Chapter

27 Amines

TYPE A : MULTIPLE CHOICE QUESTIONS

1. Identify Y in the reaction : ***[1998]***

$$C_6H_5NH_2 \xrightarrow{NaNO_2/HCl} X \xrightarrow[dil.H_2SO_4]{H_2O} Y$$

(a) $C_6H_5N_2Cl$ (b) C_6H_5OH

(c) C_6H_5NHOH (d) C_6H_6

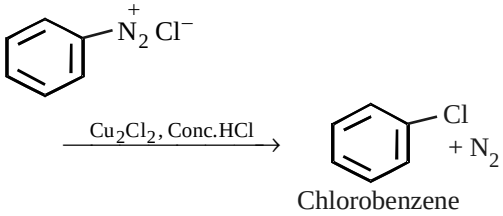
2. Dynamite is a mixture of: ***[1998]***

(a) Nitroglycerine + raw dust

(b) Nitroglycerine + HCl

(c) Hydrogen bomb + H_2SO_4

(d) Glycerine + H_2SO_4

3. 

Chlorobenzene

Above reaction is known as: ***[2000]***

(a) Strecker's reaction

(b) Sandmeyer's reaction

(c) Wohl-Ziegler reaction

(d) Stephen's reaction

4. Reduction of nitrobenzene with Sn/HCl produces: ***[2001]***

(a) azobenzene (b) azoxybenzene

(c) nitrobenzene (d) aniline

5. Hinsberg's reagent is : ***[2001]***

(a) $\begin{matrix} COOC_2H_5 \\ | \\ COOC_2H_5 \end{matrix}$

(b) $C_6H_5SO_2Cl$

(c) $C_6H_5SO_2NH_2$

(d) $CH_3COCH_2COOC_2H_5$

6. The product formed by the reaction of acetamide with bromine in presence of NaOH is : ***[2001]***

(a) CH_3CN (b) CH_3CHO

(c) CH_3CH_2OH (d) CH_3NH_2

7. Primary amine reacts with carbon disulphide and $HgCl_2$ to produce alkyl isothiocyanate. This reaction is : ***[2001]***

(a) Carbylamine reaction

(b) Hoffmann bromamide reaction

(c) Perkin reaction

(d) Hoffmann mustard oil reaction

8. Which of the following is involved in Sandmeyer's reaction? ***[2002]***

(a) ferrous salt

(b) diazonium salt

(c) ammonium salt

(d) cuprammonium salt

9. In the reaction :

$$C_6H_5CHO + C_6H_5NH_2 \longrightarrow$$

$$C_6H_5N = CHC_6H_5 + H_2O$$

The compound, $C_6H_5N = CHC_6H_5$ is known as ***[2002]***

(a) aldol (b) Schiff's base

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

10. The ortho/para directing group among the following is : ***[2003]***

(a) COOH (b) CN

(c) $COCH_3$ (d) $NHCONH_2$

11. Among the following, the weakest base is ***[2003]***

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

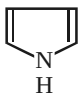
(c) $O_2N.CH_2NH_2$ (d) CH_3NHCHO

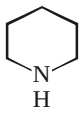
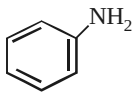
12. Nitrobenzene gives N-phenylhydroxylamine by : ***[2003]***

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

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

13. The strongest base among the following is

(a)  (b)  ***[2004]***

(c)  (d) 

14. Aromatic nitriles (ArCN) are not prepared by reaction : ***[2004]***

(a) $ArX + KCN$

(b) $ArN_2^+ + CuCN$

(c) $ArCONH_2 + P_2O_5$

(d) $ArCONH_2 + SOCl_2$

15. Melting points are normally highest for :

(a) tertiary amides (b) secondary amides

(c) primary amides (d) amines ***[2004]***

16. Which of the following chemicals are used to manufacture methyl isocyanate that caused "Bhopal Tragedy"? ***[2005]***

(i) Methylamine (ii) Phosgene

(iii) Phosphine (iv) Dimethylamine

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

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

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

(a) RNCO (b) RCON ***[2005]***

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

18. Pyridine is less basic than triethylamine because : ***[2005]***

(a) pyridine has aromatic character

(b) nitrogen in pyridine is sp^2-hybridised

(c) pyridine is a cyclic system

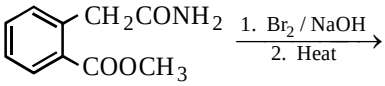
(d) in pyridine, lone pair of electrons on nitrogen is delocalised

