobenzenesulphonic acid

(*d*) sulphanilic acid (*WB JEE 2018*)

B70. Which of the following is more basic than aniline?

(*a*) Diphenylamine (*b*) Triphenylamine

(*c*) *p*-Nitroaniline (*d*) Benzylamine

(*Karnataka CET 2018*)

B71. The reaction of benzenediazonium chloride with aniline yields yellow dye. The name of the yellow dye is

(*a*) *p*-hydroxyazobenzene (*b*) *p*-aminoazobenzene

(*c*) *p*-nitroazobenzene (*d*) *o*-nitroazobenzene

(*Karnataka CET 2018*)

B72. The nitrosation of N,N-dimethylaniline takes place through the attack of electrophile

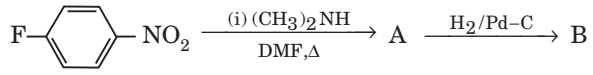
(*a*) nitronium ion (*b*) protonated nitrous acid

(*c*) nitrous acid (*d*) nitrite ion

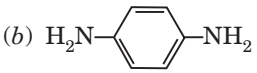
(*e*) nitrosonium ion.

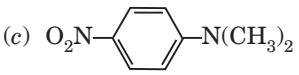
(*Kerala PET 2018*)

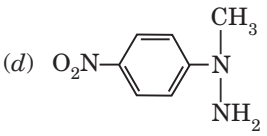
JEE (Advance) for IIT Entrance

B73. 

(*a*) 

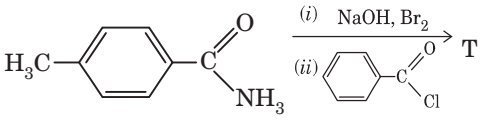
(*b*) 

(*c*) 

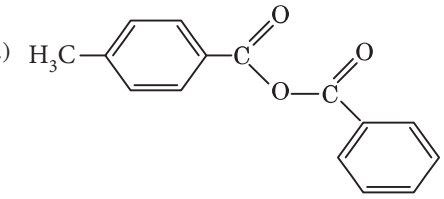
(*d*) 

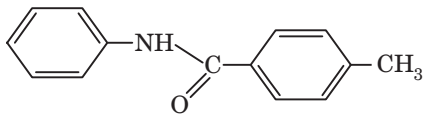
(*I.I.T. Screening 2003*)

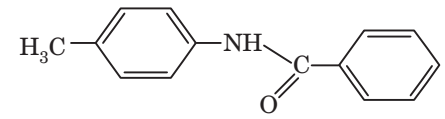
B74. In the reaction

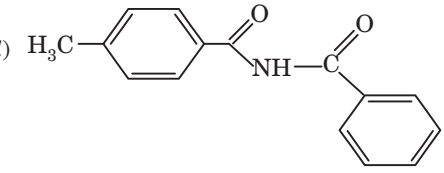


the structure of the product T is :

(*a*) 

(*b*) 

(*c*) 

(*d*) 

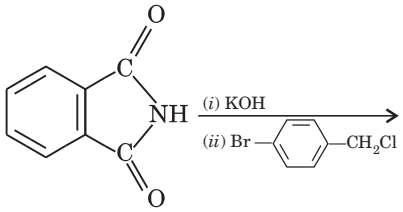
(*I.I.T. 2010*)

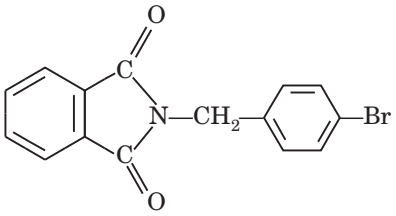
Answers

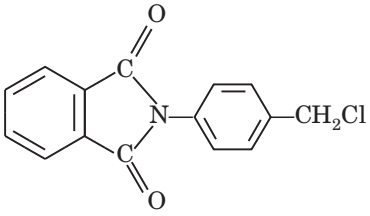
B67. (*a*) **B68.** (*b*) **B69.** (*d*) **B70.** (*d*) **B71.** (*b*) **B72** (*e*) **B73.** (*a*) **B74.** (*c*)

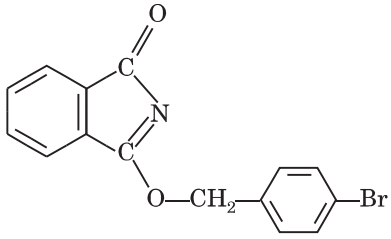
Competition File

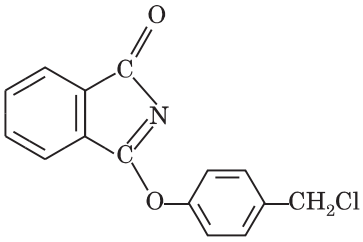
B75. The major product of the following reaction is



(a) 

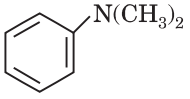
(b) 

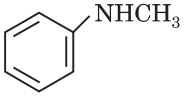
(c) 

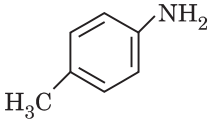
(d) 

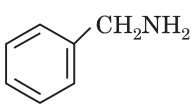
(I.I.T. 2011)

B76. 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) 

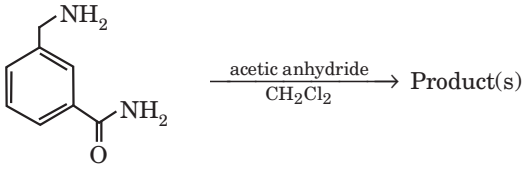
(b) 

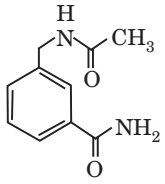
(c) 

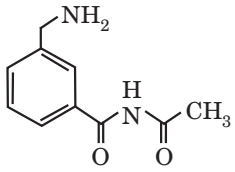
(d) 

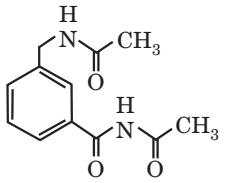
(I.I.T. 2011)

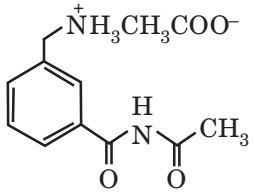
B77. In the reaction shown below, the major product(s) formed is/are



(a) 
 + CH_3COOH

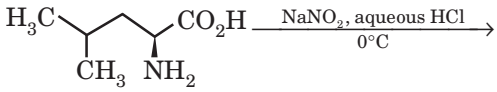
(b) 
 + CH_3COOH

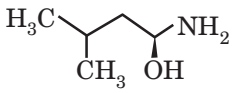
(c) 
 + H_2O

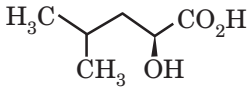
(d) 

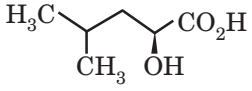
(JEE Advance 2014)

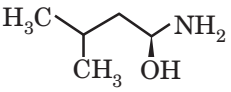
B78. The major product of the reaction is



(a) 

(b) 

c) 

(d) 

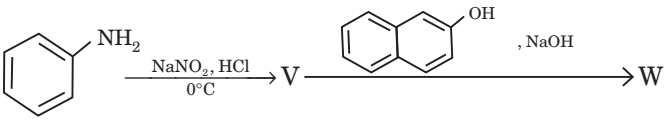
(JEE Advance 2015)

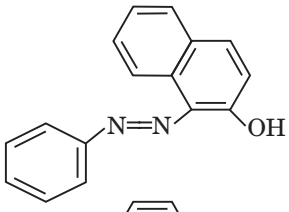
Answers

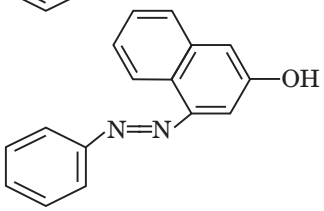
B75.(a) **B76.** (c) **B77** (a) **B78.** (c)

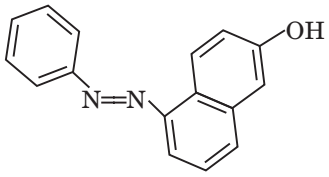
Competition File

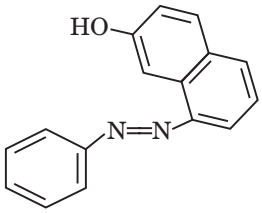
B79. In the following reactions, the major product W is



(*a*) 

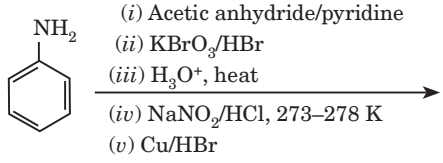
(*b*) 

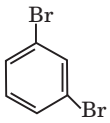
(*c*) 

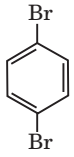
(*d*) 

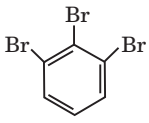
(JEE Advance 2015)

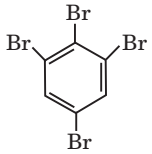
B80. The product(s) of the following reaction sequence is(are)



(*a*) 

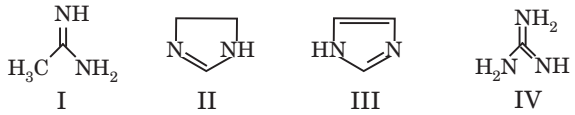
(*b*) 

(*c*) 

(*d*) 

(JEE Advance 2016)

B81. The order of basicity among the following compounds is

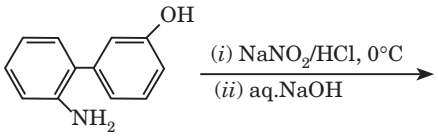


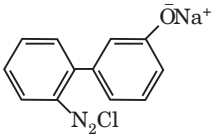
(*a*) IV > II > III > I (*b*) II > I > IV > III

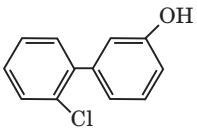
(*c*) I > IV > III > II (*d*) IV > I > II > III

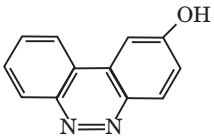
(JEE Advance 2017)

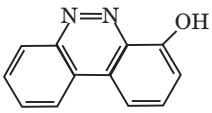
B82. The major product of the following reaction is



(*a*) 

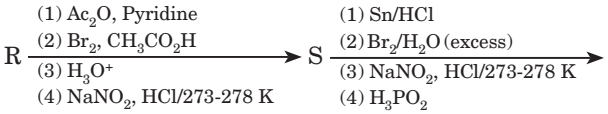
(*b*) 

(*c*) 

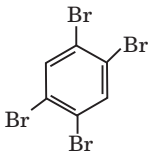
(*d*) 

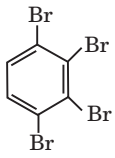
(JEE Advance 2017)

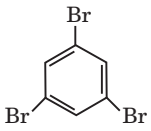
B83. Aniline reacts with mixed acid (conc. HNO_3 and conc. H_2SO_4) at 288 K to give P (51%), Q (47%) and R (2%). The major product(s) of the following reaction sequence is (are)

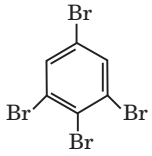


Major product(s)

(*a*) 

(*b*) 

(*c*) 

(*d*) 

(JEE Advance 2018)

Answers

B79.(*a*) **B80.** (*b*) **B81.** (*d*) **B82.** (*c*) **B83.** (*d*)

Competition File

C MULTIPLE CHOICE QUESTIONS
with more than one correct answers

C1. Examine the following structures for anilinium ion and choose the correct statement from the following :

I II

(*a*) II is an acceptable canonical structure because carbonium ions are less stable than ammonium ions.
(*b*) II is not an acceptable canonical structure because it is not aromatic.
(*c*) II is not acceptable cononical structure because the nitrogen has ten valence electrons.
(*d*) II is an acceptable cononical structure.

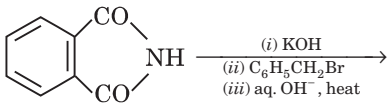
C2. A positive Carbylamine test is given by
(*a*) N, N- Dimethyl aniline
(*b*) 2, 4-Dimethyl aniline
(*c*) N-Methyl-o-methyl aniline
(*d*) *p*-Methyl benzylamine

C3. Which of the following reactions form benzylamine ?

