# 22

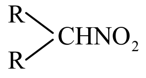
# Nitrogen Containing Compounds

## QUICK LOOK

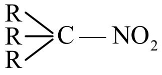
Nitro alkanes are derivatives of alkanes. They are isomeric to nitrites (esters) classified as primary, secondary and tertiary depending on the nature of carbon atom to which nitro group is linked.

$RCH_2NO_2$

Primary nitro alkane

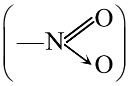


Secondary nitro alkane

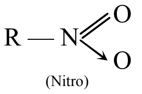


Tertiary nitro alkane

$-NO_2$ group is an ambident group.

If it attacks through  nitrogen

It is called nitro and if it attacks through oxygen atom, it is called nitrite. Hence nitrites and nitro compounds are isomers.

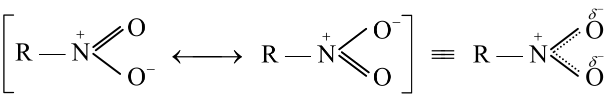


(Nitro)

is isomeric with $\underset{\text{(Nitrite)}}{R-O-N=O}$

### Structures

Evidences show that nitrogen is attached to one of the oxygen atoms by a double bond and to the other by a dative bond. The resonance hybrid is shown as under which confirms the spectroscopic evidence that both nitrogen–oxygen bonds have same bond length.

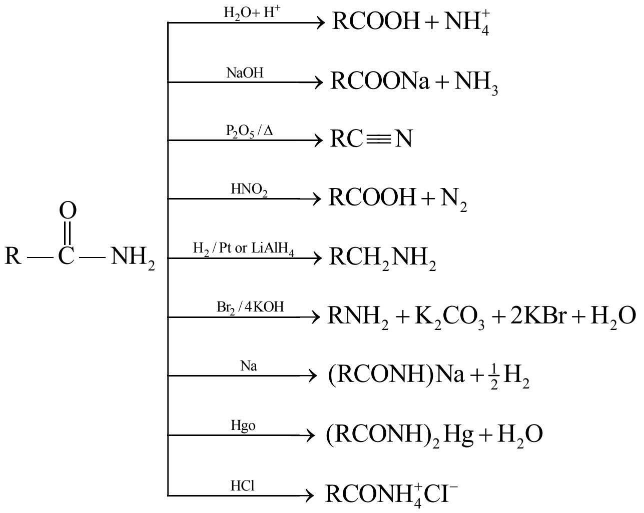


Resonating forms

Hybride structure

Out of three $sp^2$ hybrid orbitals of nitrogen one overlaps with alkyl group and two with oxygens while the unhybridized p-orbital of N-atom containing a pair of electrons and lying perpendicular to the plane of hybrid orbitals overlaps sideway with half filled 2p-orbitals of two oxygen atoms. This forms $\pi$-bond above and below the plane of molecule.

### Amides



**Cynadies (RCN) and Isocynides (RCN):** These are the compounds containing $-C\equiv N$ functional group.
They have general formula $R-C\equiv N$.

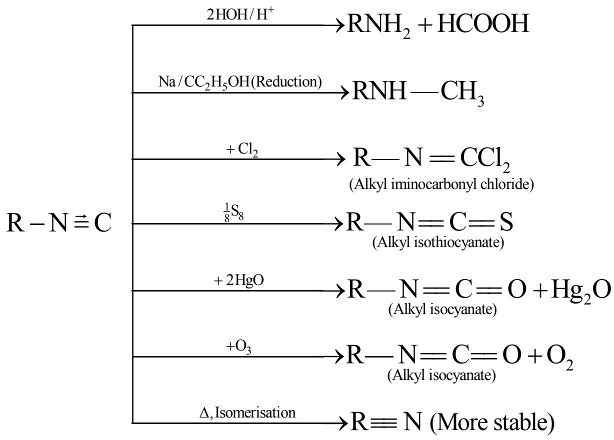
**Preparation of Cynaides:** The following methods can be employed to prepare the cynides.

- $RX + KCN(alc) \longrightarrow \underset{\text{(Main product)}}{RCN} + KX$
- Aryl cyanides cannot be prepared by this method because aryl halides are less reactive towards nucleophilic substitution.
- $RCONH_2 + P_2O_5 \xrightarrow{\text{Heat}} RCN + H_2O$
- $C_6H_5N_2^+Cl^- + CuCN \xrightarrow{KCN} C_6H_5CN + CuCl$
- $\underset{\text{(Aldoxime)}}{RCH=NOH} \xrightarrow{(CH_3CO)_2O/\Delta} RC\equiv N + H_2O$
- $RMgX + ClCN \xrightarrow{\text{Dry/ether}} R-C\equiv N + Mg(Cl)X$

**Preparation of Isocynides**

- $RX + AgCN \xrightarrow{C_2H_5OH} \underset{\text{(Major product)}}{RNC} + AgX$
- $RNH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} RNC + 3KCl + 3H_2O$
(Carbylamine reaction)

**Reactions of Isocynides:** Some of the important reactions of isocyanides are given below



$$R-N\equiv C \xrightarrow{2HOH/H^+} RNH_2 + HCOOH$$

$$R-N\equiv C \xrightarrow{Na/CC_2H_5OH(\text{Reduction})} RNH-CH_3$$

$$R-N\equiv C \xrightarrow{+Cl_2} \underset{\text{(Alkyl iminocarbonyl chloride)}}{R-N=CCl_2}$$

$$R-N\equiv C \xrightarrow{\frac{1}{8}S_8} \underset{\text{(Alkyl isothiocyanate)}}{R-N=C=S}$$

$$R-N\equiv C \xrightarrow{+2HgO} \underset{\text{(Alkyl isocyanate)}}{R-N=C=O} + Hg_2O$$

$$R-N\equiv C \xrightarrow{+O_3} \underset{\text{(Alkyl isocyanate)}}{R-N=C=O} + O_2$$

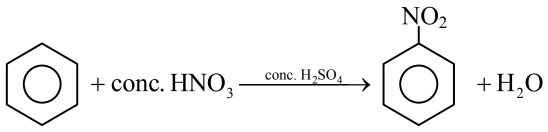
$$R-N\equiv C \xrightarrow{\Delta,\text{Isomerisation}} R\equiv N \text{ (More stable)}$$

### Nitro Compounds ($RNO_2$)

### Preparation of Aliphatic nitro Compounds

- $2RX + 2AgNO_2 \xrightarrow[\text{Heat}]{\text{Alcohol}} \underset{\substack{\text{Nntroalkane}\\ \text{(Major)}}}{RNO_2} + \underset{\substack{\text{Alkyl nitrite}\\ \text{(Minor)}}}{R-O-N=O}$
- $\underset{\substack{\text{(X may be}\\ \text{Br or I)}}}{2RX} + 2K^+(O-N=O) \longrightarrow \underset{\substack{\text{Alkyl nitrite}\\ \text{(Minor)}}}{R-O-N=O} + \underset{\substack{\text{Nntroalkane}\\ \text{(Major)}}}{RNO_2}$
- $\underset{\text{Vapour}}{CH_3-CH_3} + \underset{\text{Fuming}}{HNO_3} \xrightarrow{700K} \underset{\text{Nitroethane}}{CH_3CH_2NO_2} + H_2O$

**Preparation of Aromatic Nitro Compounds:** They are obtained by nitration of arenes with nitrating mixture $(H_2SO_4 + HNO_3)$.



This chemical reaction is typical example of electrophilic ring substitution. Here, conc. $H_2SO_4$ reacts with $HNO_3$ to produce nitronium ion $(NO_2^+)$ which acts as an electrophile while aerne behaves as the nucleophile.

**Amines:** These are derivatives of ammonia. They can be classified into primary, secondary or tertiary amines if they have functional groups $—NH_2$, $—\underset{|}{NH}—\overset{|}{\underset{|}{N}}$ respectively.

