Ordinary Thinking

Objective Questions

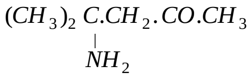
Introduction of Nitrogen Containing Compounds

1. Cyanide ion is
(a) Nucleophilic (b) Electrophilic
(c) Strongly acidic (d) Non-reactive and neutral

2. Compounds containing both amino and COOH groups are known as
(a) Diamines (b) Unknown
(c) Amino acids (d) Enzymes

3. Which of the following is 1^o amine
(a) Ethylene diamine (b) Dimethyl amine
(c) Trimethyl amine (d) *N*-methyl aniline

4. C_3H_9N represents **[AMU 1988]**
(a) Primary amine (b) Secondary amine
(c) Tertiary amine (d) All of these

5. 
$(CH_3)_2\underset{NH_2}{\underset{|}{C}}.CH_2.CO.CH_3$ is **[MP PET/PMT 1988]**
(a) Diacetone (b) Acetoneamine
(c) Diacetoneamine (d) Aminoacetone

6. A secondary amine is **[KCET 1992]**
(a) An organic compound with two $-NH_2$ groups
(b) A compound with two carbon atoms and an $-NH_2$ group
(c) A compound with an $-NH_2$ group on the carbon atom in number 2 position
(d) A compound in which two of the hydrogens of NH_3 have been replaced by organic groups

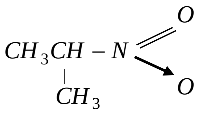
7. The structural formula of methyl aminomethane is **[MP PMT 1991]**
(a) $(CH_3)_2CHNH_2$ (b) $(CH_3)_3N$
(c) $(CH_3)_2NH$ (d) CH_3NH_2

8. Allyl isocyanide has **[IIT 1995]**
(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

9. Triaminobenzene is a **[BHU 1996]**
(a) 2^o amine (b) 3^o amine
(c) 1^o amine (d) Quarternary salt

10. $CH_2=CH-CH_2-NH-CH_3$ is a **[RPET 2000]**
(a) Secondary amine (b) Primary amine
(c) Tertiary amine (d) None of these

11. Leakage of which gas was responsible for the Bhopal tragedy in 1984
(a) $CH_3-N=C=O$ (b) $CH_3-C-N=S$
(c) $CHCl_3$ (d) C_6H_5COCl

12. Which of the following is not a nitro-derivative **[DCE 2004]**
(a) $C_6H_5NO_2$ (b) CH_3CH_2ONO
(c) 
$CH_3\underset{CH_3}{\underset{|}{CH}}-N\overset{O}{\underset{O}{\lessgtr}}$
(d) $C_6H_4(OH)NO_2$

13. Acetonitrile is: **[MP PMT 2004]**
(a) C_2H_5CN (b) CH_3CN
(c) CH_3COCN (d) $C_6H_5CH_2CN$

14. In alkyl cyanide alkyl group attached with **[BCECE 2005]**
(a) *C* of *CN* group
(b) *N* of *CN* group
(c) Either *C* or *N* of *CN* group
(d) Both *C* and *N* of *CN* group

15. Number of isomeric primary amines obtained from $C_4H_{11}N$ are
(a) 3 (b) 4
(c) 5 (d) 6

Preparation of Nitrogen Containing Compounds

1. Amides may be converted into amines by reaction named after **[CPMT 1974; MP**
(a) Perkin (b) Claisen
(c) Hoffmann (d) Kolbe

2. Reaction $CH_3CONH_2\xrightarrow{NaOBr}$ gives **[CPMT 1983, 93, 97]**
(a) CH_3Br (b) CH_4
(c) CH_3COBr (d) CH_3NH_2

3. Acetamide is treated separately with the following reagents. Which would give methyl amine **[IIT 1983; CPMT 1988, 94; MP PET 1993; MP PMT 1996; AIIMS 1998]**
(a) PCl_5 (b) $NaOH+Br_2$

(c) Sodalime (d) Hot conc. H_2SO_4

4. The amine formed from an amide by means of bromine and alkali has
(a) Same number of C atoms as that of amide
(b) One less C atom than that of amide
(c) One more C atom than that of amide
(d) Two more C atoms than that of amide

5. $CH_3CN \xrightarrow{Na+C_2H_5OH} X$

The compound *X* is **[MP PMT 1983; BHU 1984]**
(a) CH_3CONH_2 (b) $CH_3CH_2NH_2$
(c) C_2H_6 (d) CH_3NHCH_3