(*a*) $C_6H_5CONH_2 \xrightarrow[\text{Ether}]{LiAlH_4}$

(*b*) $C_6H_5CONH_2 \xrightarrow{NaOBr}$

(*c*) $C_6H_5CN \xrightarrow{H^+, H_2O}$

(*d*) 

C4. Reaction of $RCONH_2$ with a mixture of Br_2 and KOH gives RNH_2 as the main product. The intermediates involved in the reaction are :
(*a*) RCONHBr (*b*) R—NHBr
(*c*) R—N=C=O (*d*) $RCONBr_2$

C5. Which reagents among the following can affect the conversion ?
$CH_3C \equiv N \longrightarrow CH_3CH_2NH_2$
(*a*) H_2, Pt (*b*) Ammoniacal $AgNO_3$
(*c*) $LiAlH_4$ (*d*) $NaBH_4$

C6. Which of the following amines undergo acylation reaction ?
(*a*) $CH_3CH_2NH_2$ (*b*) $C_6H_5NH_2$
(*c*) $(CH_3CH_2)_2NH$ (*d*) $(CH_3)_3N$

C7. In which of the following amines, the first has lower pK_b value than the second ?
(*a*) Aniline, *m*-nitro aniline
(*b*) *m*-Toluidine, *p*-toluidine
(*c*) Aniline, *p*-chloroaniline
(*d*) Aniline, *p*-aminophenol

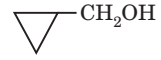
C8. $2X + B_2H_6 \longrightarrow [BH_2(X)_2]^+ [BH_4]^-$
The amine(s) X is/are
(*a*) NH_3 (*b*) CH_3NH_2
(*c*) $(CH_3)_2NH$ (*d*) $(CH_3)_3N$ *(I.I.T. 2009)*

C9. The reduction of benzene diazonium chloride to phenyl hydrazine can be accomplished by
(*a*) $SnCl_2$, HCl (*b*) Na_2SO_3
(*c*) CH_3CH_2OH (*d*) H_3PO_2 *(WB JEE 2017)*

C10. The possible product(s) to be obtained from the reaction of cyclobutyl amine with HNO_2 is/are

(*a*) 

(*b*) 

(*c*) 

(*d*) $H_2C=CH_2$ *(WB JEE 2018)*

Answers

C1. (*a, c*) **C2.** (*b, d*) **C3.** (*a, d*) **C4.** (*a, c*) **C5.** (*a, c*) **C6.** (*a, b, c*) **C7.** (*a, c*) **C8.** (*a,b,c*)
C9. (*a, b*) **C10.** (*a, c*)

D MULTIPLE CHOICE QUESTIONS
based on the given passage/comprehension

Passage I

Amines are basic in nature due to the presence of lone pair of electrons on N atom of $-NH_2$ group. The basic strength of amines can be expressed by their dissociation constant, K_b or pK_b.

$$RNH_2 + H_2O \longrightarrow R\,NH_3^+ + OH^-$$

$$K_b = \frac{[RNH_3^+][OH^-]}{[RNH_2]} \text{ and } pK_b = -\log K_b$$

Greater the K_b value or smaller the pK_b value, more is the basic strength of amine. Aliphatic amines are stronger bases than ammonia due to the electron releasing effect of alkyl groups. The basic strength among amines decreases as :

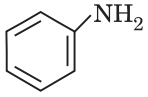
$$2° > 1° > 3°$$

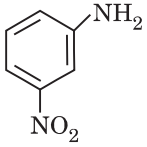
Aryl amines such as aniline are less basic than aliphatic amines due to the involvement of lone pair of electrons on N atom with the resonance in benzene. In derivatives of aniline, the electron releasing groups increase the basic strength while electron withdrawing groups decrease the basic strength. The base weakening effect of electron withdrawing group and base strengthening effect of electron releasing group is more marked at *p*-position than at *m*-position. Every *o*- substituted aniline is less basic than aniline due to *ortho* effect.

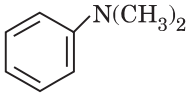
Competition File

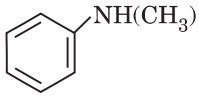
Answer the following questions :

D1. Which of the following has lowest pK_b value ?

(*a*) 

(*b*) 

(*c*) 

(*d*) 

D2. Which of the following statement is not correct ?

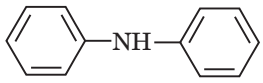
(*a*) Ethylamine is more basic than aniline

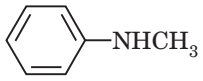
(*b*) *o*-methylaniline has lower pK_b value than aniline

(*c*) *p*-methylaniline is less basic than *m*-methylaniline

(*d*) Aniline has lower pK_b value than *o*-nitroaniline

D3. Maximum pK_b value is of

(*a*) $(CH_3CH_2)_2NH$ (*b*) 

(*c*) $(CH_3)_2NH$ (*d*) 

D4. The strongest base among the following is

(*a*) $C_6H_5NH_2$ (*b*) $p\text{-}NO_2C_6H_4NH_2$

(*c*) $m\text{-}NO_2—C_6H_4NH_2$ (*d*) $C_6H_5CH_2NH_2$

D5. Which of the following group does not decrease the basic strength of aniline ?

(*a*) $—OCH_3$ (*b*) $—NO_2$

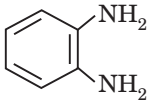
(*c*) —CN (*d*) —halogen

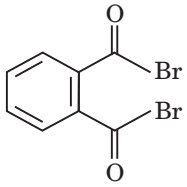
Passage II

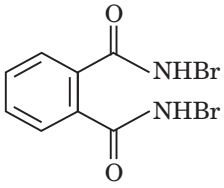
Treatment of compound O with $KMnO_4/H^+$ gave P, which on heating with ammonia gave Q. The compound Q on treatment with Br_2/NaOH produced R. On strong heating, Q gave S, which on further treatment with ethyl 2-bromopropanoate in the presence of KOH followed by acidification, gave a compound T.

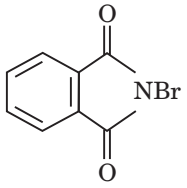
Answer the following questions :

D6. The compound R is

(*a*) 

(*b*) 

(*c*) 

(*d*) 

D7. The compound T is

(*a*) glycine (*b*) alanine

(*c*) valine (*d*) serine *(JEE Advance 2016)*

Assertion Reason Type Questions

The questions given below consist of an Assertion and a Reason. Use the following key to choose the appropriate answer.

(*a*) If both assertion and reason are CORRECT and reason is the CORRECT explanation of the assertion.

(*b*) If both assertion and reason are CORRECT, but reason is NOT THE CORRECT explanation of the assertion.

(*c*) If assertion is CORRECT but reason is INCORRECT.

(*d*) If assertion is INCORRECT but reason is CORRECT.

(*e*) If both assertion and reason are INCORRECT.

1. Assertion: *n*-Propylamine has higher boiling point than trimethylamine.

Reason : Among *n*-propylamine molecules, there is hydrogen bonding but there is no hydrogen bonding in trimethylamine.

2. Assertion : Aniline does not undergo Friedel Crafts reaction.

Reason : Friedel Crafts reaction is an electrophilic substitution reaction.

3. Assertion: Aniline is a weaker base than ammonia.

Reason : Aniline is resonance stabilized.

4. Assertion: Carbylamine reaction involves the reaction between 1° amine and chloroform in the presence of alkali.

Reason : In carbylamine reaction, $—NH_2$ group changes to —NC group.

Answers

D1. (*c*) **D2.** (*c*) **D3.** (*b*) **D4.** (*d*) **D5.** (*a*) **D6.** (*a*) **D7.** (*b*)

Competition File

5. Assertion: Tertiary amines undergo acylation reaction.
Reason : Tertiary amines have replaceable H atom.

6. Assertion : Aniline hydrogen sulphate, on heating forms a mixture of *ortho* and *para* aminosulphonic acids.
Reason : The sulphonic acid group is electron withdrawing group.

7. Assertion: Ammonolysis of alkyl halides involves reaction between alkyl halides and alcoholic ammonia.
Reason : Ammonolysis of alkyl halides mainiy produces 2° amines.

8. Assertion: Sulphonilic acid has high melting point and is practically insoluble in water.
Reason : Sulphanilic acid exists as zwitter ion salt.

9. Assertion: Alkyl cyanides and alkyl isocyanides have much higher boiling points than corresponding alkyl halides.
Reason : Cyanides and isocyanides are much more polar than alkyl halides.

10. Assertion : *p*-nitro aniline is a stronger base than *p*-toluidine.
Reason : The electron withdrawing —NO_2 group in *p*-nitroaniline makes it a stronger base.

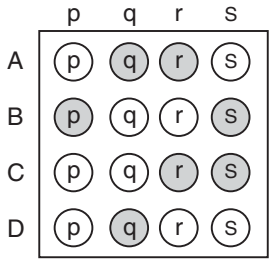
Answers

1. (*a*) **2.** (*b*) **3.** (*b*) **4.** (*a*) **5.** (*e*) **6.** (*b*) **7.** (*c*) **8.** (*a*) **9.** (*a*) **10.** (*e*)

Matrix Match Type Questions

Each question contains statements given in two columns, which have to be matched. Statements in Column I are labelled as A, B, C and D whereas statements in Column II are labelled as *p*, *q*, *r* and *s*. Match the entries of Column I with appropriate entries of Column II. Each entry in Column I may have one or more than one correct option from Column II. The answers to these questions have to be appropriately bubbled as illustrated in the following example.

If the correct matches are A-*q*, A-*r*, B-*p*, B-*s*, C-*r*, C-*s* and D-*q*, then the correctly bubbled matrix will look like the following:



1. Match the compounds in Column I with their properties/ reactions in Column II.

Column I	Column II
(A) $CH_3CH_2CH_2CN$	(*p*) Reduction with Pd—C/H_2
(B) $CH_3CH_2OCOCH_3$	(*q*) Reduction with $SnCl_2$/HCl
(C) CH_3–CH=CH–CH_2OH	(*r*) Development of foul smell on treatment with KOH and $CHCl_3$
(D) $H_3CH_2CH_2CH_2NH_2$	(*s*) Reduction with diisobutyl aluminium hydride (DIBAL–H)
	(*t*) Alkaline hydrolysis

2. Match the reaction in column-I with product formed in column-II

Column-I	Column-I
(A) Gabriel phthalimide reaction	(*p*) $CH_3CH_2NH_2$
(B) Reaction product of 1° amine with alcoholic KOH and $CHCl_3$	(*q*) $C_6H_5NH_2$
(C) Reaction product of nitrogen containing compound with $LiAlH_4$	(*r*) $C_6H_5CH_2NH_2$
(D) Reaction product of 1° amides with Br_2 and KOH	(*s*) C_6H_5NC

Answers

(1) : (A) (*p*), (*q*), (*s*), (*t*) (B) (*p*), (*s*), (*t*) (C) *p*) (D) (*r*)

(2) : (A) (*p*), (*r*) (B) (*s*) (C) (*p*),(*r*) D) (*p*), (*q*),(*r*)

Competition File

Integer Type or Numerical Value Type Questions

Integer Type: The answer to each of the following question is a **single-digit**-integer ranging from 0 to 9.

1. The number of isomeric amines corresponding to molecular formula C_3H_9N, which liberate N_2 gas on treatment with nitrous acid is

2. The number of amines having pK_b less than $C_6H_5NH_2$ among the following is

p-$CH_3C_6H_4NH_2$, *o*-$CH_3C_6H_4NH_2$, *m*-$CH_3C_6H_4NH_2$, $C_6H_5N(CH_3)_2$, $C_6H_5NHCH_3$, *p*-$NO_2C_6H_4NH_2$, *p*-$ClC_6H_4NH_2$, $C_6H_5CH_2NH_2$

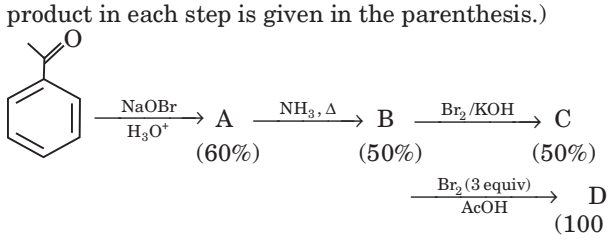
3. The number of isomeric amines of formula C_7H_9N having a benzene ring is

4. The number of isomeric amines of molecular formula $C_4H_{11}N$ which give carbylamine reaction is

5. Total number of nitrogen atoms present in reduced product obtained by reducing nitrobenzene with $LiAlH_4$ followed by aqueous work up is

Numerical Value Type: Give the correct numerical value (in decimal notation truncated/rounded off to the second decimal place).

6. In the following reaction sequence, the amount of D (in g) formed from 10 moles of acetophenone is _____ (Atomic weights in g mol^{-1} : H = 1, C = 12, N = 14, O = 16, Br = 80. (The yield (%) corresponding to the product in each step is given in the parenthesis.)