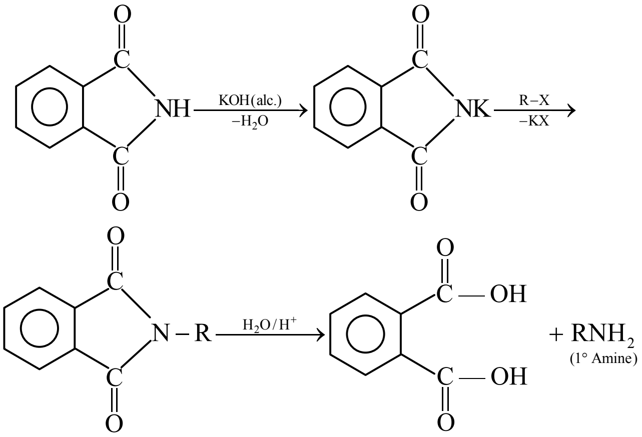
**Alkyl amines:** $RNH_2$,

**Aryl amines:** $ArNH_2$ (*e.g.* $C_6H_5NH_2$),

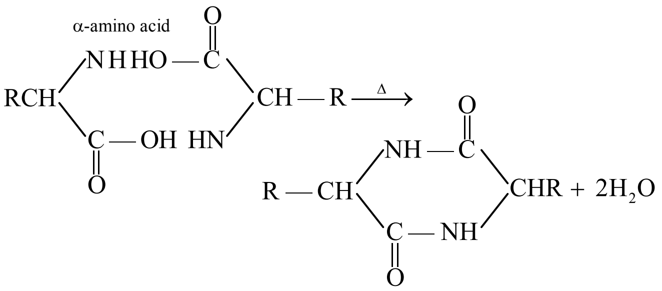
**Arlylalkyl amines:** $ArCH_2NH_2$(e.g., $C_6H_5CH_2NH_2$)

### Preparation of Amines

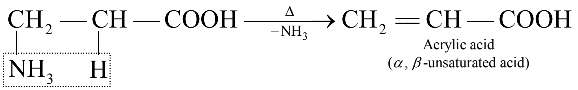
- Reduction of alkyl cyanides:
  $RCN + (H_2/Ni \text{ or } LiAlH_4) \longrightarrow RCH_2NH_2$ (1°Amine)
- Reduction of isocyanides:
  $RNC + H_2/Pt \longrightarrow RNHCH_3$ (2° Amine)
- Reduction of alkanamides:
  $RCONH_2 + (H_2/Pt \text{ or } LiAlH_4) \longrightarrow RCH_2NH_2$
- Reduction of aldoximes:
  $RCH = NOH + 4[H] \xrightarrow[\text{or } LiAlH_4]{Na/\text{alc. or } H_2/Pt} RCH_2NH_2 + H_2O$
- Hydrolysis of isocyanate:
  $R-N=C=O + 2KOH \longrightarrow RNH_2 + K_2CO_3$
- Hoffmann's bromide reaction:
  $\underset{\text{Amide}}{RCONH_2} + Br_2 + 4KOH \longrightarrow RNH_2 + 2KBr + K_2CO_3 + 2H_2O$
- Hydrolysis of isocyanides:
  $RNC + HOH \xrightarrow{HCl} RNH_2 + HCOOH$
- Ammonolysis of halides: $RX + \underset{\text{(Excess)}}{NH_3} \longrightarrow RNH_2 + HX$
- Ammonolysis of alcohols:
  $ROH + NH_3 \xrightarrow{575K,\ Al_2O_3} RNH_2 + H_2O$
- Reduction of nitro compounds:
  $C_6H_5NO_2 + 6[H] \xrightarrow{Sn/HCl} C_6H_5NH_2$
- Gabriel's Phthalimide synthesis



**Action of Heat:** α-amino acids lose two molecules of water and form cyclic amides.



*β*-amino acids lose a molecule of ammonia per molecule of amino acid to yield α,β-unsaturated acids.



$$\underset{\boxed{NH_3}}{CH_2}-\underset{\boxed{H}}{CH}-COOH \xrightarrow[-NH_3]{\Delta} \underset{\substack{\text{Acrylic acid}\\ (\alpha,\beta\text{-unsaturated acid})}}{CH_2=CH-COOH}$$

## MULTIPLE CHOICE QUESTIONS

### Amines

**1.** The correct order of basicity of amines in water is:

**a.** $(CH_3)_2NH > (CH_3)_3N > CH_3NH_2$

**b.** $CH_3NH_2 > (CH_3)_2NH > (CH_3)_3N$

**c.** $(CH_3)_3N > (CH_3)_2NH > CH_3NH_2$

**d.** $(CH_3)_3N > CH_3NH_2 > (CH_3)_2NH$

**2.** Complete the following reaction:

$R\ NH_2 + H_2SO_4 \longrightarrow$

| | |
|---|---|
| **a.** $[R\ NH_3]^+HSO_4^-$ | **b.** $[R\ NH_3]_2^+SO_4^{2-}$ |
| **c.** $R\ NH_2.H_2SO_4$ | **d.** No reaction |

**3.** Among the following which one does not act as an intermediate in Hofmann rearrangement?

| | |
|---|---|
| **a.** RNCO | **b.** $RCO\ddot{N}$ |
| **c.** $RCO\ddot{N}HBr$ | **d.** RNC |

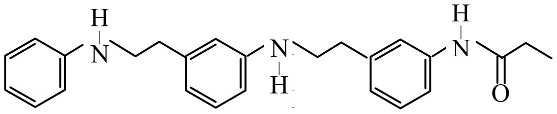
**4.** Aniline reacts with which of these to form Schiff base?

| | |
|---|---|
| **a.** Acetic acid | **b.** Benzaldehyde |
| **c.** Acetone | **d.** $NH_3$ |

**5.** Which of the following does not reduce Tollen's reagent?

| | |
|---|---|
| **a.** $CH_3CHO$ | **b.** $C_6H_5NHOH$ |
| **c.** HCOOH | **d.** $C_6H_5NO_2$ |

**6.** Which one of the following compound is most basic?



(A) (B) (C)

| | |
|---|---|
| **a.** (A) | **b.** (B) |
| **c.** (C) | **d.** All are equally basic |

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

In the given reaction what will be the product?

| | |
|---|---|
| **a.** $R-N=C=O$ | **b.** $R-\overset{+}{N}\equiv C^-$ |
| **c.** $R-C\equiv N$ | **d.** None of these |

**8.** Which of the following is secondary pollutant?

**a.** $CO_2$ **b.** $N_2O$ **c.** PAN **d.** $SO_2$

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

**a.** In electrophilic substitution reaction amino group is meta directive

**b.** Inspite of substituents nitro group always goes to *m*-position

**c.** In strong acidic medium, nitration of aniline is a nucleophic substitution reaction

**d.** In strong acidic medium aniline present as anilinium ion

**10.** Diazo-coupling is useful to prepare some:

| | |
|---|---|
| **a.** Dyes | **b.** Proteins |
| **c.** Pesticides | **d.** Vitamins |

### Introduction of Nitrogen Containing Compounds

**11.** $C_3H_9N$ represents:

| | |
|---|---|
| **a.** Primary amine | **b.** Secondary amine |
| **c.** Tertiary amine | **d.** All of these |

**12.** Allyl isocyanide has:

**a.** 9 sigma bonds and 4 pi bonds

**b.** 8 sigma bonds and 5 pi bonds

**c.** 8 sigma bonds, 3 pi bonds and 4 non-bonding electrons

**d.** 9 sigma bonds, 3 pi bonds and 2 non-bonding electrons

**13.** Acetonitrile is:

| | |
|---|---|
| **a.** $C_2H_5CN$ | **b.** $CH_3CN$ |
| **c.** $CH_3COCN$ | **d.** $C_6H_5CH_2CN$ |

**14.** Acetanilide can be prepared from aniline and which of the following?

| | |
|---|---|
| **a.** Ethanol | **b.** Acetaldehyde |
| **c.** Acetone | **d.** Acetic anhydride |

**15.** Aniline is usually purified by:

| | |
|---|---|
| **a.** Steam distillation | **b.** Simple distillation |
| **c.** Vacuum distillation | **d.** Extraction with a solvent |

### Preparation of Nitrogen Containing Compounds

**16.** Amides may be converted into amines by reaction named after**:**

| | |
|---|---|
| **a.** Perkin | **b.** Claisen |
| **c.** Hoffmann | **d.** Kolbe |

**17.** When methyl iodide is heated with ammonia, the product obtained is?

**a.** Methylamine **b.** Dimethylamine

**c.** Trimethylamine

**d.** A mixture of the above three amines

**18.** Which of the following reactions does not yield an amine?

**a.** $RX + NH_3 \longrightarrow$

**b.** $RCH = NOH + [H] \xrightarrow[C_2H_5OH]{Na}$

**c.** $RCN + H_2O \xrightarrow{H^+}$

**d.** $RCONH_2 + 4H \xrightarrow{LiAlH_4}$

**19.** Which of the following gives RNC, when reacted with $CHCl_3$ and KOH?

**a.** $RNH_2$ **b.** $R_2NH$

**c.** $R_3N$ **d.** $R_4N^+Cl^-$

**20.** Nitrobenzene combines with hydrogen in the presence of platinum to produce:

**a.** Toluene **b.** Benzene

**c.** Aniline **d.** Azobenzene

**21.** When chlorobenzene is treated with $NH_3$ in presence of $Cu_2O$ in xylene at 570 K. The product obtained is?

**a.** Benzylamine **b.** Diazonium salt

**c.** Schiff's base **d.** Aniline

**22.** In the series of reaction

$C_6H_5NH_2 \xrightarrow[0-5°C]{NaNO_2/HCl} X \xrightarrow[CH_2O]{HNO_2} Y + N_2 + HCl$ X and Y are respectively:

**a.** $C_6H_5-N=N-C_6H_5, C_6H_5N_2^{\oplus}Cl^{\ominus}$

**b.** $C_6H_5N_2^{\oplus}Cl^{\ominus}, C_6H_5-N=N-C_6H_5$

**c.** $C_6H_5N_2^{\oplus}Cl^{\ominus}, C_6H_5NO_2$

**d.** $C_6H_5NO_2, C_6H_6$

**23.** Aromatic nitriles (ArCN) are not prepared by reaction:

**a.** ArX + KCN **b.** $ArN_2^+ + CuCN$

**c.** $ArCONH_2 + P_2O_5$ **d.** $ArCONH_2 + SOCl_2$

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

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

The reducing agent used in this reaction is .......