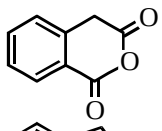
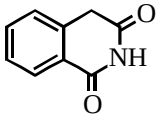
19. $C_6H_5CONHCH_3$ can be converted into $C_6H_5CH_2NHCH_3$ by : ***[2005]***

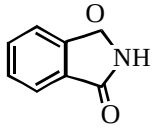
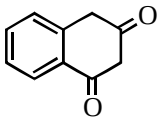
(a) $NaBH_4$ (b) H_2-Pd/C

(c) $LiAlH_4$ (d) Zn-Hg/HCl

20. The following sequence of reactions on A gives

 ***[2006]***

(a)  (b) 

(c)  (d) 

21. Nitrobenzene on treatment with zinc dust and aqueous ammonium chloride gives: ***[2006]***

(a) $C_6H_5N = NC_6H_5$

(b) $C_6H_5NH_2$

(c) C_6H_5NO

(d) C_6H_5NHOH

22. Which of the following statement is true? ***[2007]***

(a) Trimethyl amine forms a soluble compound with Hinsberg reagent and KOH.

(b) Dimethyl amine reacts with KOH and phenol to form an azo dye.

(c) Methyl amine reacts with nitrous acid and liberates N_2 from aq. solution.

(d) None of these.

23. Which of the following amines will not give N_2 gas on treatment with nitrous acid ($NaNO_2$ + HCl) ? ***[2007]***

(a) $C_2H_5NH_2$ (b) CH_3NH_2

(c) $(CH_3)_2CHNH_2$ (d) All will give N_2.

24. The compound which gives an oily nitrosoamine on reaction with nitrous acid at low temperature, is ***[2008]***

(a) CH_3NH_2 (b) $(CH_3)_2CHNH_2$

(c) $CH_3–NH–CH_3$ (d) $(CH_3)_3N$

25. Diethyl oxalate is used for distinguishing primary, secondary and tertiary ***[2009]***

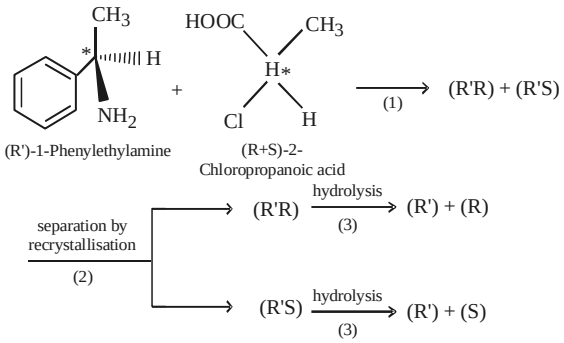
(a) alcohols

(b) amines

(c) alkyl halides

(d) hydrogens in hydrocarbons

26. Observe the following reaction : ***[2009]***



Which statement is not correct about the above observation ?

(a) The product mixture of step-1 is optically active

(b) The product R'R and R'S have identical structural formula

(c) R'R is nonsuperimposable on R'S

(d) R'R and R'S have same solubility in water

27. Fluorescein is an example of ***[2009]***

(a) azo dyes

(b) phthalein dyes

(c) triphenylmethane dyes

(d) nitro dyes

28. Urea upon hydrolysis yields: ***[2010]***

(a) acetamide

(b) carbonic acid

(c) ammonium hydroxide

(d) NO_2

29. Benzamide and benzyl amine can be distinguished by ***[2011]***

(a) cold dil. NaOH

(b) cold dil. HCl

(c) both a & b

(d) $NaNO_2$, HCl, 0°C, then β-naphthol

30. The basic character of ethyl amine, diethyl amine and triethyl amine in chlorobenzene is ***[2011]***

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

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

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

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

31. Consider the following reaction ***[2012]***

$$C_6H_5NO_2 \xrightarrow{Sn/HCl} X \xrightarrow{C_6H_5COCl} Y + HCl$$

What is Y?

(a) Acetanilide (b) Benzanilide

(c) Azobenzene (d) Hydrazobenzene

32. Which of the following gives primary amine on reduction? ***[2013]***

(a) $CH_3CH_2NO_2$

(b) $CH_3CH_2 - O - N = O$

(c) $C_6H_5N = NC_6H_5$

(d) CH_3CH_2NC

33. Which of the following compound will not undergo azo coupling reaction with benzene diazonium chloride. ***[2016]***

(a) Aniline (b) Phenol

(c) Anisole (d) Nitrobenzene

34. Which of the following are intermediates in Sandmeyer reaction ? ***[2017]***

(i) $C_6H_5N^+ \equiv NCl^-$ (ii) $C_6H_5N^+ \equiv N$

(iii) $\dot{C}_6H_5$ (iv) C_6H_5Cl

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

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

TYPE B : ASSERTION REASON QUESTIONS

Directions for (Qs. 35-41) : These questions consist of two statements, each printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following five responses.