(JEE Advance 2018)

Answers

1. (2) **2.** (5) **3.** (5) **4.** (3) **5.** (2) **6.** (495.00)

NCERT Exemplar Problems

Objective Questions

Multiple Choice Questions (Type-I)

1. Which of the following is a 3° amine?

(*a*) 1-methylcyclohexylamine

(*b*) Triethylamine

(*c*) *tert*-butylamine

(*d*) N-methylaniline

2. The correct IUPAC name for $CH_2{=}CHCH_2\ NHCH_3$ is

a) Allylmethylamine

(*b*) 2-amino-4-pentene

(*c*) 4-aminopent-1-ene

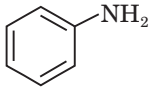
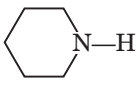
(*d*) N-methylprop-2-en-1-amine

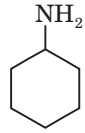
3. Amongst the following, the strongest base in aqueous medium is _____.

(*a*) CH_3NH_2 *b*) $NCCH_2NH_2$

c) $(CH_3)_2NH$ (*d*) $C_6H_5NHCH_3$

4. Which of the following is the weakest Brönsted base?

(*a*)  (*b*) 

c)  (*d*) CH_3NH_2

5. Benzylamine may be alkylated as shown in the following equation :

$C_6H_5CH_2NH_2 + R{-}X \longrightarrow C_6H_5CH_2NHR$

Which of the following alkyl halide is best suited for this reaction through S_N1 mechanism?

(*a*) CH_3Br (*b*) C_6H_5Br

c) $C_6H_5CH_2Br$ (*d*) C_2H_5Br

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

(*a*) H_2(excess)/Pt (*b*) $LiAlH_4$ in ether

(*c*) Fe and HCl (*d*) Sn and HCl

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

(*a*) Sodium amide, $NaNH_2$

b) Sodium azide, NaN_3

(*c*) Potassium cyanide, KCN

(*d*) Potassium phthalimide, $C_6H_4(CO)_2N^-K^+$

Answers

1 (*b*) **2.** (*d*) **3.** (*c*) **4.** (*a*) **5.** (*c*) **6** (*b*) **7.** (*c*)

Competition File

8. The source of nitrogen in Gabriel synthesis of amines is _____.
(*a*) Sodium azide, NaN_3
(*b*) Sodium nitrite, $NaNO_2$
(*c*) Potassium cyanide, KCN
(*d*) Potassium phthalimide, $C_6H_4(CO)_2N^-K^+$

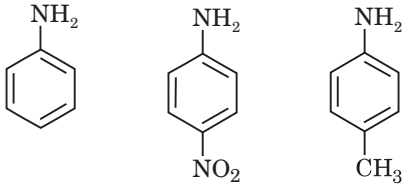
9. Amongst the given set of reactants, the most appropriate for preparing 2° amine is _____.
(*a*) 2° R—Br + NH_3
(*b*) 2° R—Br + NaCN followed by H_2/Pt
(*c*) 1° R—NH_2 + RCHO followed by H_2/Pt
(*d*) 1° R—Br (2 mol) + potassium phthalimide followed by H_3O^+/heat

10. The best reagent for converting 2–phenylpropanamide into 2-phenylpropanamine is _____.
(*a*) excess H_2
(*b*) Br_2 in aqueous NaOH
(*c*) iodine in the presence of red phosphorus
(*d*) $LiAlH_4$ in ether

11. The best reagent for converting, 2-phenyl propanamide into 1- phenylethanamine is ____.
(*a*) excess H_2/Pt (*b*) NaOH/Br_2
(*c*) $NaBH_4$/methanol (*d*) $LiAlH_4$/ether

12. Hoffmann bromamide degradation reaction is shown by _____.
(*a*) $ArNH_2$ (*b*) $ArCONH_2$
(*c*) $ArNO_2$ (*d*) $ArCH_2NH_2$

13. The correct increasing order of basic strength for the following compounds is _____.



(I) II) III)

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

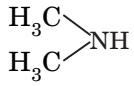
14. Methylamine reacts with HNO_2 to form _____.
(*a*) CH_3—O—N=O (*b*) CH_3—O—CH_3
(*c*) CH_3OH (*d*) CH_3CHO

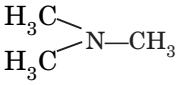
15. The gas evolved when methylamine reacts with nitrous acid is _____.
(*a*) NH_3 (*b*) N_2
(*c*) H_2 (*d*) C_2H_6

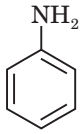
16. In the nitration of benzene using a mixture of conc. H_2SO_4 and conc. HNO_3, the species which initiates the reaction is _____.
(*a*) NO_2 (*b*) NO^+
(*c*) NO_2^+ (*d*) NO_2^-

17. Reduction of aromatic nitro compounds using Fe and HCl gives _____.
(*a*) aromatic oxime
(*b*) aromatic hydrocarbon
(*c*) aromatic primary amine
(*d*) aromatic amide

18. The most reactive amine towards dilute hydrochloric acid is _____.

(*a*) CH_3—NH_2 (*b*) 

(*c*) 

(*d*) 

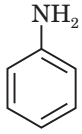
19. Acid anhydrides on reaction with primary amines give _____.
(*a*) amide (*b*) imide
(*c*) secondary amine (*d*) imine

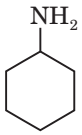
20. The reaction $Ar\overset{+}{N}_2Cl^- \xrightarrow{Cu/HCl} ArCl + N_2 + CuCl$ is named as _____.
(*a*) Sandmeyer reaction
(*b*) Gattermann reaction
(*c*) Claisen reaction
(*d*) Car lamine reaction

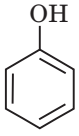
21. Best method for preparing primary amines from alkyl halides without changing the number of carbon atoms in the chain is
(*a*) Hoffmann Bromamide reaction
(*b*) Gabriel phthalimide synthesis
(*c*) Sandmeyer reaction
(*d*) Reaction with NH_3

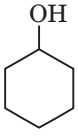
22. Which of the following compound will not undergo azo coupling reaction with benzene diazonium chloride.
(*a*) Aniline (*b*) Phenol
(*c*) Anisole (*d*) Nitrobenzene

23. Which of the following compounds is the weakest Bronsted base?

(*a*) 

(*b*) 

(*c*) 

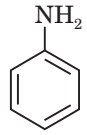
(*d*) 

Answers

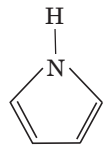
8. (*d*) **9.** (*c*) **10.** (*d*) **11.** (*b*) **12.** (*b*) **13.** (*d*) **14.** (*c*) **15.** (*b*) **16.** (*c*) **17.** (*c*) **18.** (*b*)
19. (*a*) **20.** (*b*) **21.** (*b*) **22.** (*d*) **23.** (*c*)

Competition File

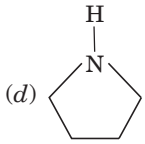
24 Among the following amines, the strongest Bronsted base is _____.



(*a*) (*b*) NH_3



(*c*)



(*d*)

25. The correct decreasing order of basic strength of the following species is _____.

H_2O, NH_3, OH^-, NH_2^-

(*a*) $NH_2^- > OH^- > NH_3 > H_2O$

(*b*) $OH^- > NH_2^- > H_2O > NH_3$

(*c*) $NH_3 > H_2O > NH_2^- > OH^-$

(*d*) $H_2O > NH_3 > OH^- > NH_2^-$

26. Which of the following should be most volatile?

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

(III) CH_3CH_2, CH_3 >NH (IV) $CH_3CH_2CH_3$

(*a*) II (*b*) IV

(*c*) I (*d*) III

27. Which of the following methods of preparation of amines will give same number of carbon atoms in the chain of amines as in the reactant?

(*a*) Reaction of nitrite with $LiAlH_4$.

(*b*) Reaction of amide with $LiAlH_4$ followed by treatment with water.

(*c*) Heating alkylhalide with potassium salt of phthalimide followed by hydrolysis.

(*d*) Treatment of amide with bromine in aqueous solution of sodium hydroxide.

Answers

24. (*d*) **25.** (*a*) **26.** (*b*) **27.** (*c*)

Multiple Choice Questions (Type-II)

Note : *In the following questions two or more options may be correct.*

28. Which of the following cannot be prepared by Sandmeyer's reaction?

(*a*) Chlorobenzene (*b*) Bromobenzene

(*c*) Iodobenzene (*d*) Fluorobenzene

29. Reduction of nitrobenzene by which of the following reagent gives aniline?

(*a*) Sn/HCl (*b*) Fe/HCl

(*c*) H_2-Pd (*d*) Sn/NH_4OH

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

(*a*) R—NC (*b*) $CHCl_3$

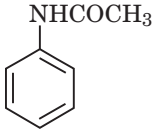
(*c*) $COCl_2$ (*d*) $NaNO_2$ + HCl

31. The reagents that can be used to convert benzenediazonium chloride to benzene are _____.

(*a*) $SnCl_2/HCl$ *b*) CH_3CH_2OH

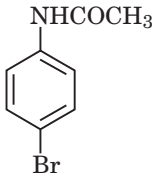
(*c*) H_3PO_2 (*d*) $LiAlH_4$

32. The product of the following reaction is _____.

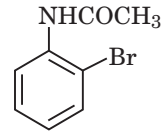


+ Br_2/CH_3COOH

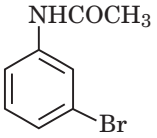
(*a*)



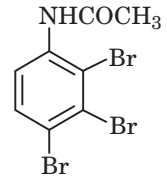
(*b*)



(*c*)

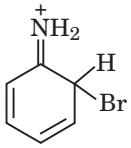


(*d*)

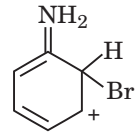


33. Arenium ion involved in the bromination of aniline is _____.

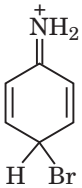
(*a*)



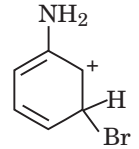
(*b*)



(*c*)



(*d*)



Answers

28. (*c*), (*d*) **29.** (*a*), (*b*), (*c*) **30.** (*a*), (*b*) **31.** (*b*), (*c*) **32.** (*a*), (*b*) **33.** (*a*), (*b*), (*c*)

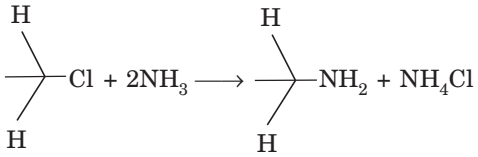
Competition File

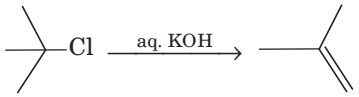
34. Which of the following amines can be prepared by Gabriel synthesis.

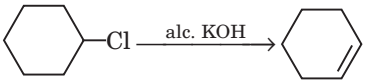
(*a*) Isobutyl amine (*b*) 2-Phenylethylamine

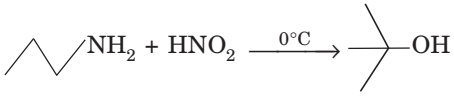
c) N-methylbenzylamine *d*) Aniline

35. Which of the following reactions are correct?

(*a*) 

(*b*) 

(*c*) 

(*d*) 

36. Under which of the following reaction conditions, aniline gives *p*-nitro derivative as the major product?

(*a*) Acetyl chloride/pyridine followed by reaction with conc. H_2SO_4 + conc. HNO_3.

(*b*) Acetic anhydride/pyridine followed by conc. H_2SO_4 + conc. HNO_3.

(*c*) Dil. HCl followed by reaction with conc. H_2SO_4 + conc. HNO_3.

(*d*) Reaction with conc. HNO_3 + conc.H_2SO_4.

37. Which of the following reactions belong to electrophilic aromatic substitution?

(*a*) Bromination of acetanilide

(*b*) Coupling reaction of aryldiazonium salts

(*c*) Diazotisation of aniline

(*d*) Acylation of aniline

Answers

34. (*a*), (*b*) **35.** (*a*), (*c*) **36.** (*a*), (*b*) **37.** (*a*), (*b*)

Matching Type Questions

Note : *Match the items of Column I and Column II in the following questions.*

38. Match the reactions given in Column I with the statements given in Column II.

Column I	Column II
(*a*) Ammonolysis	(*i*) Amine with lesser number of carbon atoms.
b) Gabriel phthalimide synthesis	(*ii*) Detection test for primary amines.
(*c*) Hoffmann Bromamide reaction	(*iii*) Reaction of phthalimide with KOH and R—X.
(*d*) Carbylamine reaction with NH_3.	(*iv*) Reaction of alkylhalides

39. Match the compounds given in Column I with the items given in Column II.

Column I	Column II
(*a*) Benzene sulphonyl chloride	(*i*) Zwitter ion
(*b*) Sulphanilic acid	(*ii*) Hinsberg reagent
(*c*) Alkyl diazonium salts	(*iii*) Dyes
(*d*) Aryl diazonium salts	(*iv*) Conversion to alcohols

Answers

38. (*a*) — (*iv*); (*b*) — (*iii*); (*c*) — (*i*); (*d*) — (*ii*)

39. (*a*) — (*ii*); (*b*) — (*i*); (*c*) — (*iv*); (*d*) — (*iii*).