**a.** $LiAlH_4$ **b.** Sn/HCl

**c.** Na/alcohol **d.** $H_2/Ni$

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

What is Z ?

**a.** $CH_3CH_2NH_2$ **b.** $CH_3CH_2NC$

**c.** $CH_3CH_2CH_3$ **d.** $NH_2CONH_2$

**26.** Ethylamine can be prepared by the action of bromine and caustic potash on**:**

**a.** Acetamide **b.** Propionamide

**c.** Formamide **d.** Methyl cyanide

**27.** Which one of the following compound gives a secondary amine on reduction?

**a.** Nitromethane **b.** Nitrobenzene

**c.** Methyl isocyanide **d.** Methyl cyanide

**28.** In this reaction

$C_6H_5NH_2 + HCl + NaNO_2 \longrightarrow X.$ Product X is:

**a.** Aniline hydrochloride

**b.** Nitro aniline

**c.** Benzenediazonium chloride

**d.** None of these

**29.** Which of the following compound is the strongest base?

**a.** Ammonia **b.** Aniline

**c.** Methylamine **d.** *N*-methyl aniline

### Properties of Nitrogen Containing Compounds

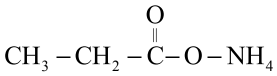
**30.** Which of the following compound is expected to be most basic?

**a.** Aniline **b.** Methylamine

**c.** Hydroxylamine **d.** Ethylamine

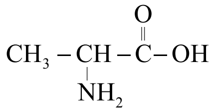
**31.** Which of the following compounds is an amino acid?

**a.**



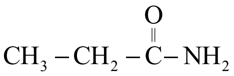
$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-O-NH_4$

**b.**



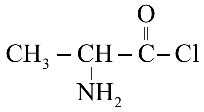
$CH_3-\underset{\underset{NH_2}{|}}{CH}-\overset{\overset{O}{\|}}{C}-OH$

**c.**



$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-NH_2$

**d.**



$CH_3-\underset{\underset{NH_2}{|}}{CH}-\overset{\overset{O}{\|}}{C}-Cl$

**32.** Which of the following amines would undergo diazotisation?

**a.** Primary aliphatic amines

**b.** Primary aromatic amines

**c.** Both a. and b.

**d.** None of these

**33.** Which one is weakest base?

**a.** Ammonia **b.** Methylamine

**c.** Dimethylamine **d.** Trimethylamine

**34.** Which of following is not an usual method for preparation of primary amine?

**a.** Hofmann's method

**b.** Curtius reaction

**c.** Schmidt reaction

**d.** Friedel-Craft's reaction

**35.** A solution of methyl amine:

**a.** Turns blue litmus red

**b.** Turns red litmus blue

**c.** Does not affect red or blue litmus

**d.** Bleaches litmus

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

**37.** Methyl amine reacts with $HNO_2$ giving**:**
**a.** $CH_3O-N=O$ **b.** $CH_3-O-CH_3$
**c.** $CH_3OH$ **d.** a. and b. both

**38.** Unpleasant smelling carbylamines are formed by heating alkali and chloroform with:
**a.** Any amine **b.** Any aliphatic amine
**c.** Any aromatic amine **d.** Any primary amine

**39.** The amine which does not react with acetyl chloride is or Which of the following cannot be acetylated?
**a.** $CH_3NH_2$ **b.** $(CH_3)_2NH$
**c.** $(CH_3)_3N$ **d.** None of these

**40.** Which of the following compounds does not react with $NaNO_2$ and HCl?
**a.** $C_6H_5OH$ **b.** $C_6H_5NH_2$
**c.** $(CH_3)_3CNO_2$ **d.** $(CH_3)_3CHNO_2$

**41.** In the diazotisation of aniline with sodium nitrite and hydrochloric acid, an excess of hydrochloric acid is used primarily to:
**a.** Suppress the concentration of free aniline available for coupling
**b.** Suppress hydrolysis of phenol
**c.** Insure a stoichiometric amount of nitrous acid
**d.** Neutralize the base liberated

**42.** Aniline and methyl amine can be differentiated by:
**a.** Reaction with chloroform and aqueous solution of KOH
**b.** Diazotisation followed by coupling with phenol
**c.** Reaction with $HNO_2$
**d.** None of these

**43.** Methyl isocyanide on hydrolysis gives:
**a.** $CH_3NH_2$ **b.** HCOOH
**c.** $CH_3COOH$ **d.** Both a. and b.

**44.** *p*-chloro aniline and anilinium hydrogen chloride can be distinguished by:
**a.** Sandmaeyer reaction **b.** Carbyl amine reaction
**c.** Hinsberg's reaction **d.** $AgNO_3$

**45.** The alkyl cyanides when hydrolysed to the corresponding acid, the gas evolved is?
**a.** $N_2$ **b.** $O_2$ **c.** $NH_3$ **d.** $CO_2$

**46.** Which of the following compound reacts with chloroform and a base to form phenyl isocyanide?
**a.** Phenol **b.** Aniline
**c.** Benzene **d.** Nitro benzene

**47.** The reduction of which of the following compound would yield secondary amine?
**a.** Alkyl nitrite
**b.** Carbylamine
**c.** Primary amine
**d.** Secondary nitro compound

**48.** $C_6H_5NH_2 \xrightarrow{NaNO_2HCl} X \xrightarrow{Cu_2(CN)_2} Y \xrightarrow{H_2O/H^+} Z$
*Z* is identified as:
**a.** $C_6H_5-NH-CH_3$ **b.** $C_6H_5-COOH$
**c.** $C_6H_5-CH_2-NH_2$ **d.** $C_6H_5-CH_2-COOH$

**49.** In the reaction
$CH_3CN + 2H \xrightarrow[\text{Ether}]{\text{HCl}} X \xrightarrow[H_2O]{\text{Boiling}} Y$; the term Y is:
**a.** Acetone **b.** Ethyl amine
**c.** Acetaldehyde **d.** Dimethyl amine

**50.** Reduction of alkyl nitrites yields:
**a.** Alcohol **b.** Base
**c.** Amine **d.** Acid

**51.** The correct order of basicity in amines:
**(i)** $C_4H_5NH_2$ **(ii)** $CH_3NH_2$
**(iii)** $(CH_3)_2NH$ **(iv)** $(CH_3)_3N$
**a.** (i) < (iv) < (ii) < (iii) **b.** (iv) < (iii) < (ii) < (i)
**c.** (i) < (ii) < (iii) < (iv) **d.** (ii) < (iii) < (iv) < (i)

**52.** The product of mustard oil reaction is:
**a.** Alkyl isothiocyanate
**b.** Dithio carbonamide
**c.** Dithio ethylacetate
**d.** Thioether

**53.** When methyl cyanide is hydrolysed in presence of alkali, the product is?
**a.** Acetamide **b.** Methane
**c.** $CO_2 + H_2O$ **d.** Acetic acid

**54.** Primary and secondary amines are distinguished by:
**a.** $Br_2/KOH$ **b.** $HClO_4$
**c.** $HNO_2$ **d.** $NH_3$

**55.** Hydrolysis of acetonitrile in acidic medium produces:
**a.** $CH_3CH_2OH$ **b.** $CH_3COOH$
**c.** $CH_3NC$ **d.** $CH_3COOCH_3$

**56.** Reduction of methyl isocyanide gives:

**a.** Ethylamine **b.** Methylamine

**c.** Dimethylamine **d.** Trimethylamine

**57.** A primary amine can be converted to an alcohol by the action of:

**a.** Alkali **b.** Nitrous acid

**c.** Reducing agent **d.** Oxidising agent

**58.** Which of the following is not used as an explosive?

**a.** Trinitrotoluene **b.** Trinitrobenzene

**c.** Picric acid **d.** Nitrobenzene

**59.** Which of following do not react with $HNO_2$?

**a.** Primary nitroalkanes

**b.** Secondary nitroalkanes

**c.** Tertiary nitroalkanes

**d.** All of these

**60.** When an organic compound was treated with sodium nitrite and hydrochloric acid in the ice cold, nitrogen gas was evolved copiously. The compound is?