6. Ethylamine can be prepared by the action of bromine and caustic potash on **[CPMT 1994]**
(a) Acetamide (b) Propionamide
(c) Formamide (d) Methyl cyanide

7. Ethylamine can be obtained by the **[CPMT 1985]**
(a) Action of NH_3 on ethyl iodide
(b) Action of NH_3 on ethyl alcohol
(c) Both (a) and (b)
(d) None of the above

8. Aniline is usually purified by **[CPMT 1983, 93; JIPMER 1997]**
(a) Steam distillation (b) Simple distillation
(c) Vacuum distillation (d) Extraction with a solvent

9. Reduction of nitroalkanes yields
(a) Acid (b) Alcohol
(c) Amine (d) Diazo compounds

10. Acetamide changes into methylamine by
(a) Hofmann bromamide reaction
(b) Hofmann reaction
(c) Friedel-Craft's reaction
(d) Hinsberg reaction

11. When methyl iodide is heated with ammonia, the product obtained is
(a) Methylamine
(b) Dimethylamine
(c) Trimethylamine
(d) A mixture of the above three amines

12. Acetanilide can be prepared from aniline and which of the following
(a) Ethanol (b) Acetaldehyde
(c) Acetone (d) Acetic anhydride

13. Reduction of nitroalkanes in neutral medium (e.g. Zn / NH_4Cl) forms mainly
(a) $R-NH_2$ (b) $R-NHOH$
(c) $R-N=N-Cl$ (d) All of these

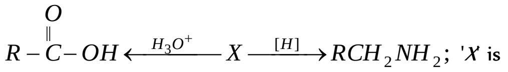
14. Nitrosobenzene can be prepared by oxidizing aniline from
(a) H_2SO_4 (b) H_2SO_5
(c) H_2SO_3 (d) $K_2Cr_2O_7$

15. The Hinsberg's method is used for
(a) Preparation of primary amines
(b) Preparation of secondary amines
(c) Preparation of tertiary amines
(d) Separation of amine mixtures

16. Which one of the following compound gives a secondary amine on reduction
(a) Nitromethane (b) Nitrobenzene
(c) Methyl isocyanide (d) Methyl cyanide

17. Chloropicrin is manufactured by the reaction between Cl_2, $NaOH$ and
(a) Nitromethane (b) Nitroethane
(c) Nitrophenol (d) Nitrostyrene

18. In the reaction


$R-\overset{\overset{O}{\|}}{C}-OH \xleftarrow{H_3O^+} X \xrightarrow{[H]} RCH_2NH_2$; '*X*' is

[MP PMT 1990]
(a) Isonitrile (b) Nitrile
(c) Nitrite (d) Oxime

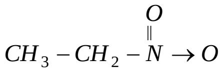
19. When ethanol is mixed with ammonia and passed over alumina the compound formed is **[CBSE PMT 1990]**
(a) $C_2H_5NH_2$ (b) C_2H_4
(c) $C_2H_5OC_2H_5$ (d) CH_3OCH_3

20. Which of the following reactions does not yield an amine **[CPMT 1989, 93]**
(a) $RX+NH_3 \longrightarrow$
(b) $RCH=NOH+[H] \xrightarrow[C_2H_5OH]{Na}$
(c) $RCN+H_2O \xrightarrow{H^+}$
(d) $RCONH_2+4H \xrightarrow{LiAlH_4}$

21. Identify '*B*' in the reaction

Acetamide $\xrightarrow[\Delta]{P_2O_5} A \xrightarrow{4H} B$ **[MP PET 1995]**
(a) CH_3NH_2 (b) $CH_3CH_2NH_2$
(c) CH_3CN (d) CH_3COONH_4

22. Which of the following gives primary amine on reduction **[MP PMT 1995]**


(a) $CH_3-CH_2-\overset{\overset{O}{\|}}{N}\rightarrow O$
(b) $CH_3-CH_2-O-N=O$
(c) $CH_3CH_2NO_3$
(d) None of these

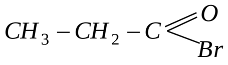
23. Which of the following is converted into an alcohol on treatment with HNO_2 **[MP PET 1996; MP PMT 1999]**
(a) Methyl amine (b) Aniline
(c) Dimethyl amine (d) Triethyl amine