Assertion and Reason Type Questions

Note : *In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.*

(*a*) *Both assertion and reason are wrong.*

(*b*) *Both assertion and reason are correct statements but reason is not correct explanation of assertion.*

(*c*) *Assertion is correct statement but reason is wrong statement.*

(*d*) *Both assertion and reason are correct statements and reason is correct explanation of assertion.*

(*e*) *Assertion is wrong statement but reason is correct statement.*

Competition File

40. **ssertion :** Acylation of amines gives a monosubstituted product whereas alkylation of amines gives polysubstituted product.
Reason : Acyl group sterically hinders the approach of further acyl groups.

41. **Assertion :** Hoffmann bromamide reaction is given by primary amines.
Reason : Primary amines are more basic than secondary amines.

42. **ssertion :** N-Ethylbenzene sulphonamide is soluble in alkali.
Reason : Hydrogen attached to nitrogen in sulphonamide is strongly acidic.

43. **Assertion :** N, N-Diethylbenzene sulphonamide is insoluble in alkali.
Reason : Sulphonyl group attached to nitrogen atom is strong electron withdrawing group.

44. **Assertion :** Only a small amount of HCl is required in the reduction of nitro compounds with iron scrap and HCl in the presence of steam.
Reason : $FeCl_2$ formed gets hydrolysed to release HCl during the reaction.

45. **Assertion :** Aromatic 1° amines can be prepared by Gabriel phthalimide synthesis.
Reason : Aryl halides undergo nucleophilic substitution with anion formed by phthalimide.

46. **ssertion :** Acetanilide is less basic than aniline.
Reason : Acetylation of aniline results in decrease of electron density on nitrogen.

Answers

40. (*c*) **41.** (*c*) **42.** (*d*) **43.** (*b*) **44.** (*d*) **45.** (*a*) **46.** (*d*)

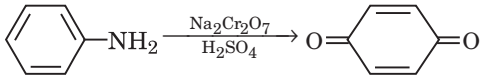
Hints & Explanations for *Difficult Objective Type Questions*

A. *mcq with only one correct answer*

A2. (*a*) : Only primary amines give carbylamine reaction.

A3. (*d*) : $C_6H_5NH_2 + C_6H_5CHO \longrightarrow \underset{\text{Schiff's base}}{C_6H_5N{=}CHC_6H_5} + H_2O$
Benzaldehyde

A4. (*c*) : $R{-}N{\equiv}C \xrightarrow[\text{reduction}]{4[H]} \underset{\text{sec-amine}}{RNHCH_3}$

A5. (*d*) : 

Benzoquinone

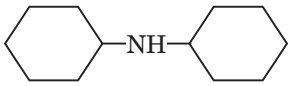
A6. (*b*) : $C_2H_5NH_2 + HONO \longrightarrow C_2H_5OH + N_2 + H_2O$

A8. (*b*) : Only primary amines give carbylamine reaction.

A9. (*c*) : $-NH_2$ group is protected by acetylation by reacting with CH_3COCl.

A11. (*c*) : $AgCl + 2CH_3NH_2 \longrightarrow \underset{\text{soluble}}{[Ag(CH_3NH_2)_2]^+ Cl^-}$

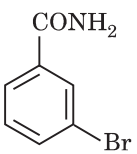
A12. (*b*) : $(C_2H_5)_2NH + HONO \longrightarrow (C_2H_5)_2N{-}N{=}O + H_2O$

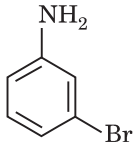
A13. (*c*) : 

is least basic and therefore has maximum value of pK_b.

A15. (*b*) : $CH_3CH_2NH_2 + CHCl_3 + 3KOH\ (alc.) \longrightarrow CH_3CH_2NC + 3KCl + 3H_2O$

A16. (*d*) : $CH_3CONH_2 + Br_2 + 4\ KOH \longrightarrow CH_3NH_2 + 2\ KBr + K_2CO_3 + 2H_2O$

A17 (*b*) : 

$+ Br_2 + 4KOH \longrightarrow$ 

$+ 2KBr + K_2CO_3 + 2H_2O$
m-Bromoaniline

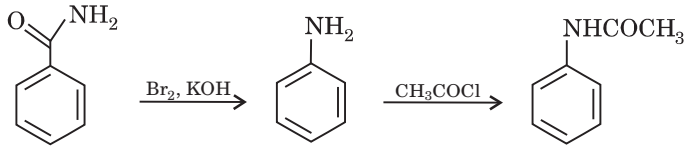
A18. (*c*) : $\underset{\text{Alkyl isothiocyanate}}{R{-}N{=}C{=}S} + HgS + 2HCl$

This reaction is called Hoffmann mustard oil reaction.

Competition File

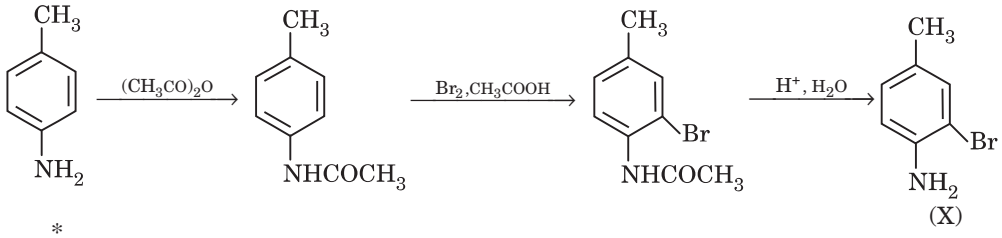
A1 (*c*) : *Refer A.18.* Phenyl isothiocyanate.

A20 (*b*) :



A21 (*d*) : Because it is primary amine.

A22. (*b*) :



(X)

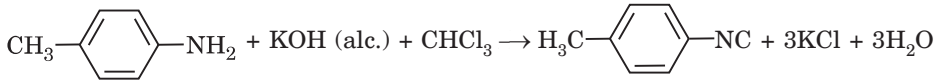
A23. (*b*) : $CH_3\overset{*}{C}HCH_2CH_2CH_3$ (2 – Aminopentane)

NH_2

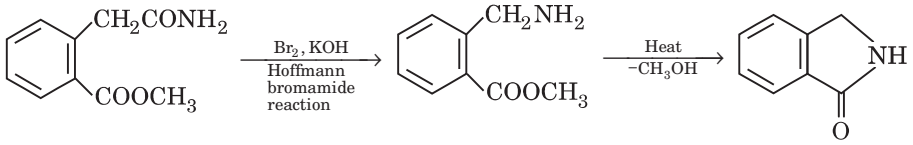
A25. (*d*) : Sandmeyer's reaction with chloroaniline gives *p*-dichlorobenzene which is solid (m.p. 325 K) while that with anilinium chloride gives chlorobenzene, which is liquid (m.p. 405 K). Anilinium hydrochloride is an acid salt and therefore, liberates CO_2 with $NaHCO_3$ and gives white ppt. of AgCl with $AgNO_3$. However, both are primary amines and give carbylamine test and therefore, cannot be distinguished.

A26. (*a*) : $CH_3CH_2Cl \xrightarrow{NaCN} CH_3CH_2CN \xrightarrow{Ni,H_2} CH_3CH_2NH_2 \xrightarrow{(CH_3CO)_2O} CH_3CH_2NHCOCH_3$

A27. (*a*) :



A28. (*d*) :



A29. (*a*) : Primary amines form benzene sulphonamides which are soluble in alkalies.

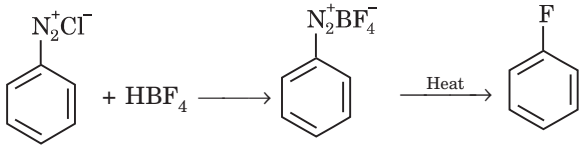
A30. (*d*) : Secondary amines can be prepared by reduction of isonitriles.

$R–N\equiv C \xrightarrow{4[H]} RNHCH_3$

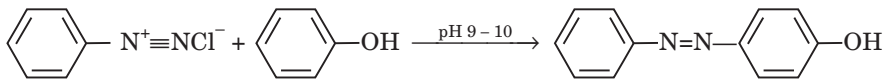
Isonitrile 2°–Amine

A31. (*c*) : Aromatic diazonium salts are more stable than aliphatic diazonium salts because of resonance.

A32. (*c*) :

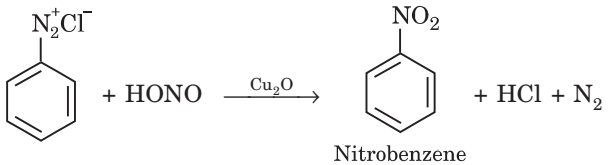


A34. (*b*) :



p-Hydroxyazobenzene

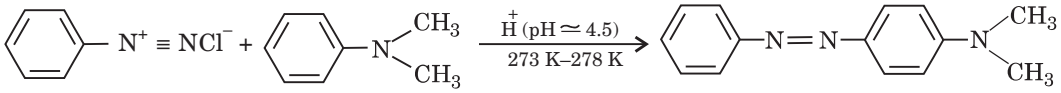
A35. (*c*) :



Nitrobenzene

Competition File

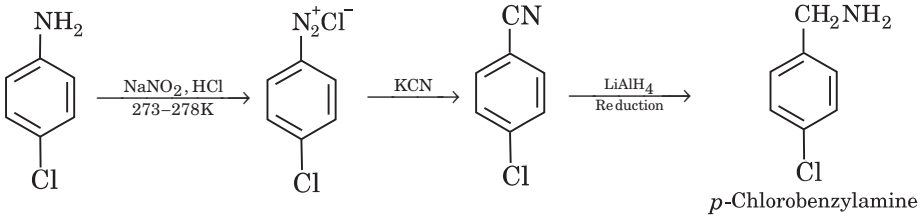
A37. (*b*) :



Dimethylaniline

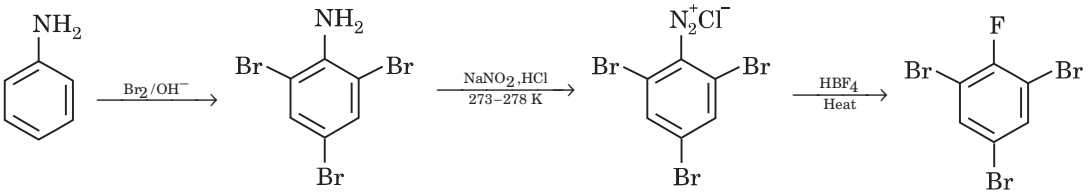
A38. (*d*) : Electron releasing groups increase the stability of diazonium cations by dispersing the positive charge on the N-atom.

A39. (*a*) :



p-Chlorobenzylamine

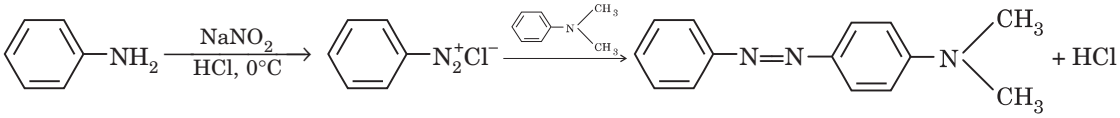
A40. (*c*) :



B. *mcq from Competitive Examinations*

B1. (*a*) : Methylisocyanide on reduction with $LiAlH_4$ gives dimethylamine, which is a secondary amine.

B2. (*c*) :



B3. (*d*) : Secondary aliphatic and aromatic amines react with nitrous acid to form N-nitrosoamine.

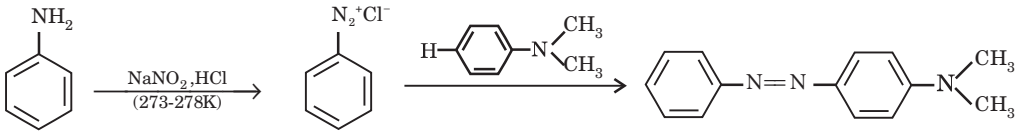
B4. (*b*) : $HNO_3 + H_2SO_4 \longrightarrow NO_2^+ + H_2O + HSO_4^-$

Here HNO_3 loses OH^- to give NO_2^+. Hence it acts as a base.