**a.** A nitro compound

**b.** A primary amine

**c.** An aliphatic primary amine

**d.** An aromatic primary amine

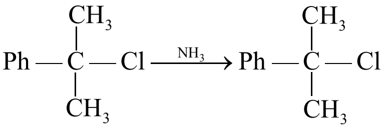
## NCERT EXEMPLAR PROBLEMS

### More than One Answer

**61.** Choose the incorrect reaction:

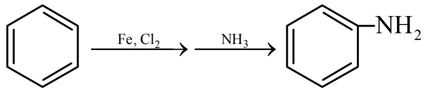
**a.** ${}_3N$

**b.**

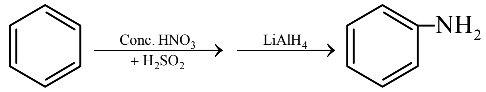


$$Ph-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-Cl \xrightarrow{NH_3} Ph-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-Cl$$

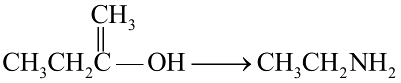
**c.**



**d.**



**62.**



$$CH_3CH_2\overset{\overset{CH_3}{\|}}{C}-OH \longrightarrow CH_3CH_2NH_2$$

Which of the following is/are effective for this conversion?

**a.** $NH_3$ (excess), heat, Na, $C_2H_5OH$

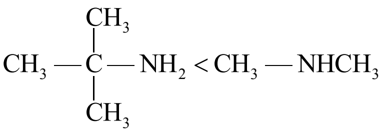
**b.** $N_3H$, cold conc. $H_2SO_4$

**c.** $NH_3$ (excess), heat, $NaOH, Br$

**d.** $NH_2-NH_2, H^+; NaNO_2, HCl; OH^-, H_2O$

**63.** Choose the correct comparisons (s).

**a.**



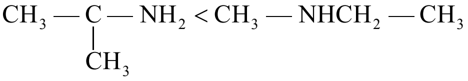
$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-NH_2 < CH_3-NHCH_3$$

basicity in aqueous medium

**b.** $CH_3CH_2CH_2NH_2 > (CH_3)N$

basicity in aqueous medium

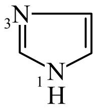
**c.**



$$CH_3-\underset{CH_3}{\underset{|}{C}}-NH_2 < CH_3-NHCH_2-CH_3$$

basicity in aqueous medium

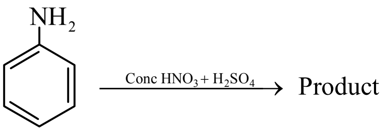
**d.**



N(1) > N(3)

basicity in aqueous medium

**64.**



Mark out the incorrect statement: (s)

**a.** In the reaction, $NO_2$ is the electrophile and it is electrophilic substitution.

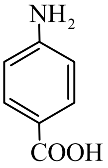
**b.** In the electrophilic substitution, nitration proceeds faster than that over benzene

**c.** In the electrophilic substitution, nitration proceeds slower than that over benzene

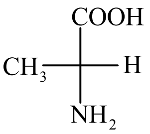
**d.** The reaction gives Meta substituted product as the predominant product.

**65.** Which of the following basically exist(s) as dipolar ion(s)?

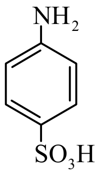
**a.**



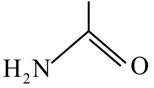
**b.**



**c.**



**d.**



**66.** The amine formed from an amide by means of bromine and alkali has:

**a.** Same number of C atoms as that of amide

**b**. One less C atom than that of amide

**c.** One more C atom than that of amide

**d.** Two more C atoms than that of amide

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

**a.** $CH_3NH_2$ **b.** $CH_3CH_2NH_2$

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

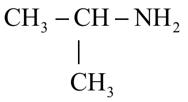
**68.** KCN reacts readily to give cyanide with:

**a.** Ethyl alcohol **b.** Ethyl bromide

**c.** Bromobenzene **d.** Chlorobenzene

**69.** Which of the following amine will not react with nitrous acid to give nitrogen?

**a.** $CH_3NH_2$ **b.** $CH_3-CH_2-NH_2$

**c.** 
$CH_3-CH(CH_3)-NH_2$

**d.** $(CH_3)_3N$

**70.** Primary amines can be distinguished from secondary and tertiary amines by reacting with:

**a.** Chloroform and alcoholic KOH

**b.** Methyl iodide

**c.** Chloroform alone

**d.** Zinc dust

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

**a.** Phenol **b.** Aniline

**c.** Nitrobenzene **d.** Benzene

**72.** The amine which can react with $C_6H_5-SO_2-Cl$ to form a product insoluble in alkali shall be?

**a.** Primary amine

**b.** Secondary amine

**c.** Tertiary amine

**d.** Both primary and secondary amines

**73.** Which one of the following compounds when heated with KOH and a primary amine gives carbylamine test?

**a.** $CHCl_3$ **b.** $CH_3Cl$

**c.** $CH_3OH$ **d.** $CH_3CN$

**74.** When acetamide reacts with $Br_2$ and caustic soda, then we get?

**a.** Acetic acid **b.** Bromoacetic acid

**c.** Methyl amine **d.** Ethyl amine

### Assertion and Reason

**Note:** Read the Assertion (A) and Reason (R) carefully to mark the correct option out of the options given below:

**a.** If both assertion and reason are true and the reason is the correct explanation of the assertion.

**b.** If both assertion and reason are true but reason is not the correct explanation of the assertion.

**c.** If assertion is true but reason is false.

**d.** If the assertion and reason both are false.

**e.** If assertion is false but reason is true.

**75.** **Assertion:** Nitrating mixture used for carrying our nitration of benzene consists of conc. $HNO_3$ + conc. $H_2SO_4$.

**Reason:** In presence of $H_2SO_4, HNO_3$ acts as a base and produces $NO_2^+$ ions.

**76.** **Assertion:** In order to convert R—Cl to pure $R-NH_2$, Gabriel pthalimide synthesis can be used.

**Reason:** With proper choice of alkyl halides, pthalimide synthesis can be used to prepare 1°, 2° or 3° amines.

**77.** **Assertion:** Lower aldehydes and ketones are soluble in water but the solubility decreases as the molecular mass increases.

**Reason:** Distinction between aldehydes and ketones can be made by Tollen's test.

**78.** **Assertion:** Aniline hydrogen sulphate on heating forms a mixture of ortho and para aminobenzene sulphonic acids.

**Reason:** The sulphonic acid group is electron withdrawing.

**79.** **Assertion:** Alkyl isocyanides in acidified water give alkyl formamides.

**Reason:** In isocyanides, carbon first acts as a nuclephile and then as an electrophile.

**80.** **Assertion:** Benzene diazonium chloride does not give tests for nitrogen:

**Reason:** $N_2$ gas lose takes place during heating

**81.** **Assertion:** Amines are basic in nature.

**Reason:** Presence of lone pair of electron on nitrogen atom.

**82.** **Assertion:** Nitrobenzene does not undergo Friedel Craft alkylation.

**Reason:** Nitrobenzene is used as solvent in laboratory and industry.

**83.** **Assertion:** The reaction between a diazo salt and an aromatic amine or a phenol, giving an aminoazo or hydroxyazo compounds is called coupling reaction.

**Reason:** Condensation of diazonium salt with phenol is carried out in weakly acidic medium.

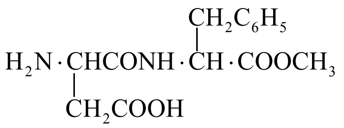
**84.** **Assertion:** *p*-Anisidine is weaker base than aniline.