24. Which of the following gives *RNC*, when reacted with $CHCl_3$ and *KOH* **[MP PET 1996]**
(a) RNH_2 (b) R_2NH
(c) R_3N (d) $R_4N^+Cl^-$

25. When aniline reacts with $NaNO_2$ and dil. *HCl* at 0^o-5^oC, the product formed is **[MP PMT 1996; AIIMS 1996]**
(a) Nitroaniline
(b) Benzene diazonium chloride
(c) Benzene
(d) Trinitroaniline

26. Starting from propanoic acid, the following reactions were carried out

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

What is the compound *Z*
(a) CH_3-CH_2-Br
(b) $CH_3-CH_2-NH_2$
(c) 
(d) $CH_3-CH_2-CH_2-NH_2$

27. In the reaction

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

the final product (C) is

(a) Ammonium acetate (b) Acetamide

(c) Amino methane (d) Ethanal

28. In the following reaction, X is

$$X \xrightarrow{\text{Bromination}} Y \xrightarrow{NaNO_2+HCl} Z \xrightarrow[C_2H_5OH]{\text{Boiling}} \text{Tribromobenzene}$$

[CPMT 1999]

(a) Benzoic acid (b) Salicylic acid

(c) Phenol (d) Aniline

29. Which of the following reactions will not give primary amine [CPMT 1999]

(a) $CH_3CONH_2 \xrightarrow{KOH.Br_2}$

(b) $CH_3CN \xrightarrow{LiAlH_4}$

(c) $CH_3NC \xrightarrow{LiAlH_4}$

(d) $CH_3CONH_2 \xrightarrow{LiAlH_4}$

30. Carbylamine reaction is given by [BHU 1996; EAMCET 1990]

(a) 1^o amine (b) 3^o amine

(c) 2^o amine (d) Quarternary salts

31. The reaction

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

is known as [BHU 1996]

(a) Carbylamine reaction

(b) Reimer-Tiemann reaction

(c) Kolbe reaction

(d) Hofmann's degradation

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

What is Z? [CPMT 1996]

(a) $CH_3CH_2NH_2$ (b) CH_3CH_2NC

(c) $CH_3CH_2CH_3$ (d) NH_2CONH_2

33. Which of the following reacts with chloroform and a base to form phenyl isocyanide [AFMC 1997]

(a) Aniline (b) Phenol

(c) Benzene (d) Nitrobenzene

34. Aromatic primary amine when treated with cold HNO_2 gives [Pb. CET 2002; DCE 1999]

(a) Benzyl alcohol (b) Nitro benzene

(c) Benzene (d) Diazonium salt

35. Which of the following compound is the strongest base [BHU 1999]

(a) Ammonia (b) Aniline

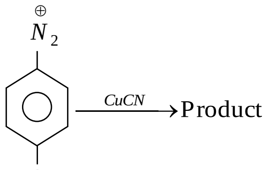
(c) Methylamine (d) *N*-methyl aniline

36. Nitrobenzene combines with hydrogen in the presence of platinum to produce [BHU 1999]

(a) Toluene (b) Benzene

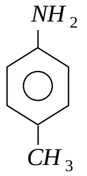
(c) Aniline (d) Azobenzene

37.

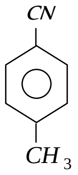


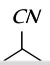
The product is [RPET 2000]

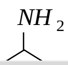
(a)



(b)







(c) (d)

38. Ethyl amine on heating with CS_2 in presence of $HgCl_2$ forms

(a) C_2H_5NCS (b) $(C_2H_5)_2S$

(c) $(C_2H_5)_2CS$ (d) $C_2H_5(CS)_2$

39. Which of the following reacts with $NaNO_2 + HCl$ to give phenol [MP PMT 2000]

(a) $C_6H_5CH_2NHCH_3$ (b) $(CH_3)_2NH$

(c) CH_3NH_2 (d) $C_6H_5NH_2$

40. Which of the following reactions give $RCONH_2$ [Roorkee 2000]

(a) $R - C \equiv N + H_2O \xrightarrow{HCl}$

(b) $RCOONH_4 \xrightarrow{\text{heat}}$

(c) $R - COCl + NH_3 \longrightarrow$

(d) $(RCO)_2O + NH_3 \longrightarrow$

41. When chlorobenzene is treated with NH_3 in presence of Cu_2O in xylene at 570 *K*. The product obtained is [Pb. PMT 2000]