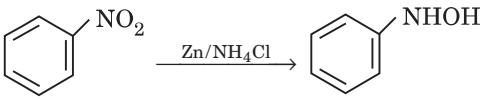
B5. (*c*) : $CH_3—\underset{\underset{O}{\|}}{C}—NH_2 \xrightarrow[Br_2]{NaNO_2} CH_3NH_2$

This reaction is Hoffmann degradation reaction.

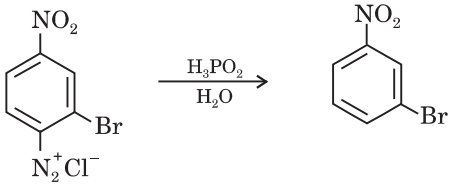
B6. (*c*) :



B8. (*a*) :

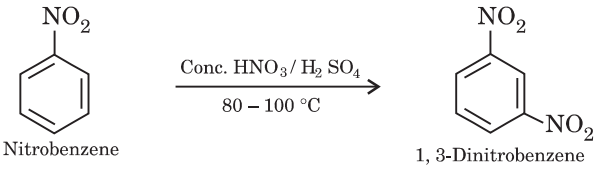


B9 (*a*) :



Competition File

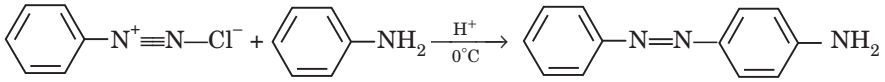
B1 (*d*) :



Nitrobenzene — 1, 3-Dinitrobenzene

B11. (*b*) : $C_6H_5N_2^+X^-$ is most stable diazonium salt because of resonance stabilization.

B12. (*d*) :

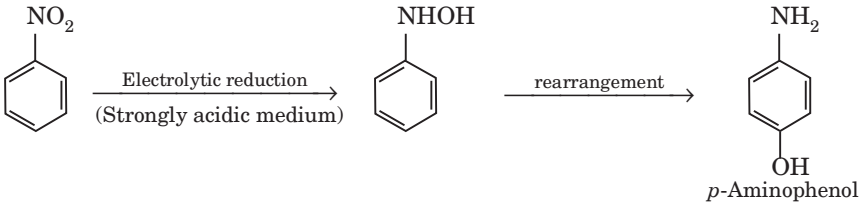


B13. (*c*) : Four isomers

$CH_3CH_2CH_2NH_2$,	$CH_3—\underset{\displaystyle CH_3}{\overset{\displaystyle \vert}{CH}}—NH_2$,	$CH_3CH_2—NH—CH_3$	$CH_3—\underset{\displaystyle CH_3}{\overset{\displaystyle \vert}{N}}—CH_3$,
Propan-1-amine	Propan-2-amine	N-Methylethanamine	N, N –Dimethylmethanamine

B15. (*b*) : Chlorobenzene does not react with potassium phthalimide because aryl halides are less reactive towards nucleophilic substitution reaction.

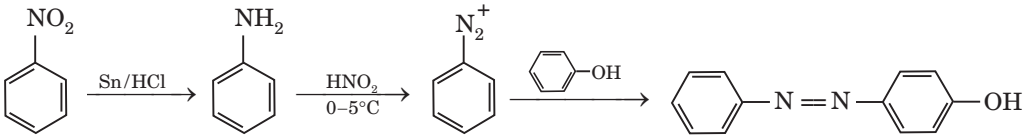
B16. (*c*) : Under strongly acidic medium, nitrobenzene on electrolytic reduction gives *p*-aminophenol.



p-Aminophenol

B18. (*c*) : Tertiary nitro compounds do not react with nitrous acid because they do not have α-hydrogen.

B19. (*b*) :



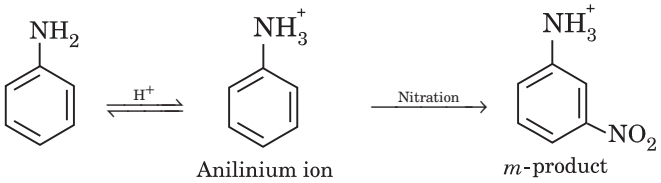
(A) (B) Azo dye (Coloured compound)

B20. (*a*) : $CH_3CONH_2 + Br_2 + 4KOH \xrightarrow{Heat} CH_3NH_2 + 2KBr + K_2CO_3 + 3H_2O$

Acetamide — Methanamine

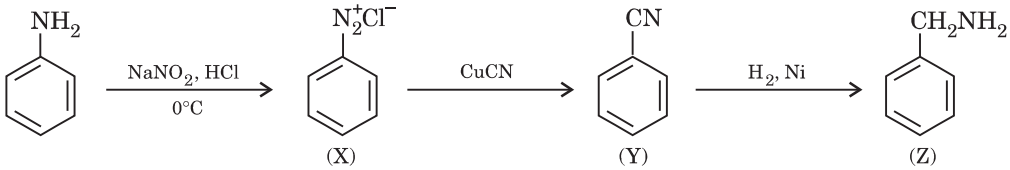
This is Hoffmann bromide reaction.

B22 (*d*) : In strongly acidic medium, anilinium ion is formed which is meta directing.



Anilinium ion — *m*-product

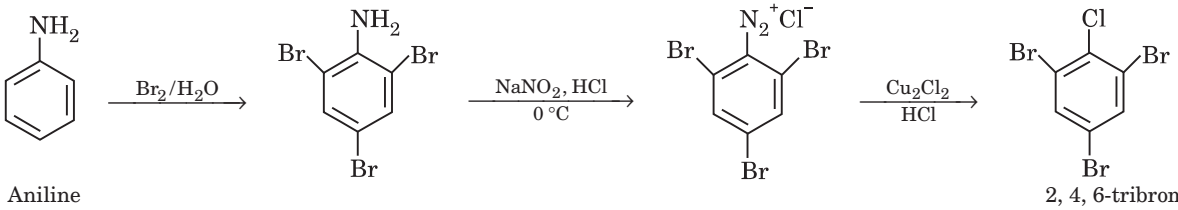
B23. (*b*) :



(X) (Y) (Z)

B2 (*b*) : 2° amines are strongest bases than other amines. Therefore, $(C_2H_5)_2NH$ *i.e.*, N-ethylethanamine is the strongest base.

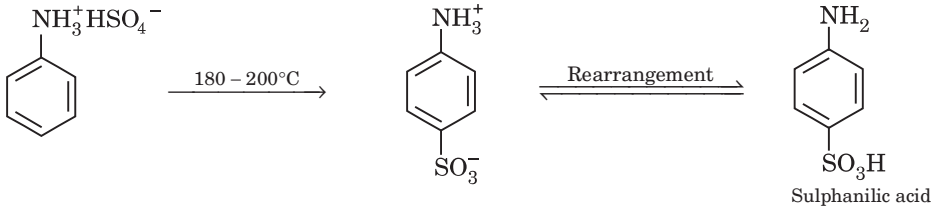
B25. (*d*) :



Aniline — 2, 4, 6-tribromo chlorobenzene

Competition File

B26 (*e*) :



Sulphanilic acid

B27 (*d*) : Secondary amines could be prepared by reduction of isonitriles.

$$R{-}N \equiv C \xrightarrow{4[H]} \underset{\text{sec-Amine}}{RNH\,CH_3}$$

B28. (*d*) : Gabriel phthalimide synthesis is used for the preparation of 1° aliphatic amines. Ethylmethylamine is a 2° amine and hence cannot be prepared by this method.

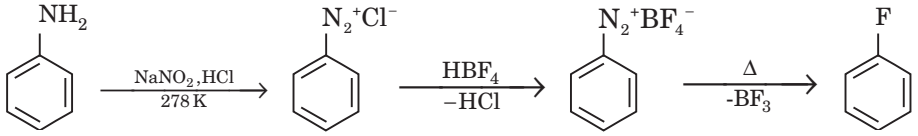
B29. (*d*) : Secondary amines (diethylamine) give an alkali insoluble product with *p*-toluenesulphonyl chloride.

B30. (*b*) : Cyclohexyl amine is an aliphatic amine. Aliphatic amines are more basic than aromatic amines.

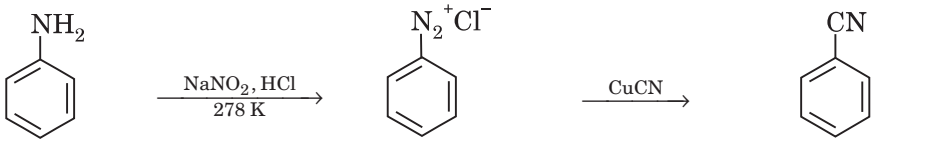
B32. (*c*) : $CH_3CH_2NH_2 + CHCl_3 + 3KOH \longrightarrow CH_3CH_2NC + 3KCl + 3H_2O$

This is Carbylamine reaction.

B33. (*a*) :



B34. (*a*) :



Benzenediazonium chloride (A) Benzonitrile (B)

B35. (*c*) :

$$R{-}NH_2 + Cl{-}\overset{\overset{O}{\|}}{C}{-}CH_3 \longrightarrow R{-}NH{-}\overset{\overset{O}{\|}}{C}{-}CH_3 + HCl$$

Each $CH_3{-}\overset{\overset{O}{\|}}{C}{-}$ group increases the molecular mass by 42

Total increase in molecular mass = 390 – 180 = 210

Number of NH_2 groups = $\frac{210}{42} = 5$.

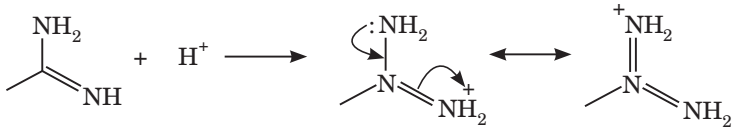
B36. (*b*) : $(CH_3)_2NH$ is most basic and therefore has the smallest pK_b value.

B38. (*d*) : $RCONH_2 + 4NaOH + Br_2 \longrightarrow RNH_2 + Na_2CO_3 + 2NaBr + 2H_2O$ *i.e*,

4 mole of NaOH and 1 mole of Br_2.

B39. (*c*) : Aniline in acidic medium gets protonated to anilinium ion. Anilinium ion is strongly deactivating group and is meta directing. Therefore, meta nitration product is obtained in significant amount.

B40. (*c*) : The conjugate acid obtained by addition of proton to amine (C) is stabilized by resonance and therefore, it is most basic.



The amine (D) is secondary amine and it is more basic than primary amine (A). The amine (B) is least basic because N atom in it is sp^2 hybridised. Since a sp^2 hybridised N has more *s*-character (more electronegative) than sp^3 hybridised N in amine (A), then N in amine (B) has lesser tendency to donate its electron pair than amine (A). In other words, it is less basic than primary amine (A). Combining these trends, the basicity of four amines increases as:

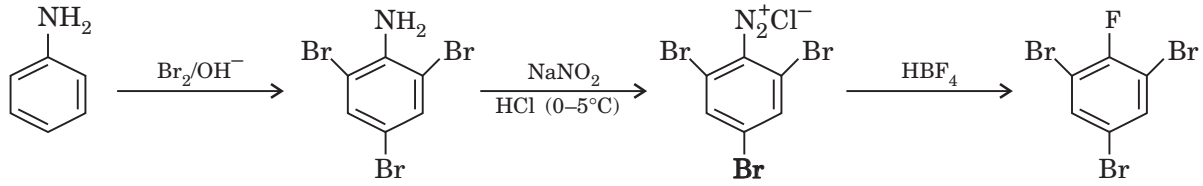
(B) < (A) < (D) < (C)

Competition File

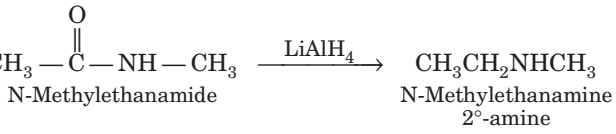
B4 (*a*) : The presence of electron withdrawing group like $-NO_2$ at *p*-position will decrease the basic character, so (2) will be least basic. Presence of electron donating group like $-OCH_3$ at *p*-position will increase the basic character and therefore, (4) is the most basic. The order is :

$$2 < 5 < 1 < 3 < 4$$

B42. (*c*) :



B43. (*b*) :

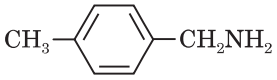


N-Methylethanamide — N-Methylethanamine (2°-amine)

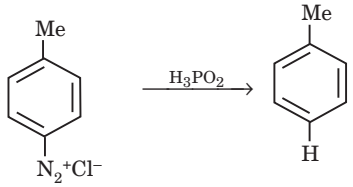
B4 (*a*) : Only treatment of amide with Br_2 in aqueous NaOH or KOH will give amine with lesser number of carbon atoms.

$$RCONH_2 \xrightarrow[\Delta]{Br_2, KOH} RNH_2$$

B4 (*d*) : Primary aliphatic and aromatic primary amines give positive carbylamine test. *p*-methylbenzylamine is a primary amine and hence gives this test.