**Reason:** $-OCH_3$ group in anisidine exerts –R effect.

## Comprehension Based

### Paragraph –I

Aspartame is an artificial sweetener having peptide bound in its structure given below:



$$\mathrm{H_2N\cdot \underset{\displaystyle CH_2COOH}{CH}CONH\cdot \overset{\displaystyle CH_2C_6H_5}{CH}\cdot COOCH_3}$$

**85.** It contains the functional group:

**A.** Amino **B.** Carboxylic

**C.** Ester **D.** Amine

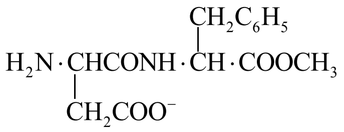
**E.** Benzyl

**a.** A, B, C, D, E **b.** A, B, C, D

**c.** A, B, E **d.** A, B, D, E

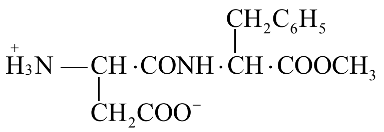
**86.** It zwitter ion structure is:

**a.**



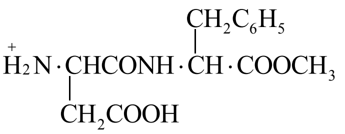
$$\mathrm{H_2N\cdot \underset{\displaystyle CH_2COO^-}{CH}CONH\cdot \overset{\displaystyle CH_2C_6H_5}{CH}\cdot COOCH_3}$$

**b.**



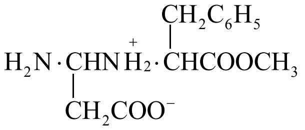
$$\mathrm{\overset{+}{H_3}N — \underset{\displaystyle CH_2COO^-}{CH}\cdot CONH\cdot \overset{\displaystyle CH_2C_6H_5}{CH}\cdot COOCH_3}$$

**c.**



$$\mathrm{\overset{+}{H_2}N\cdot \underset{\displaystyle CH_2COOH}{CH}CONH\cdot \overset{\displaystyle CH_2C_6H_5}{CH}\cdot COOCH_3}$$

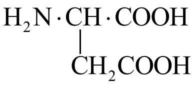
**d.**



$$\mathrm{H_2N\cdot \underset{\displaystyle CH_2COO^-}{CH}\overset{+}{N}H_2\cdot \overset{\displaystyle CH_2C_6H_5}{CH}COOCH_3}$$

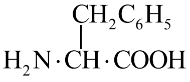
**87.** Aspartame on hydrolysis forms two amino acids:

**A.**



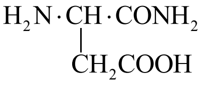
$$\mathrm{H_2N\cdot \underset{\displaystyle CH_2COOH}{CH}\cdot COOH}$$

**B.**



$$\mathrm{H_2N\cdot \overset{\displaystyle CH_2C_6H_5}{CH}\cdot COOH}$$

**C.**



$$\mathrm{H_2N\cdot \underset{\displaystyle CH_2COOH}{CH}\cdot CONH_2}$$

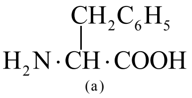
**D.**

$$\mathrm{H_2N\cdot CHCONH\cdot \overset{\displaystyle CH_2C_6H_5}{CH}\cdot COOH}$$

**a.** A, B **b.** C, D

**c.** A, C **d.** B, D

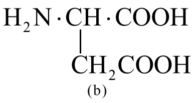
**88.** Which is correct for?



$$\mathrm{H_2N\cdot \overset{\displaystyle CH_2C_6H_5}{CH}\cdot COOH}$$

(a)

and



$$\mathrm{H_2N\cdot \underset{\displaystyle CH_2COOH}{CH}\cdot COOH}$$

(b)

?

**A.** (a) is less hydrophobic

**B.** (a) is more hydrophobic

**C.** $C_6H_5 — CH_2^-$ is more hydrophobic than $CH_2COOH$

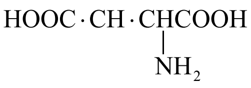
**D.** $C_6H_5 - CH_2 -$ is more hydrophobic than $CH_2COOH$

**a.** B, C **b.** A, D

**c.** B, D **d.** A, C

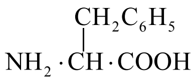
**89.** Aspartic acid has the structure:

**a.**



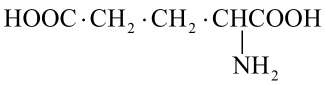
$$\mathrm{HOOC\cdot CH\cdot \underset{\displaystyle NH_2}{CH}COOH}$$

**b.**



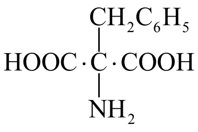
$$\mathrm{NH_2\cdot \overset{\displaystyle CH_2C_6H_5}{CH}\cdot COOH}$$

**c.**



$$\mathrm{HOOC\cdot CH_2\cdot CH_2\cdot \underset{\displaystyle NH_2}{CH}COOH}$$

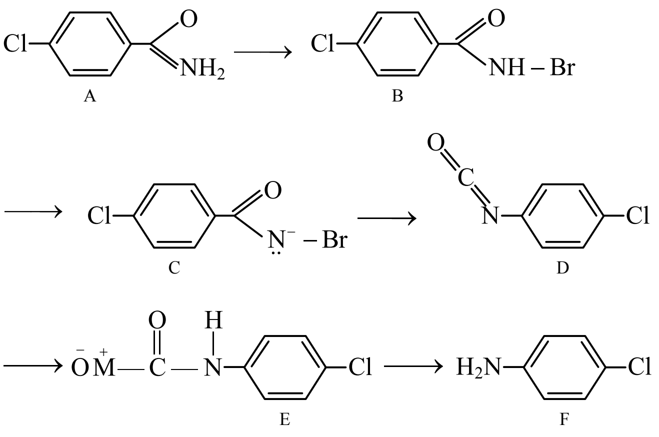
**d.**



$$\mathrm{HOOC\cdot \overset{\displaystyle CH_2C_6H_5}{\underset{\displaystyle NH_2}{C}}\cdot COOH}$$

### Paragraph –II

*R*CONH$_2$ is converted into RNH$_2$ by means of Hofmann bromamide degradation.



In this reaction, RCONHBr is formed form which this reaction has derived its name. Electron donating group at phenyl activates the reaction. Hofmann degradation reaction is an intra-molecular reaction.

**90.** How can the conversion of A to B be brought about?

**a.** KBr **b.** KBr + $CH_3ONa$

**c.** KBr + KOH **d.** $Br_2$ + KOH

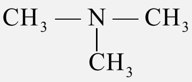
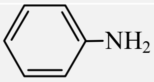
**91.** Which is the rate determining step in Hofmann bromamide degradation?

**a.** Formation of A **b.** Formation of B

**c.** Formation of C **d.** Formation of D

## Match the Column

**92.** Match the statement of Column with those in Column II:

| Column I<br>(Amines) | Column II<br>(Characteristics) |
|---|---|
| **(A)** $CH_3CH_2CH_2NH_2$ | **1.** Treatment of $NaNO_2$, HCl give N-nitroso compound |
| **(B)** $CH_3CH_2NHCH_3$ | **2.** Treatment of $NaNO_2$, HCl gives diazonium chloride |
| **(C)**  $CH_3-\underset{\displaystyle CH_3}{\underset{\vert}{N}}-CH_3$ | **3.** Treatment of $CH_3$1 (excess) followed by AgOH; heat gives out alkene |
| **(D)**  | **4.** Treatment of HCl, heat gives dealkylation |

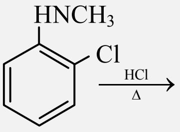
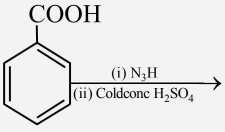
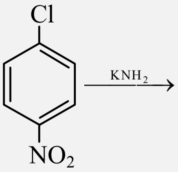
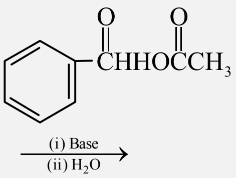
**a.** A-3,4; B→1,3,4; C→4; D→2

**b.** A→2,3,4; B→1,4; C→1,4; D→2

**c.** A→2,3,4; B→4; C→2; D→4

**d.** A→1,3,4; B→2,3,4; C→4; D→2

**93.** Match the statement of Column with those in Column II:

| Column I<br>(Reactants) | Column II<br>(Characteristics of Reaction) |
|---|---|
| **(A)**  | **1.** Para substituted product |
| **(B)**  | **2.** Inter molecular re-arrangement |
| **(C)**  | **3.** Reaction involves Ph–N = C–O as an inter-mediate |
| **(D)**  | **4.** Biomolecular reaction |

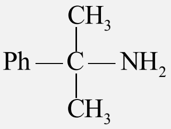
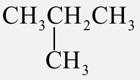
**a.** A→1,4; B→2,3; C→2,4; D→1,3

**b.** A→1,4; B→2,3; C→1,4; D→2,3

**c.** A→3,4; B→1,2,3; C→2,4; D→2,3

**d.** A→1,2; B→2,4; C→3,2; D→1,4

**94.** Match the statement of Column with those in Column II:

| Column I<br>(Amines) | Column II<br>(Characteristics) |
|---|---|
| **(A)**  $Ph-\overset{\displaystyle CH_3}{\overset{\vert}{\underset{\displaystyle CH_3}{\underset{\vert}{C}}}}-NH_2$ | **1.** Treatment of $CS_2$, $HgCl_2$ gives out alkyliso-thiocyanate |
| **(B)** $CH_3CH_2NH_2$ | **2.** Treatment of p-toluene sulphonyl chloride produces the compound insoluble in alkali |
| **(C)**  $CH_3\underset{\displaystyle CH_3}{\underset{\vert}{C}}H_2CH_3$ | **3.** Treatment of $H_2O_2$; heat gives out alkene |
| **(D)** $CH_3CH_2NHCH_3$ | **4.** Treatment of carbon disulphide produces dithiocarbamic acid |