(a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.

(b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.

(c) If the Assertion is correct but Reason is incorrect.

(d) If both the Assertion and Reason are incorrect.

(e) If the Assertion is incorrect but the Reason is correct.

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

Reason : Presence of lone pair of electrons on nitrogen atom. ***[1999]***

36. **Assertion :** Benzene diazonium chloride does not give test for nitrogen.

Reason : Loss of N_2 gas takes place during heating. ***[1999]***

37. **Assertion :** *p*-$O_2N.\ C_6H_4.COCH_3$ is prepared by Friedel Craft's acylation of nitrobenzene.
Reason : Nitrobenzene easily undergoes electrophilic substitution reaction. ***[2005]***

38. **Assertion :** Alkyl isocyanides in acidified water give alkyl formamides.
Reason : In isocyanides, carbon first acts as a nucleophile and then as an electrophile. ***[2005]***

39. **Assertion :** Anilinium chloride is more acidic than ammonium chloride.
Reason : Anilinium ion is resonance stabilized. ***[2006]***

40. **Assertion :** Benzene diazonium salt on boiling with water forms phenol.
Reason : C – N bond is polar. ***[2007]***

41. **Assertion :** Nitrobenzene is used as a solvent in Friedel-Craft's reaction.
Reason : Fusion of nitrobenzene with solid KOH gives a low yield of a mixture of *o*-and *p*-nitrophenols. ***[2008]***

Directions for (Qs.42-46) : Each of these questions contains an Assertion followed by Reason. Read them carefully and answer the question on the basis of following options. You have to select the one that best describes the two statements.

(a) If both Assertion and Reason are correct and Reason is the correct explanation of Assertion.
(b) If both Assertion and Reason are correct, but Reason is not the correct explanation of Assertion.
(c) If Assertion is correct but Reason is incorrect.
(d) If both the Assertion and Reason are incorrect.

42. **Assertion :** Nitration of aniline can be conveniently done by protecting the amino group by acetylation.
Reason : Acetylation increases the electron-density in the benzene ring. ***[2010]***

43. **Assertion :** Acetamide reacts with Br_2 in presence of methanolic CH_3ONa to form methyl N-methylcarbamate.
Reason : Methyl isocyanate is formed as an intermediate which reacts with methanol to form methyl N-methylcarbamate. ***[2014]***

44. **Assertion :** 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 ***[2016]***

45. **Assertion :** Aniline does not undergo Friedel-Crafts reaction. ***[2017]***
Reason : $-NH_2$ group of aniline reacts with $AlCl_3$ (Lewis acid) to give acid-base reaction.

46. **Assertion :** Aniline is better nucleophile than anilium ion. ***[2017]***
Reason : Anilium ion have +ve charge.

HINTS & SOLUTIONS

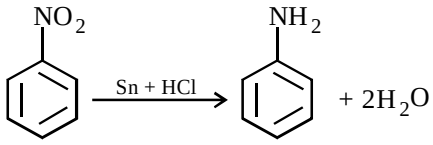
Type A : Multiple Choice Questions

1. (b) $C_6H_5NH_2 \xrightarrow{NaNO_2+HCl} \underset{X}{C_6H_5N_2Cl} \xrightarrow{H_2O} \underset{Y}{C_6H_5OH}$

2. (a) Dynamite is a mixture of nitroglycerine and raw dust.

3. (b) The given reaction is known as Sandmeyer's reaction.

4. (d) Reduction of nitrobenzene with Sn/HCl produces aniline.



5. (b) Hinsberg's reagent is $C_6H_5SO_2Cl$ which is used to distinguish primary, secondary and tertiary amines.

6. (d) $CH_3CONH_2 + 2NaOH + Br_2 \longrightarrow$

$CH_3NH_2 + Na_2CO_3 + 2NaBr + H_2O$

7. (d) The reaction is known as Hoffmann mustard oil reaction.

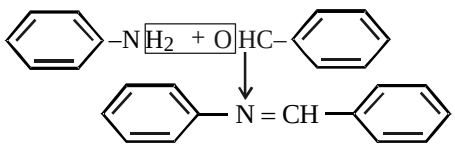
$$R{-}NH_2 + S{=}C{=}S \longrightarrow R{-}NH{-}\overset{\overset{S}{\|}}{C}{-}SH \xrightarrow{HgCl_2} R{-}N{=}C{=}S + HgS + 2HCl$$

Alkyl isothiocyanate

8. (b) Diazonium salt is involved in Sandmeyer's reaction.