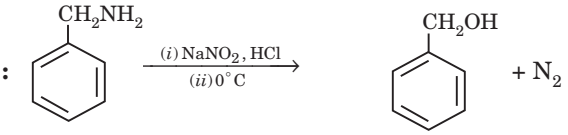


B4 (*a*) :



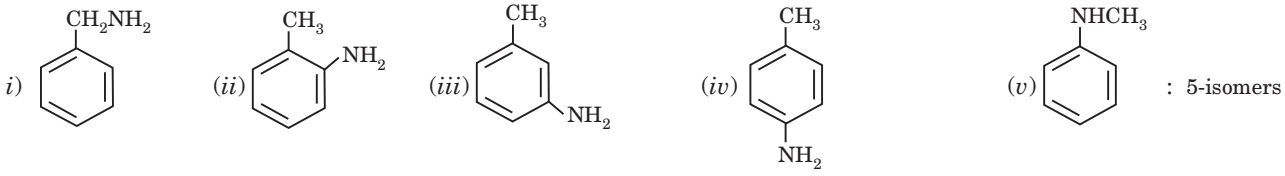
B50 (*b*) : 2° amine reacts with benzene sulphonyl chloride and the product formed is insoluble in NaOH. Therefore, the amine should have only one H-atom attached to nitrogen atom.

B51. (*a*) :



Benzyl amine (C_7H_9N) (A) — Benzyl alcohol

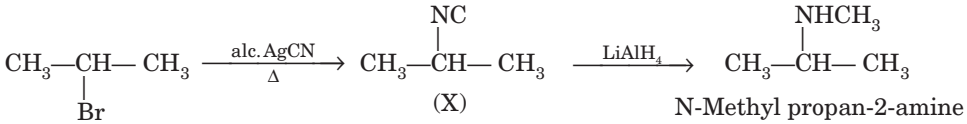
The possible isomers are :



: 5-isomers

B5 (*a*) : Only primary amides undergo Hoffmann bromamide reaction.

B53. (*b*) :



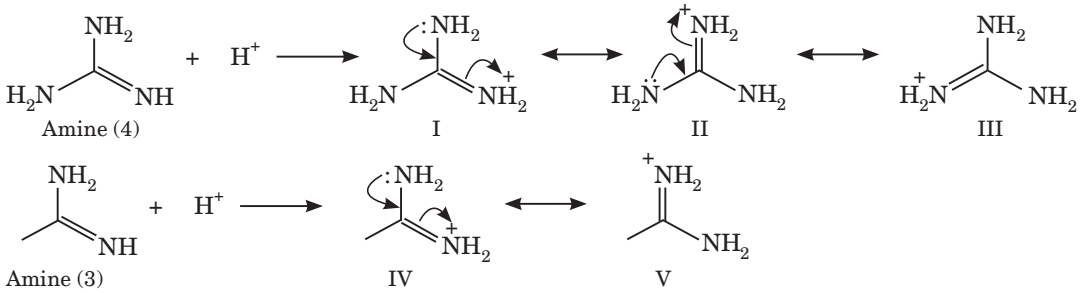
2-Bromopropane — (X) — N-Methyl propan-2-amine

B54. (*c*) : $(C_2H_5)_2NH + HONO \longrightarrow (C_2H_5)_2N{-}N{=}O + H_2O$

N-Nitrosodiethylamine

Competition File

B55. (*c*) : The conjugate acids obtained by addition of proton to amine (4) is resonance stabilized by three equivalent structures (I, II and III) while that obtained from amine (3) is resonance stabilized by two equivalent structures (IV and V).

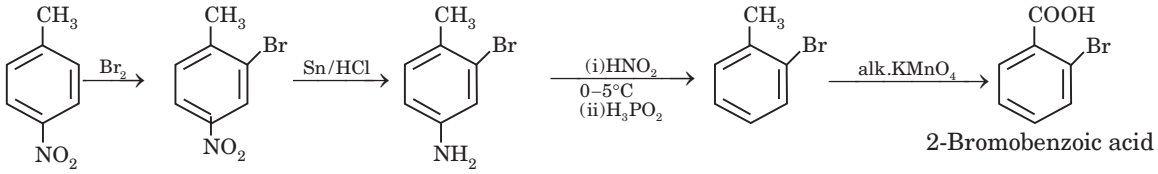


Therefore, amine (4) is more basic than amine (3). In amine (1), lone pair of electrons is present on a sp^3 hybridized N while in amine (2), it is present on a sp^2 hybridised N. Since a sp^2 hybridised N has more *s*-character (more electronegative) than a sp^3 hybridised N, therefore, amine (2) has lesser tendency to donate its electron pair than amine (1). In other words, amine (2) is less basic than amine (1). Combining these trends, the basicity of four amines increases as:

(2) < (1) < (3) < (4)

B56. (*c*) : Only primary aliphatic amines can be prepared by Gabriel phthalimide synthesis. Therefore, benzylamine is prepared by this method.

B57 (*e*) :

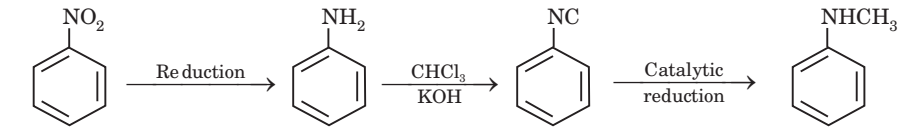


2-Bromobenzoic acid

B58. (*b*) : $CH_3CN \xrightarrow{\text{Reduction}} CH_3CH_2NH_2 \xrightarrow{HNO_2} CH_3CH_2OH + N_2 + H_2O$

Ethane nitrile (A) (B)

B59. (*a*) :

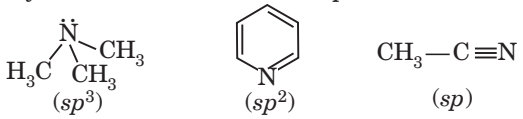


Nitrobenzene (A) — Aniline (B) — Phenyl isocyanide (C) — N-Methyl benzenamine

B60. (*c*) : Primary aliphatic and aromatic amines react with $CHCl_3$ in the presence of alcolic KOH and give isocyanides which have nauseating smell/odour

$PhNH_2 \xrightarrow[\text{alc.KOH}]{CHCl_3} PhNC$ (Phenyl isocyanide)

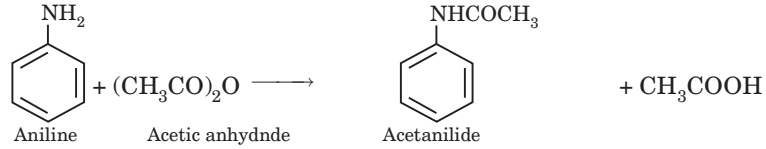
B61. (*a*) : Hybridisation of N is the compounds are



As percentage of *s*-character increases, the electronegativity increases. Therefore, electronegativity order is

$MeCN > C_5H_5N > Me_3N$

B62. (*b*) :

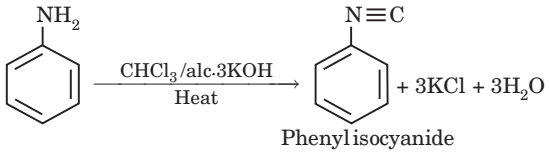


Aniline — Acetic anhydnde — Acetanilide

Initial moles	2	1	0	0
After reaction	1	0	1	1

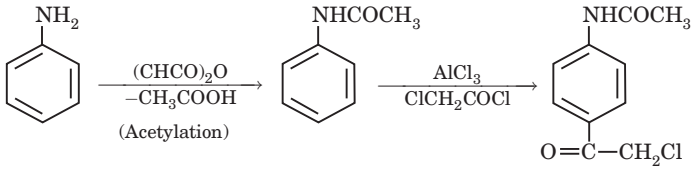
1 mole of acetanilide = 135 g

B63. (*c*) :

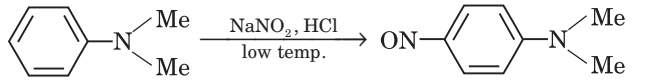


Phenyl isocyanide

B64. (*a*) :

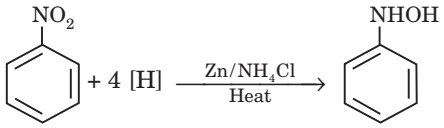


B65. (*a*) : N, N – Dimethylamine (3° amine) forms p-nitroso derivative with HNO_2



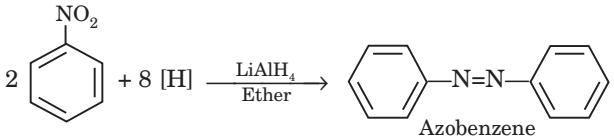
p-nitroso–N, N–dimethylaniline

B66. (*d*) :

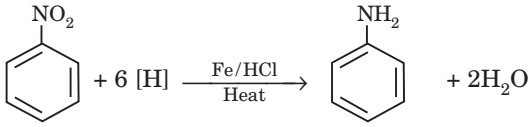


Phenylhydroxylamine

(a), (b) and (c) are not correct.

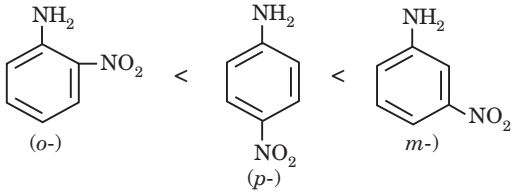


Azobenzene



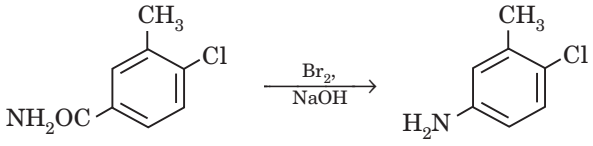
Aniline

B67. (*a*) :

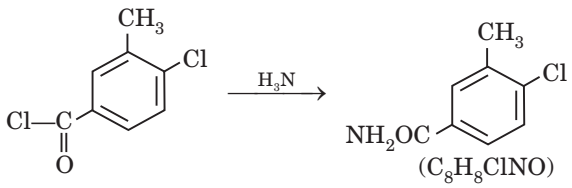


Ortho substituted anilines are weaker bases than others due to ortho effect, which is combination of steric and electronic factors.

B68. (*b*) : Problem can be solved by using back reaction. Hoffmann degradation reaction (Br_2, NaOH) converts amides to amines (one carbon atom less).



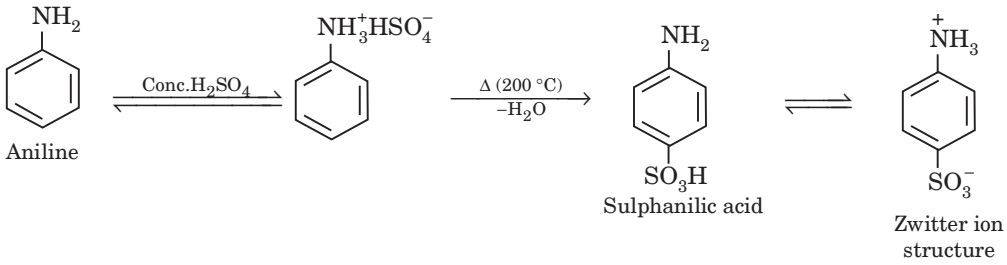
(C_8H_8ClNO)



$(C_8H_6Cl_2O)$
(M)

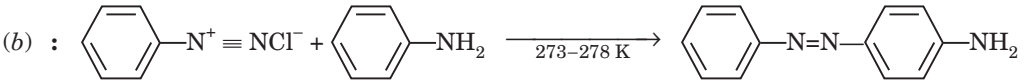
(C_8H_8ClNO)

B69. (*d*) :



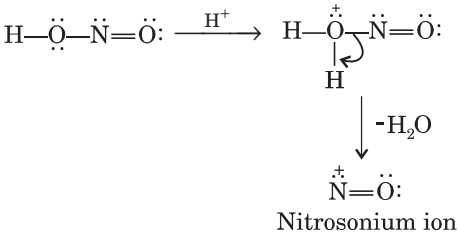
B70. (*d*) : Benzylamine is most basic among these.