**a.** A→1,2; B→3,4; C→3; D→4

**b.** A→2,3; B→1,2; C→1,3; D→2,4

**c.** A→1,4; B→1,4; C→3; D→4

**d.** A→1,4; B→2,4; C→3; D→2,3

## Integer

**For 95 to 100**

The ammonia evolved from the treatment of 0.30 g of an organic compound for the estimation of nitrogen was passed in 100 ml of 0.1 sulphuric acid. The excess of acid required 20 mL of 0.5M sodium hydroxide solution for complete neutralization. For the organic compound:

**95.** Acetamide:

**96.** Benzamide:

**97.** Urea:

**98.** Thiourea:

**99.** Number of isomeric primary amines obtained from $C_4H_{11}N$ are:

**100.** The maximum number of $-NO_2$ groups that can be introduced by nitration in benzene is usually

## ANSWER

| 1. | 2. | 3. | 4. | 5. | 6. | 7. | 8. | 9. | 10. |
|---|---|---|---|---|---|---|---|---|---|
| a | b | d | b | d | b | b | c | d | a |
| **11.** | **12.** | **13.** | **14.** | **15.** | **16.** | **17.** | **18.** | **19.** | **20.** |
| d | d | b | b | d | c | d | c | a | c |
| **21.** | **22.** | **23.** | **24.** | **25.** | **26.** | **27.** | **28.** | **29.** | **30.** |
| d | c | a | b | a | b | c | c | c | d |
| **31.** | **32.** | **33.** | **34.** | **35.** | **36.** | **37.** | **38.** | **39.** | **40.** |
| b | b | a | d | b | a | d | d | c | c |
| **41.** | **42.** | **43.** | **44.** | **45.** | **46.** | **47.** | **48.** | **49.** | **50.** |
| a | b | d | d | c | b | b | b | c | a |
| **51.** | **52.** | **53.** | **54.** | **55.** | **56.** | **57.** | **58.** | **59.** | **60.** |
| a | a | d | c | b | c | b | d | c | c |
| **61.** | **62.** | **63.** | **64.** | **65.** | **66.** | **67.** | **68.** | **69.** | **70.** |
| b,c,d | b,c,d | a,b,c | b | b,c | b | c | b | d | a |
| **71.** | **72.** | **73.** | **74.** | **75.** | **76.** | **77.** | **78.** | **79.** | **80.** |
| b | b | a | c | a | c | b | d | a | a |
| **81.** | **82.** | **83.** | **84.** | **85.** | **86.** | **87.** | **88.** | **89.** | **90.** |
| a | b | c | d | b | b | a | a | a | d |
| **91.** | **92.** | **93.** | **94.** | **95.** | **96.** | **97.** | **98.** | **99.** | **100.** |
| d | a | b | c | 24 | 11 | 47 | 37 | 4 | 6 |

## SOLUTION

### Multiple Choice Questions

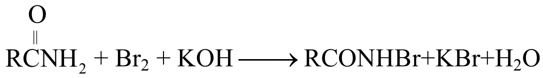
**1.** **(a)** Basicity of amines increase with increase in number of $-CH_3$ groups (or any group which cause +I effect), due to increase in electron density on N atom. As a rule, the basicity of *t*-amine should be more than that of *s*-amine, but actually it is found to be lesser than *s*-amines.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

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

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

$$2RNH_2 + H_2SO_4 \longrightarrow [RNH_3^+]_2SO_4^{2-}$$

**3.** **(d)** (i)



$$R\overset{O}{\overset{\|}{C}}NH_2 + Br_2 + KOH \longrightarrow RCONHBr + KBr + H_2O$$

(ii) $RCONHBr + KOH \rightarrow RNCO + KBr + H_2O$

(iii) $RNCO + 2KOH \rightarrow RNH_2 + K_2CO_3$

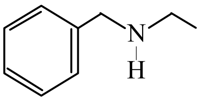
$RCONH_2 + Br_2 + 4KOH \rightarrow RNH_2 + 2KBr + K_2CO_3 + 2H_2O$

**4.** **(b)** Aniline reacts with benzaldehyde and forms Schiff's base (benzal aniline) or anils.

$$C_6H_5-NH_2 + O=CHC_6H_5 \xrightarrow[-H_2O]{\Delta} \underset{\text{Benzylidine aniline}}{C_6H_5N=CHC_6H_5}$$

**5.** **(d)** $\underset{\text{Acetamide}}{CH_3CONH_2} + Br_2 + 4KOH \xrightarrow[-2H_2O]{} \underset{\text{(Methyl amine)}}{CH_3NH_2} + 2KBr + 2K_2CO_3$

**6.** **(b)**

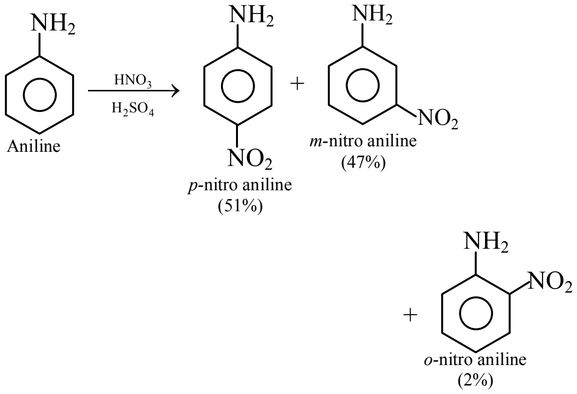


is most basic

**7.** **(b)** N-alkyl formamides when dehydrated with $POCl_3$ in presence of pyridine give isocyanides.

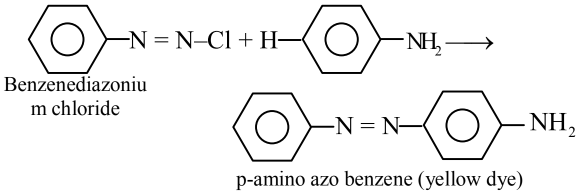
**8.** **(c)** Pollutants which are formed by reaction amongst the primary pollutants (persist in the environment in the form they are passed into it) are called as secondary pollutants. *e.g.*, peroxyacyl nitrates (PAN) are formed through reaction between nitrogen oxides and hydrocarbons in the presence of sunlight.

**9.** **(d)**



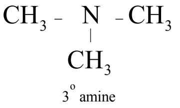
The reason for this is that, in acidic condition protonation of–$NH_2$ group gives anilinium ion ($+NH_3$), which is of deactivating nature and of *m*-directive nature.

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



**11.** **(d)** $C_3H_9N$ can form all the 3 amines.

$\underset{1^o \text{ amine}}{CH_3CH_2CH_2-NH_2}$, $\underset{2^o \text{ amine}}{CH_3-CH_2-NH-CH_3}$



$$\underset{3^o \text{ amine}}{CH_3-\underset{CH_3}{\underset{|}{N}}-CH_3}$$

**12.** **(d)** Allyl isocyanide. $CH_2=CH-CH_2-N\stackrel{\rightharpoonup}{=}C$

**13.** **(b)** $CH_3CN$ is called acetonitrile....

**14.** **(b)** $CH_3CH_2-O-N=O$ is a nitrite derivative, hence it is not a nitro derivative.

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

**16.** **(c)** Hofmann's bromamide reaction

$$\underset{\text{Acetamide}}{CH_3-CO-NH_2}+Br_2+4KOH$$

$$\xrightarrow{H_2O}\underset{\text{Methyl amine}}{CH_3NH_2}+K_2CO_3+2KBr+2H_2O$$

**17.** **(d)** $CH_3I\xrightarrow[\Delta]{NH_3}\underset{\text{Methylamine}}{CH_3NH_2}\xrightarrow{CH_3I}\underset{\text{Dimethyl amine}}{(CH_3)_2NH}$

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

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

It yield amine when reduced as –

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

**19.** **(a)** $\underset{1^\circ-\text{amine}}{R-NH_2}+CHCl_3+3KOH\longrightarrow R-NC+3KCl+3HO$

**20.** **(c)** $\underset{\text{Nitrobenzene}}{C_6H_5NO_2}+6H\xrightarrow{pt/H_2}\underset{\text{Aniline}}{C_6H_5NH_2}+2H_2O$