$Ar - N_2 - X + Cu_2Cl_2 / HCl \longrightarrow ArCl + N_2 + X^-$

9. (b) Primary amines react with aldehydes or ketones to form compound known as Schiff's base

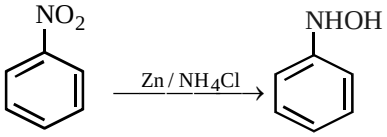


Schiff's base

10. (d) $-NH-CONH_2$ group is ortho para directing. Nitrogen shares its lone pair with benzene ring and makes this group ortho para directing.

11. (c) As $-NO_2$ is strong electron withdrawing group.

12. (d)



Phenyl hydroxylamine

13. (c) The lone pair of electrons on nitrogen is not involved in the formation of π-electron cloud of the ring.

14. (a) Aryl halide (ArX) does not undergo nucleophilic substitution because they have strong C—X bond due to resonance.

15. (d) Although amines as well as amides form intermolecular H-bonding, H-bonding in amides is less prominent because of $-\overset{\overset{O}{\|}}{C}-$ group of $-\overset{\overset{O}{\|}}{C}-\ddot{N}H_2$

16. (c)

$$CH_3NH_2 + \underset{\text{Phosgene}}{COCl_2} \longrightarrow \underset{\text{Methyl isocyanate}}{CH_3NCO} + 2HCl$$

17. (d) Hofmann rearrangement

$$R-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow{Br_2} R-\overset{\overset{O}{\|}}{C}-NHBr \xrightarrow{KOH} R-\overset{\overset{O}{\|}}{C}-N^-\!\!-Br \xrightarrow[(-Br^-)]{}$$

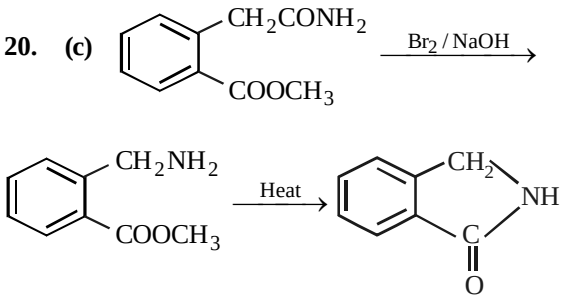
$$R-\overset{\overset{O}{\|}}{C}-\ddot{N} \longrightarrow \underset{\text{Alkyl isocyanate}}{\overset{\overset{O}{\|}}{C}=N-R}$$

$$\overset{\overset{O}{\|}}{C}=N-R \xrightarrow[H_2O]{OH^-} RNH_2 + CO_3^{2-}.$$

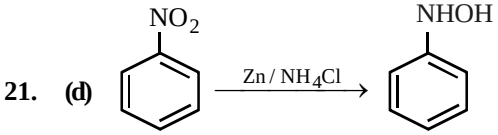
18. (b) Pyridine is less basic because nitrogen in pyridine is sp^2 hybridised, and sp^2 hybridised orbital is more acidic in character than sp^3 hybridised orbital in $(C_2H_5)_3N$.

19. (c) $C_6H_5CONHCH_3 \xrightarrow{LiAlH_4} C_6H_5CH_2NHCH_3$

20. (c)



21. (d)



22. (c) Among the given statements only (c) is true. As methyl amine liberates N_2 on reaction with nitrous acid.

$CH_3-NH_2+2HONO \xrightarrow{} CH_3-ONO+N_2+2H_2O$

While dimethyl amine and trimethyl amine form insoluble compound with Hinsberg reagent and KOH.

$$R_2NH + C_6H_5SO_2Cl \xrightarrow{OH^-} C_6H_5SO_2NR_2$$

$$R_3N + C_6H_5SO_2Cl \xrightarrow{OH^-} \underset{\text{insoluble}}{R_3N}$$

Azo dyes are not formed by secondary amines.

23. (d) All aliphatic primary amines liberate N_2 on treatment with nitrous acid ($NaNO_2 + HCl$)

$RNH_2 + HONO \xrightarrow{} R-OH + N_2 + H_2O$

24. (c) **Out of** primary, secondary and tertiary amines, the secondary amines, on reaction with HNO_2, produce yellow oily *compounds* called *nitrosoamines*.

$$\underset{(2^\circ \text{ amine})}{CH_3-NH-CH_3} + HNO_2 \longrightarrow \underset{\substack{\text{dimethyl nitrosoamine}\\(\text{oily})}}{CH_3-\overset{\overset{NO}{|}}{N}-CH_3} + H_2O$$

25. (b) Diethyl oxalate is used for distinguishing 1°, 2° and 3° amines as three amines react differently as discussed below.