B71. (*b*) :



Benzene diazonium chloride Aniline *p*-Aminoazobenzene (yellow dye)

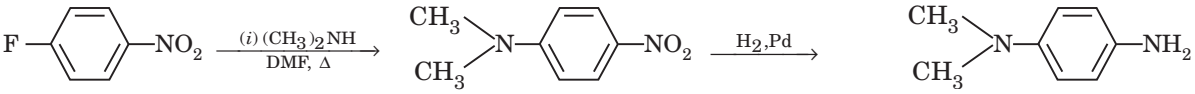
B72 (*e*) :



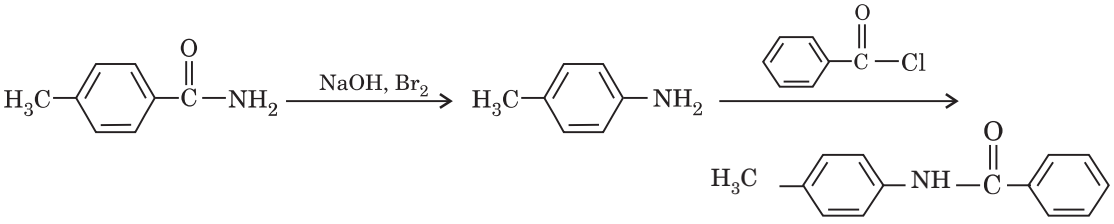
Nitrosonium ion

Aromatic tertiary amine *i.e.*, N, N–dimethylaniline undergoes electrophilic substitution with nitrosonium ion at *p*-postion of the phenyl ring.

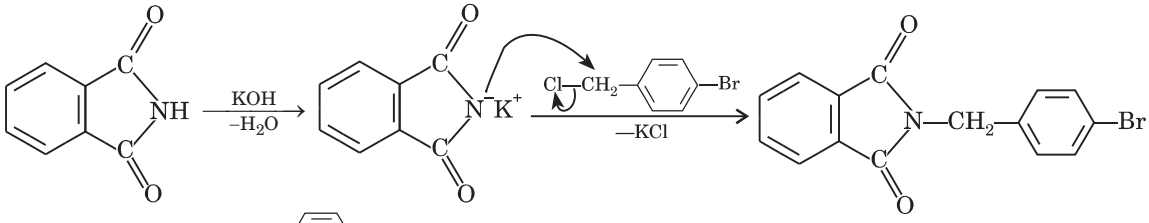
B73. (*a*) :



B74. (*c*) :

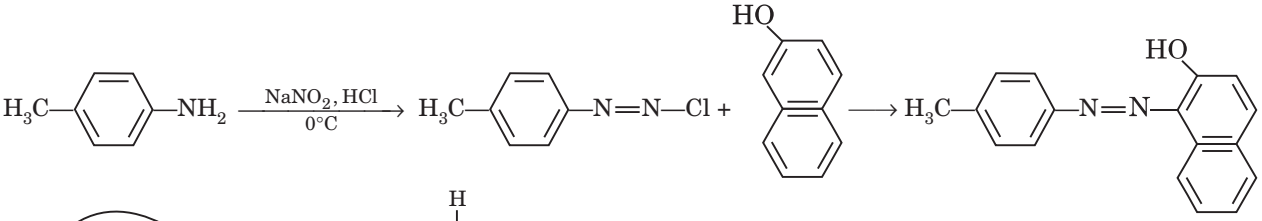


B75. (*a*) :

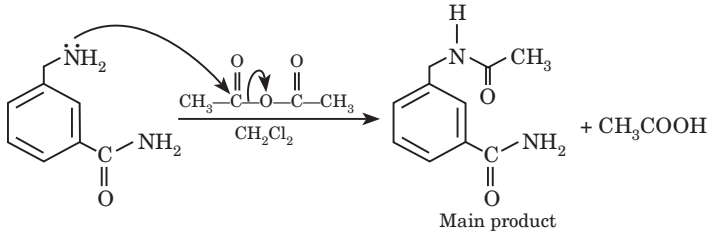


During the attack of Br—C6H4—CH2—Cl, C—Br bond is shorter due to resonance and hence is strong. Therefore, it cannot take part in the reaction. The Cl takes part in the reaction.

B76. (*c*) :



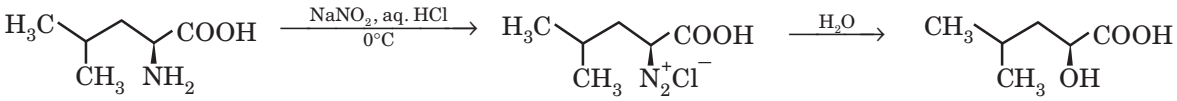
B77. (*a*) :



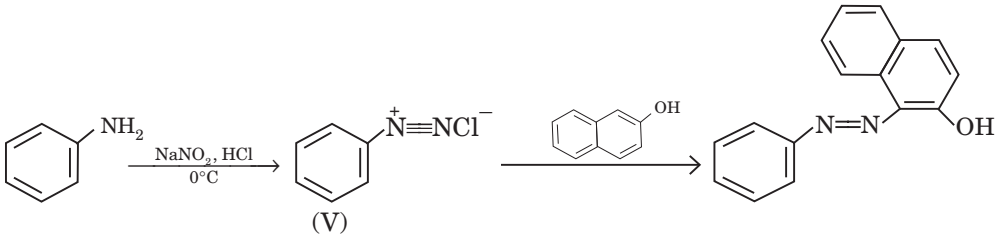
Main product

Acetylation takes place when amine (not amide) reacts with acetyl chloride or acetic anhydride.

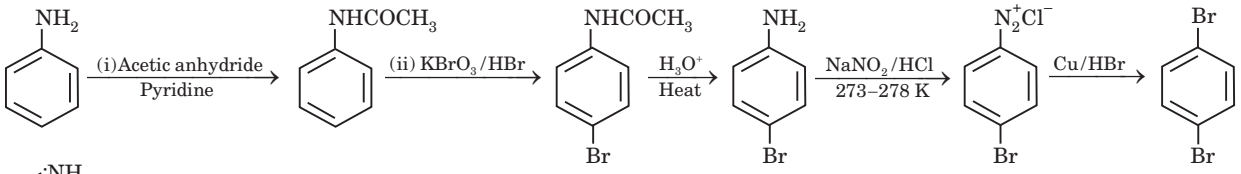
B78 (*c*) :



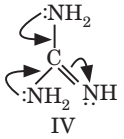
B79. (*a*) :



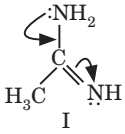
B80 (*b*) :



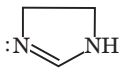
B81. (*d*) :



Resonance with two NH_2 groups increases electron density on N of =NH.



Resonance with one NH_2 group increases electron density on N to lesser extent (than IV) of =NH.

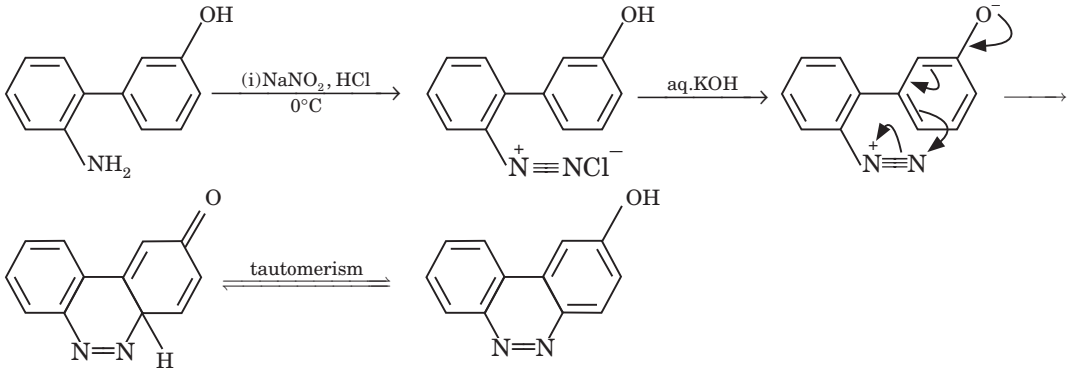


Electron density on N of NH increases due to resonance

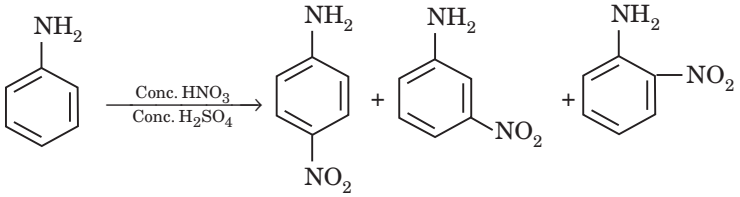
The lone pair is not available because it is involved in aromatic sextet.

Hence, correct order is IV > I > II > III

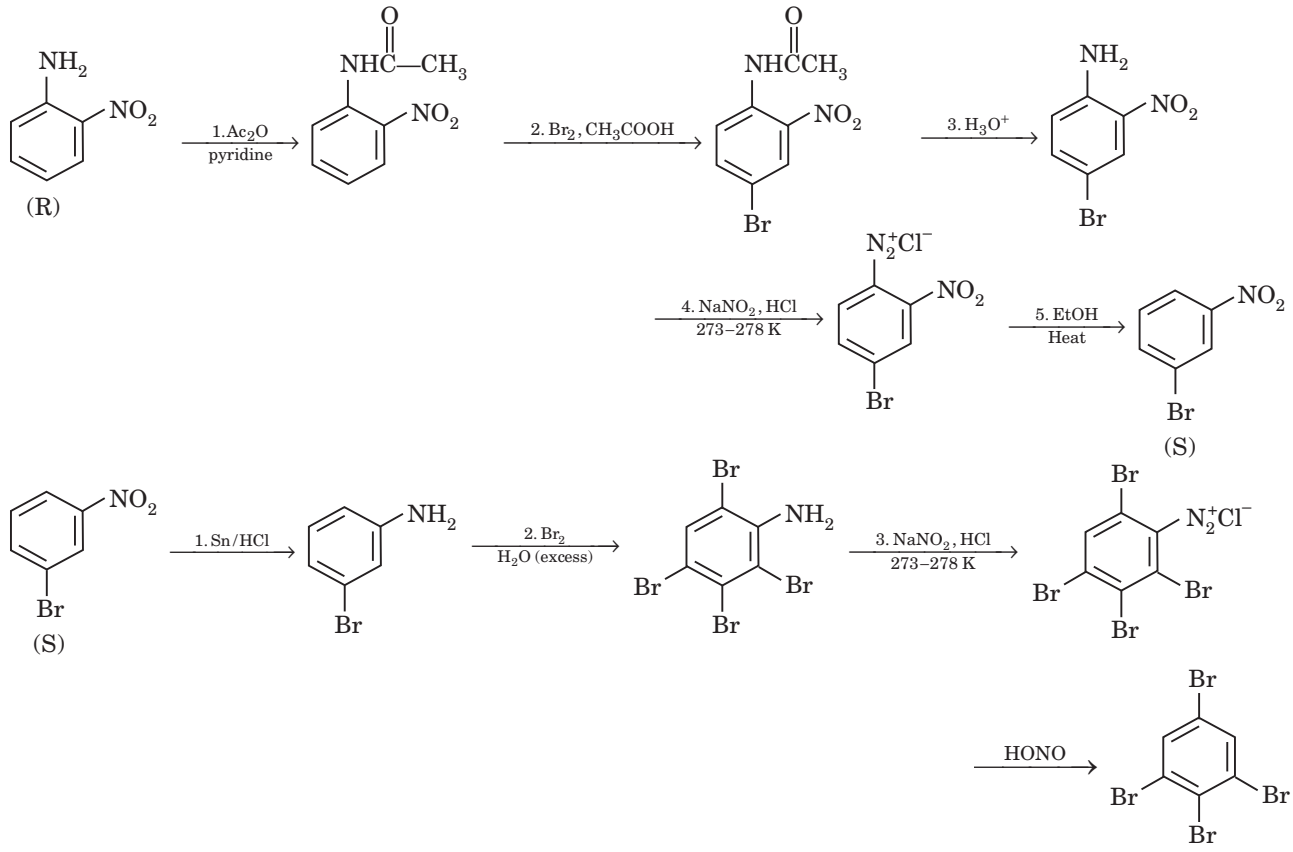
B8 (*c*) :



B83. (*d*) :



51% (P) 47% (Q) 2% (R)

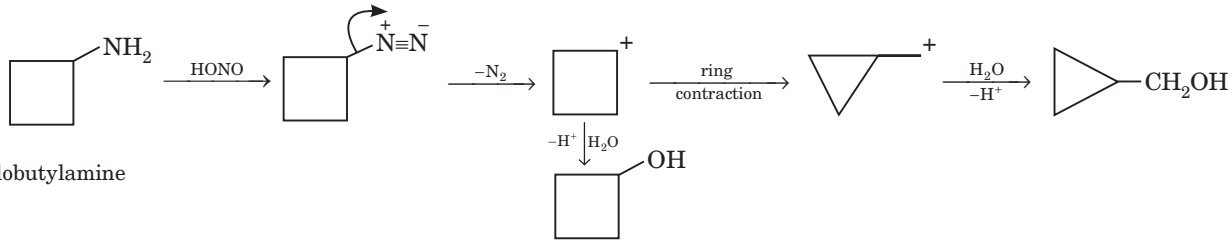


C. *mcq with more than one correct answer*

C8. (*a*,*b*,*c*): $2NH_3 + B_2H_6 \longrightarrow \left[H_2B(NH_3)_2 \right]^+ BH_4^-$

Similarly, it forms ionic compounds, with 1° and 2° amines. But with 3° amines, it forms adduct.