**21.** **(d)** $\underset{\text{chlorobenzene}}{2C_6H_5Cl}+2NH_3\xrightarrow[\text{in xylene }570^\circ K]{H_2O}$

$$\underset{\text{(Aniline)}}{C_6H_5NH_2}+Cu_2Cl_2+H_2O$$

**22.** **(c)** $C_6H_5NH_2\xrightarrow[0^\circ C-5^\circ C]{NaNO_2\ /\ HCl}\underset{(X)}{C_6H_5N_2^+Cl^-}$

$$\xrightarrow[H_2O]{HNO_2}\underset{(Y)}{C_6H_5NO_2}+N_2+HCl$$

**23.** **(a)** Halogen have –*I* and +*M* effect by which its electron delocalized in benzene ring by resonance & due to its –*I* effect its bonded with benzene ring and cannot be substitute by $CN^-$ and show the inertness against KCN while other option gives Aromatic nitrile

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

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

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

**24.** **(b)** $C_6H_5NO_2+6H\xrightarrow{Sn+HCl}C_6H_5-NH_2+2H_2O$

**25.** **(a)** $CH_3CONH_2\xrightarrow{Na+ROH}CH_3CH_2OH+H_2O$

**26.** **(b)** $\underset{\text{Propionamide}}{CH_3-CH_2-CO-NH_2}+Br_2+4KOH\longrightarrow$

$$CH_3CH_2NH_2+K_2CO_3+2KBr+2H_2O$$

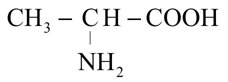
**27.** **(c)** $CH_3-N=C+4[H]\xrightarrow{\text{Reduction}}\underset{2^\circ\text{ amine}}{CH_3-NH-CH_3}$

**28.** **(c)** $C_6H_5NH_2+HCl+NaNO_2\longrightarrow C_6H_5N_2Cl$

**29.** **(c)** Methyl amine is the strongest base.

**30.** **(d)** Due to +ve I.E. of alkyl group, *N*-atom of amines acquires patrial –ve charge and thus electron pair is easily donated.

**31.** **(b)**



$CH_3-\underset{\underset{NH_2}{|}}{C}H-COOH$

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

**32.** **(b)** Only primary aromatic amines can undergo diazotisation.

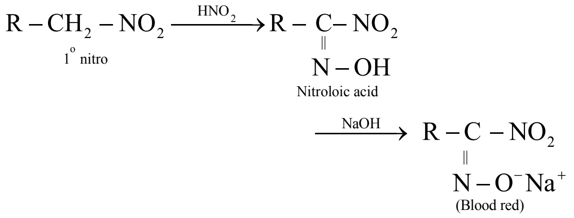
**33.** **(a)** $\underset{\text{2°amine is most basic}}{(CH_3)_2NH}>\underset{1^\circ\text{amine}}{CH_3NH_2}>\underset{3^\circ\text{ amine}}{(CH_3)_3N}>\underset{\text{Ammonia is least basic}}{\overset{..}{N}H_3}$

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

**35.** **(b)** $\underset{\text{(Litmus paper)}}{\text{Red}}\xrightarrow{CH_3NH_2}\text{Blue}$

This litmus paper test shows basic nature of amine.

**36.** **(a)**



$\underset{1^\circ\text{ nitro}}{R-CH_2-NO_2}\xrightarrow{HNO_2}\underset{\text{Nitroloic acid}}{R-\underset{\underset{N-OH}{\|}}{C}-NO_2}$

$\xrightarrow{NaOH}\underset{\text{(Blood red)}}{R-\underset{\underset{N-O^-Na^+}{\|}}{C}-NO_2}$

**37.** **(d)** $CH_3NH_2+2HNO_2\longrightarrow CH_3-O-N=O+N_2+2H_2O$

$2CH_3NH_2+2HNO_2\longrightarrow CH_3-O-CH_3+2N_2+3H_2O$

**38.** **(d)** $R-NH_2+CHCl_3+3NaOH\longrightarrow RN\equiv C+3NaCl+3H_2O$

The unpleasant smell is due to the formation of isocyanide.

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

**40.** **(c)** Replacable $H^-$is absent.

**41.** **(a)** To supress the concentration of the aniline available for coupling other rise coupling occurs.

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

**43.** **(d)** $CH_3-NC+2H_2O\longrightarrow CH_3NH_2+HCOOH$

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

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

46. **(b)** We know that

$$\underset{\text{Aniline}}{C_6H_5NH_2}+\underset{\text{Chloroform}}{CHCl_3}+3KOH \rightarrow \underset{\text{phenyl isocyanide}}{C_6H_5NC}+3KCl+3H_2O$$

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

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

$$\underset{\text{Carbylamine}}{R-N \stackrel{\rightarrow}{=} C} \xrightarrow{Ni/H_2} \underset{\text{Secondary amine}}{R-NH-CH_3}$$

48. **(b)** $C_6H_5NH_2 \xrightarrow{NaNO_2/HCl} \underset{(X)}{C_6H_5N_2Cl}$

$$\xrightarrow{Cu_2(CN)_2} \underset{(Y)}{C_6H_5\,CN} \xrightarrow{H_2O/H^+} \underset{\text{Benzoic acid (Z)}}{C_6H_5-COOH}$$

Thus product *Z* is identified as

49. **(c)** $CH_3CN+2H \xrightarrow[\text{Ether}]{HCl} HC\equiv CH$

$$\xrightarrow{\text{Boiling } H_2O} \underset{\text{Acetaldeyde}}{CH_3CHO}$$

50. **(a)** $\underset{\text{Alkyl nitrite}}{R-O-N=O}+6[H] \xrightarrow{Sn/HCl} \underset{\text{Alcohol}}{ROH}+NH_3+H_2O$

51. **(a)** Basicity order is

$$C_4H_5NH_2 < (CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$$

$(CH_3)_3N$ is less basic due to steric effect while $C_4H_5NH_2$ is less basic due to resonance.

52. **(a)** Mustard oil reaction

$$CH_3-CH_2-\underset{\text{Ethyl amine}}{NH_2}+CS_2 \xrightarrow{HgCl_2}$$

$$\underset{\text{Ethyl isothiocyanate}}{CH_3-CH_2-N=C=S}+H_2S$$

53. **(d)** $\underset{\text{Methyl cyanide}}{CH_3-C\equiv N}+2H_2O \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH}+NH_3$

54. **(c)** $\underset{1^\circ}{CH_3CH_2-NH_2}+HNO_2 \longrightarrow \underset{\text{Alcohol}}{CH_3CH_2-OH}+N_2+H_2O$

$$\underset{2^\circ}{(CH_3CH_2)_2NH}+HNO_2 \longrightarrow \underset{\text{Nitroso amine}}{(CH_3CH_2)_2N-N=O}+H_2O$$

55. **(b)** $CH_3CN+2H_2O \xrightarrow{HCl} CH_3COOH+NH_3$

56. **(c)** $CH_3NC+4H \xrightarrow[\text{ether}]{LiAlH_4} (CH_3)_2NH$ .

57. **(b)** $R-NH_2+HNO_2 \longrightarrow \underset{\text{alcohol}}{R-OH}+N_2+H_2O$ .

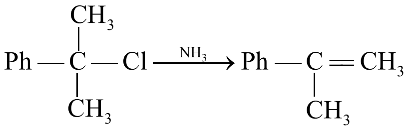
58. **(d)** Nitro compounds are not explosive but stable compound.

59. **(c)** Because in tertiary nitroalkanes $\alpha-H$ atom is absent.

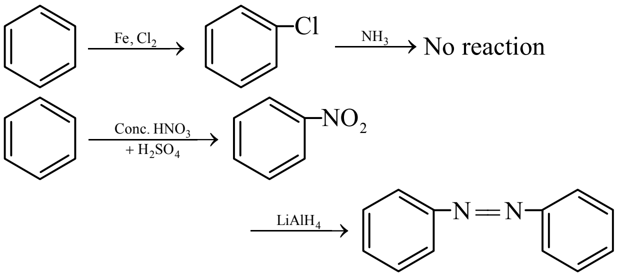
60. **(c)** $RNH_2+NaNO_2+HCl \longrightarrow R-OH+NaCl+N_2+H_2O$

## NCERT Exemplar Problems

### More than One Answer

61. **(b,c,d)** 

$$Ph-\overset{CH_3}{\underset{CH_3}{C}}-Cl \xrightarrow{NH_3} Ph-\underset{CH_3}{C}=CH_3$$



62. **(b,c,d)** (a) given corresponding amine

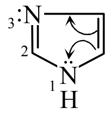
$CH_3CH_2-CH_2-NH_2$,

(b) Schmidt reaction

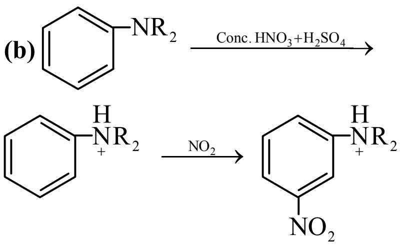
(c) Hoffmann's bromamide degradation

(d) Curtius reaction.