The 1° amine forms corresponding substituted oxamide which is a crystalline solid; while 2° amine forms a diethyl oxamic ester which is a liquid and 3° amine does not react with diethyl oxalate since it does not contain a replacable hydrogen atom.

$$\underset{1^\circ \text{ amine}}{RNH_2} + \begin{matrix}COOC_2H_5\\|\\COOC_2H_5\end{matrix} \longrightarrow \underset{\substack{\text{oxamide}\\\text{crystalline}\\\text{solid}}}{\begin{matrix}CONHR\\|\\CONHR\end{matrix}} + 2C_2H_5OH$$

$$\underset{2^\circ \text{ amine}}{R_2NH} + \begin{matrix}COOC_2H_5\\|\\COOC_2H_5\end{matrix} \longrightarrow \underset{\substack{\text{N, N–dialkyl}\\\text{oxamic ester}}}{\begin{matrix}CO-NR_2\\|\\COOC_2H_5\end{matrix}} + C_2H_5OH$$

$$\underset{3^\circ \text{ amine}}{R_3N} + \begin{matrix}COOC_2H_5\\|\\COOC_2H_5\end{matrix} \longrightarrow \text{No reaction}$$

26. (d) R'R and R'S are diastereomers and have different physical properties like water solubility, B.P., M.P. etc.

Mixture of diastereomers is optically active hence the product mixture in step 1 is optically active.

27. (b) Fluorescein also called resorcinolphthalein is an example of phthalein dye. It is prepared by heating phthalic anhydride and resorcinol over a zinc catalyst, and it crystallizes as a deep red powder.

28. (b) $NH_2-\overset{\overset{O}{||}}{C}-NH_2 \xrightarrow[\text{acid or base}]{\text{hydrolysis}}$

$$CO_2 + 2H_3 \xrightarrow{H_2O} \underset{\text{Carbonic acid}}{H_2CO_3}$$

Note: The enzyme urease (occurs in soyabean) brings about the same change.

29. (b) Cold dil. NaOH does not attack to either of the compound, while cold dil. HCl reacts only with benzyl amine $C_6H_5CH_2NH_2$.

30. (a) In presence of chlorobenzene, hydrogen bonding is not possible between the protonated amine and the solvent and thus the stabilization factor (solvation effect) is absent. Hence basicity is explained on the basis of the number of electron releasing groups in an amine.

31. (b) **32. (a)** **33. (d)** **34. (a)**

Type B : Assertion Reason Questions

35. (a) Amines are basic in nature due to presence of a lone pair of electrons on nitrogen.

36. (a) Benzene diazonium chloride does not give test of nitrogen as nitrogen gas is evolved on heating.

37. (d) Nitrobenzene undergoes electrophilic substitution reaction with difficulty because NO_2 group is electron withdrawing & therefore, it deactivates the benzene ring.

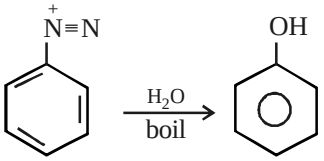
38. (a) $R-N^+\equiv C^- \xrightarrow{H^+} R-N^+\equiv CH \xrightarrow{H_2O}$

$\rightarrow R-N=C(H)(OH) \rightleftharpoons R-NH-\underset{\underset{O}{\|}}{C}-H$ (Alkyl formamide)

In the first step due to partial nagative charge on carbon it acts as nucleophile and therefore attacked by H^+ of the acid. Once it acquires positive charge, it becomes electrophile as is shown in the next step.

39. (c) Anilinium chloride is more acidic than ammonium chloride because it liberates aniline (resonance stabilized) when heated with strong base.

Anilinium ions does not show resonance because charge dispersion at ring may involve pentavalent nitrogen structure.

40. (b) 

benzene diazonium salt

Although C–N bond is polar but it is not exact reason for the substitution.

41. (b) Nitrobenzene is used as a solvent in Friedel-Craft's reaction because its $-NO_2$ group deactivates benzene ring for electrophilic substitution.

Although the given staement of the reason is correct, it is not correct explanation of the given statement.

42. (c) Acetylation decreases the electron density in the benzene ring thereby preventing oxidation.

43. (a) **44. (c)** **45. (a)**

46. (a) It is fact that aniline is better nucleophile than anilium ion. Anilium ion contain +ve charge, which reduces the tendency to donate lone pair of electron $C_6H_5NH_3^+$ (Anilium ion).