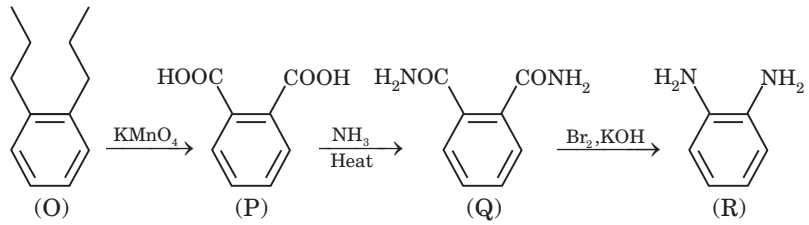
C10. (*a*,*c*):



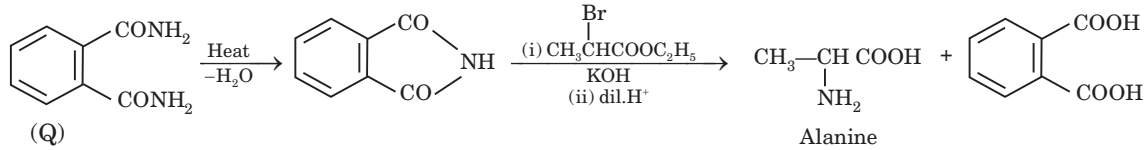
Cyclobutylamine

D. *mcq based on the given passage/comprehension*

D6. (*a*) :

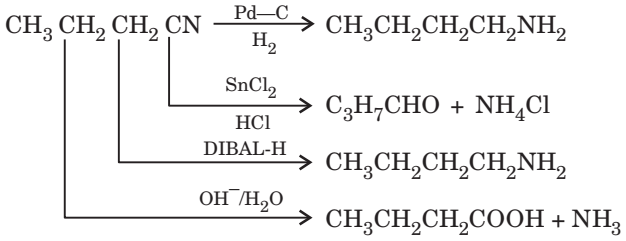


D7. (*b*) :

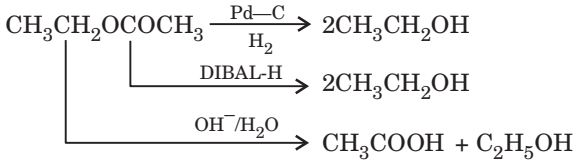


Matrix Match Type Questions

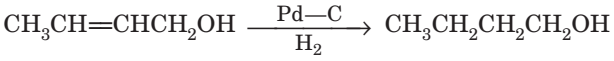
1. (A) : (*p*), (*q*), (*s*), (*t*)



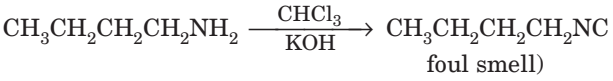
(B) : (*p*), (*s*), (*t*)



(C) : (*p*)

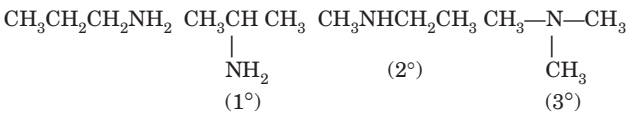


(D) : (*r*)



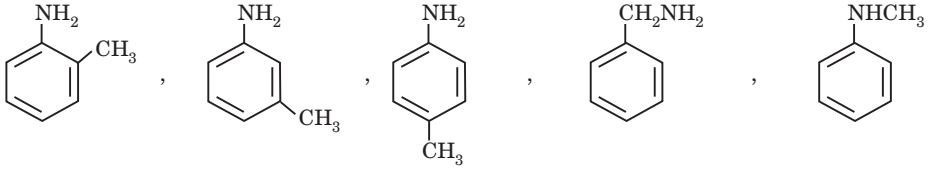
nteger Type or Numerical Value Type Questions

1. (2) Isomeric amines are

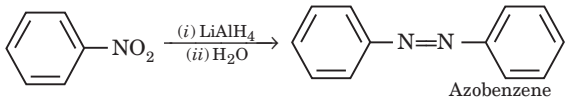


Only primary amine (*i.e.* 2°) react with HNO_2 to liberate N_2 gas.

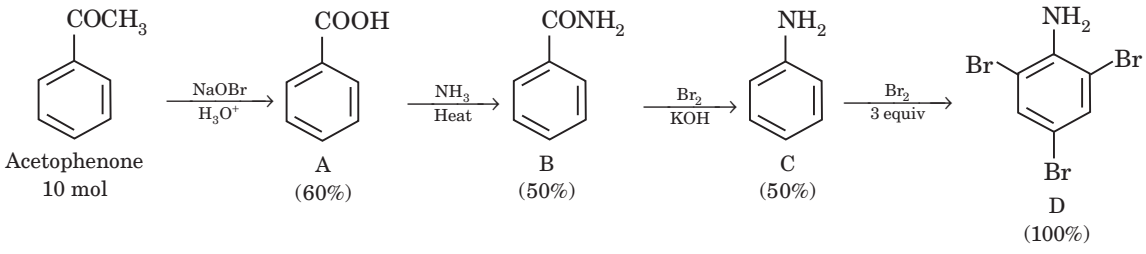
2. (5 The amines *p*-$CH_3C_6H_4NH_2$, *m*-$CH_3C_6H_4NH_2$, $C_6H_5N(CH_3)_2$, $C_6H_5NHCH_3$, $C_6H_5CH_2NH_2$ are more basic than aniline and hence have lower pK_b values.

3. (5 

4. (3) There are eight isomeric amines of molecular formula $C_4H_{11}N$. Out of these only three are primary which give carbylamine reaction.

5. (2 

Azobenzene

6. (495.00) 

Acetophenone 10 mol — A (60%) — B (50%) — C (50%) — D (100%)

Moles of A formed $= \dfrac{10 \times 60}{100} = 6$ mol

Moles of B formed $= \dfrac{6 \times 50}{100} = 3$ mol

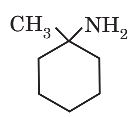
Moles of C formed $= \dfrac{3 \times 50}{100} = 1.5$ mol

Moles of D formed $= \dfrac{1.5 \times 100}{100} = 1.5$ mol

Molecular mass of D ($C_6H_2Br_3NH_2$) = 6 × 12 + 2 × 1 + 3 × 80 + 14 + 2 × 1 = 330

Amount of D formed = 330 × 1.5 = 495.00g

NCERT Exemplar Problems : MCQs Type-I

1. (*b*)  $(C_2H_5)_3N$ $(CH_3)_3C—NH_2$ $C_6H_5NH(CH_3)$

1° amine 3°amine 1°amine 2°amine

2. (*d*) $\overset{3}{C}H_2{=}\overset{2}{C}(CH_3)\,\overset{1}{C}H_2\,\overset{*}{N}H$ N-methylprop-2-en-1-amine

4. (*a*) Due to delocalisation of a lone pair of electrons present on the N-atom into the benzene ring, $C_6H_5NH_2$ is a weak base.

5. (c) because of the stability of $C_6H_5CH_2^+$ carbocation

8. (d) $C_6H_4(CO)_2N^-K^+$

9. (*c*) $R—\underset{H}{C}{=}O + H_2NR \xrightarrow[\text{amination}]{\text{Reductive}} RCH{=}NR \xrightarrow{H_2, Pt} RCH_2NHR$

Schiff base 2° amine

10. (*d*) $CH_3\underset{C_6H_5}{CH}CONH_2 \xrightarrow[\text{ether}]{LiAlH_4} CH_3—\underset{C_6H_5}{CH}CH_2NH_2$

2-Phenyl propanamide 2-Phenyl propanamine

11. (*b*) $CH_3\underset{C_6H_5}{CH}CONH_2 \xrightarrow[Br_2]{NaOH} CH_3—\underset{C_6H_5}{CH}—NH_2$

13. (*d*) Electron donating group (—CH_3) increases the basicity of amines while electron-withdrawing group (—NO_2) decreases the basicity.

16. (*c*) $\overset{+}{N}O_2$ is an electrophile.

$HNO_3 + H_2SO_4 \longrightarrow \overset{+}{N}O_2 + HSO_4^- + H_2O$

18. (*b*) The amine which is most basic is most reactive, *i.e.* $(CH_3)_2NH$.

19. (*a*) $RNH_2 + (RCO)_2O \longrightarrow R—\overset{O}{\overset{\|}{C}}—\underset{H}{N}—R$

Amides

22. (*d*) Nitrobenzene does not undergo azo coupling reaction.

26. (*b*) $(CH_3)_3N$ *i.e.* tertiary amine does not form associated molecules.

NCERT Exemplar Problems : MCQs Type-II

29. (*a*), (*b*), (*c*) : $C_6H_5NO_2 \xrightarrow{Zn, NH_4OH} C_6H_5NHOH$, while all other reagents give aniline.

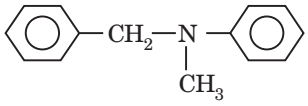
32. (*a*), (*b*) : Ortho and para products are formed.

34. (*a*), (*b*) : Only primary aliphatic amines are prepared by Gabriel synthesis.

Unit Practice Test

for Board Examination

Time Allowed : 2 Hrs. Maximum Marks : 35

1. Write the IUPAC name of  (1)
2. Arrange the following in order of their basic strength in aqueous solution.
   aniline, *p*-nitroaniline, *p*-toluidine. (1)
3. How will you convert aniline into chlorobenzene? Give equation. (1
4. Why do amines act as nucleophiles? (1)
5. niline dissolves in aqueous HCl. Why? (1
6. Explain:
   (*i*) Why does the reactivity of —NH_2 group get reduced in acetanilide?
   (*ii*) Why does methylamine has lower boiling point than methanol? (2)
7. Convert the following :
   (*i*) 3-Methylaniline to 3-nitrotoluene
   (*ii*) Aniline into 1, 3, 5-tribromobenzene. (2)
8. What is Gabriel phthalimide synthesis? Why aromatic primary amines cannot be prepared by this method? (2)
9. How do aromatic and aliphatic primary amines react with nitrous acid? (2)
10. Why are aromatic amines weaker bases than aliphatic amines? (2)
11. How will you convert :
    (*i*) Benzyl chloride to 2-phenylethanamine (*ii*) Aniline to *p*-bromoaniline
    (*iii*) Benzoic acid to aniline? (3)
12. Explain the following reactions by giving one example :
    (*i*) Carbylamine reaction (*ii*) Sandmeyer's reaction
    (*iii*) Balz-Schiemann reaction (3)
13. Explain the following :
    (*a*) Ethylamine is soluble in water, whereas aniline is not.
    (*b*) Although amino group is *o*- and *p*-directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of *m*-nitroaniline.
    (*c*) Aniline does not undergo Friedel Crafts reaction. (3)
14. onvert the following :
    (*i*) 4-Nitrotoluene to 2-bromobenzoic acid
    (*ii*) *p*-toluidine into 2-bromo-4-methylaniline
    (*iii*) acetaldehyde to ethylamine. (3
15. Starting with aniline and using suitable reagents, outline the synthesis of (3)
    (*i*) *m*-bromochlorobenzene *ii*) *p*-nitrobenzene
    (*iii*) 1, 2, 3-tribromobenzene
16. (*a*) How does benzene diazonium chloride react with
    (*i*) phenol (*ii*) aniline
    (*b*) Describe the method for the identification of primary, secondary and tertiary amines. Also write chemical equations for the reactions involved. (5)

► To check your performance, see HINTS AND SOLUTIONS TO SOME QUESTIONS at the end of Part II of the book.