63. **(a,b,c)** $2^\circ > 1^\circ > 3^\circ > NH_3$ (in aqueous medium),3°>2°>1° (in the gaseous state)



N(1) containing lone pair is delocalized to impart aromaticity.

64. **(b)** 

Reaction medium is strongly acidic; $-NR_2$ group gets converted first into $-NHR_2$ which is deactivating and Meta directing.

65. **(b,c)** Aromatic amines are usually weaker bases, so cannot neutralise the acid, although the more acidic group $-SO_4H$ is neutralized and dipolar ion is formed with what. Aliphatic a-amino acids form dipolar ion as the amine is sufficiently basic.

66. **(b)** $\underset{(2c)}{CH_3 - CO - NH_2} \xrightarrow[\text{Hofmann's bromamide}]{NaOH / Br_2} \underset{(1c)}{CH_3 - NH_2}$

67. **(c)** Secondary amines give oily nitrosomine with nitrous acid.

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

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

69. **(d)** Tertiary amine does not react with nitrous acid because in it $\alpha$-H atom is absent.

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

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

72. **(b)** $C_6H_5SO_2Cl$ is called Hinsberg's reagent they react with sec amine to form a product in soluble in alkalies. This reaction used to separate 1°, 2° and 3° amine from their mixture.

73. **(a)** $CHCl_3$ gives carbylamine test.

$$RNH_2 + CHCl_3 + 3KOH(alc.)$$

$$\xrightarrow{\Delta} \underset{\text{alkyl isocyanide}}{RN \overset{\rightarrow}{=} C} + 3KCl + 3H_2O$$

74. **(c)** This is Hofman-bromide reaction. In this reaction one carbon less amines are formed from amides.

$$CH_3CONH_2 \xrightarrow{Br_2 / KOH} CH_3NH_2$$

**Assertion and Reason**

75. **(a)** $HNO_3 + 2H_2SO_4 \rightleftharpoons 2HSO_4^- + NO_2^+ + H_3\overset{+}{O}$

76. **(c)** Only primary aliphatic amines can be prepared by Gabriel phthalimide reaction.

77. **(b)** Solubility of aldehydes and ketones decrease as the molecular mass increase.

78. **(d)** The nitro group strongly deactivates the benzene ring towards electrophilic substitution. Nitrobenzene does not undergo Friedel-Craft acylation reaction.

79. **(a)** In an isocyanide, first an electrophile and then a nucleophile add at the carbon to form a species which usually undergoes further transformations.

$$R\overset{+}{N} \equiv \overset{-}{C} + E^+ \longrightarrow R\overset{+}{N} \equiv CE \xrightarrow{Nu} RN \equiv C(Nu)E$$

$$R\overset{+}{N} \equiv \overset{-}{C} + H_2O \longrightarrow RN = CHOH \longrightarrow \underset{\text{alkylformamide}}{RNHCHO}$$

80. **(a)** It is true that benzene diazonium chloride does not respond Lassaigne test of nitrogen because benzene diazonium chloride losses $N_2$ on Slight heat and thus it can't react with sodium metal.

81. **(a)** Amines are basic due to the presence of a lone pair of electrons on nitrogen atom. The lone pair can be easily donated.

82. **(b)** Nitrobenzene does not undergo Friedel Craft reaction because nitro group deactivate the ring towards electrophilic substitution and drastic conditions are needed to carry out the electrophilic substitution reactions.

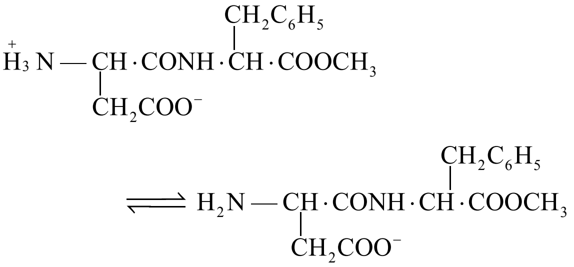
83. **(c)** Condensation of diazonium salt with phenol is carried out in weakly alkaline medium, $(pH = 9)$. This is due to the fact that in strongly acid medium the $-OH$ of a phenol remains unionised, and an amine forms a salt. Phenol exists as phenoxide ion and the latter is readily substituted by electrophiles than phenol itself. Thus, in phenol, coupling is carried out in alkaline medium.

84. **(d)** *p*-Anisidine is a stronger base than aniline. $-OCH_3$ group in anisidine exerts +R-effect.

**Comprehension Based**

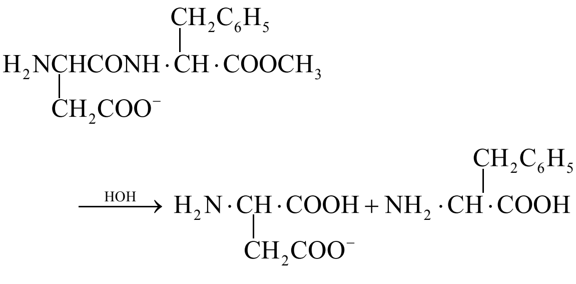
85. **(b)** Benzyl is not functional group.

86. **(b)**



$$\overset{+}{H_3}N - \underset{CH_2COO^-}{CH} \cdot CONH \cdot \overset{CH_2C_6H_5}{CH} \cdot COOCH_3 \rightleftharpoons H_2N - \underset{CH_2COO^-}{CH} \cdot CONH \cdot \overset{CH_2C_6H_5}{CH} \cdot COOCH_3$$

87. **(a)**



$$H_2N\underset{CH_2COO^-}{C}HCONH \cdot \overset{CH_2C_6H_5}{CH} \cdot COOCH_3 \xrightarrow{HOH} H_2N \cdot \underset{CH_2COO^-}{CH} \cdot COOH + NH_2 \cdot \overset{CH_2C_6H_5}{CH} \cdot COOH$$

88. **(a)** $C_6H_5 \cdot CH_2$ — is more hydrophobic

89. **(a)** Aspartic acid is 2-amino butan-dioic acid

90. **(d)** Hofmann bromamide reaction takes place with $Br_2$ + KOH

91. **(d)** Also red mechanism of reaction

**Match the Column**

**92.** **(a)** A→3,4; B→1,3,4; C→4; D→2

**93.** **(b)** A→1,4; B→2,3; C→1,4; D→2,3

**94.** **(c)** A→1,4; B→1,4; C→3; D→4

**Integer**

**For 95 to 100**

Let unreacted 0.1 M $(= 0.2\ \text{N})$ $H_2SO_4 = V'$ mL

$\therefore$ 20 mL of 0.5 M NaOH $= V'$ mL of 0.2 $H_2SO_4$

$\therefore$ $20 \times 0.5 = V' \times 0.2$

$\therefore$ $V' = 50$ mL

Used $H_2SO_4 = 100 - 50 = 50$ mL

$$\%\ \text{Nitrogen} = \frac{1.4\ \text{NV}}{\text{w}}$$

Where, N = normality of $H_2SO_4$ and V = volume of $H_2SO_4$

$$\therefore\ \%\ \text{Nitrogen} = \frac{14 \times 0.2 \times 50}{0.30}$$

= 46.67% of nitrogen in

**95.** **(24)** $CH_3CONH_2 = \dfrac{14 \times 100}{59}$

= 23.73% ≈ 24

**96.** **(11)** $C_6H_5CONH_2 = \dfrac{14 \times 100}{122}$

= 11.48% ≈ 11

**97.** **(47)** $NH_2CONH_2 = \dfrac{28 \times 100}{60}$

= 46.67% ≈ 17

**98.** **(37)** $NH_2CSNH_2 = \dfrac{28 \times 100}{76}$

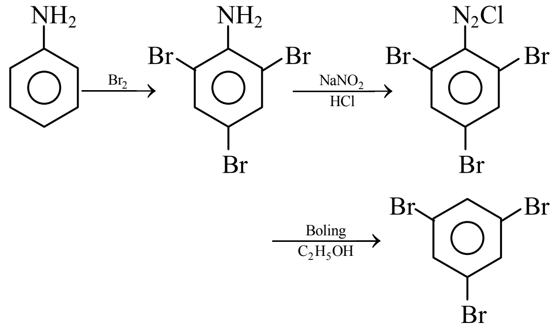
= 36.84% ≈ 37

**99.** **(4)** Four 1° amines are possible

$CH_3CH_2CH_2CH_2NH_2, (CH_3)_2CHCH_2NH_2,$

$CH_3CH(NH_2)CH_2CH_3, (CH_3)_3CNH_2$

**100.** **(6)**



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