(a) Benzylamine (b) Diazonium salt

(c) Schiff's base (d) Aniline

42. Nitrobenzene can be prepared from benzene by using a mixture of conc. HNO_3 and conc. H_2SO_4. In the nitrating mixture, HNO_3 acts as a [BHU 2001]

(a) Base (b) Acid

(c) Catalyst (d) Reducing agent

43. The rate determining step for the preparation of nitrobenzene from benzene is [AIIMS 2001]

(a) Removal of $\overset{+}{NO}_2$ (b) Removal of $\overset{+}{NO}_3$

(c) Formation of $\overset{+}{NO}_2$ (d) Formation of $\overset{+}{NO}_3$

44. In this reaction $C_6H_5NH_2 + HCl + NaNO_2 \rightarrow X$. Product X is [RPMT 2002; AFMC 2002]

(a) Aniline hydrochloride

(b) Nitro aniline

(c) Benzenediazonium chloride

(d) None of these

45. The diazonium salts are the reaction products in presence of excess of mineral acid with nitrous acid and [MP PET 2002]

(a) Primary aliphatic amine

(b) Secondary aromatic amine

(c) Primary aromatic amine

(d) Tertiary aliphatic amine

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

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

The reducing agent used in this reaction is .... [Orissa JEE 2002]

(a) $LiAlH_4$ (b) Sn/HCl

(c) *Na*/alcohol (d) H_2/Ni

47. When aniline is treated with sodium nitrite and hydrochloric acid at $0^\circ C$, it gives [Orissa JEE 2003]

(a) Phenol and N_2 (b) Diazonium salt

(c) Hydrazo compound (d) No reaction takes place

48. $CH_3NO_2 \xrightarrow{Sn+HCl} CH_3X$, the '*X*' contain

[CPMT 2003]

(a) $-NH_2$ (b) $-COOH$

(c) $-CHO$ (d) $(CH_3CO)_2O$

49. In the series of reaction

$C_6H_5NH_2 \xrightarrow[0-5^\circ C]{NaNO_2/HCl} X \xrightarrow[CH_2O]{HNO_2} Y + N_2 + HCl$ X and Y are respectively [EAMCET 2003]

(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) $C_6H_5NO_2, C_6H_6$

50. Aromatic nitriles ($ArCN$) are not prepared by reaction [AIIMS 2004]

(a) $ArX + KCN$ (b) $ArN_2^+ + CuCN$

(c) $ArCONH_2 + P_2O_5$ (d) $ArCONH_2 + SOCl_2$

51. An organic amino compound reacts with aqueous nitrous acid at low temperature to produce an oily nitroso amine. The compound is : [DCE 2003]

(a) CH_3NH_2 (b) $CH_3CH_2NH_2$

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

52. Azo-dyes are prepared from : [BHU 2004; Pb. CET 2001]

(a) Aniline (b) Salicylic acid

(c) Benzaldehyde (d) Chlorobenzene

53. Gabriel's phthalimide synthesis is used for the preparation of [CPMT 1982; DPMT 1983]

(a) Primary aromatic amine (b) Secondary amine

(c) Primary aliphatic amine (d) Tertiary amine

54. For the preparation of *p*-nitroiodobenzene from *p*-nitroaniline, the best method is [Orissa JEE 2005]

(a) $NaNO_2 / HCl$ followed by KI

(b) $NaNO_2 / HCl$ followed by $CuCN$

(c) $LiAlH_4$ followed by I_2

(d) $NaBH_4$ followed by I_2

55. KCN reacts readily to give a cyanide with [J & K 2005]

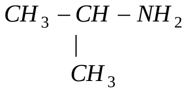
(a) Ethyl alcohol (b) Ethyl bromide

(c) Bromobenzene (d) Chlorobenzene

Properties of Nitrogen Containing Compounds

1. Which of the following amine will not react with nitrous acid to give nitrogen [NCERT 1984]

(a) CH_3NH_2 (b) $CH_3-CH_2-NH_2$

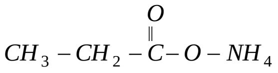
(c) 
$CH_3-\underset{\underset{CH_3}{|}}{CH}-NH_2$ (d) $(CH_3)_3N$

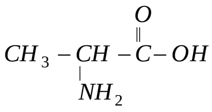
2. Which of the following compound is expected to be most basic

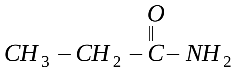
(a) Aniline (b) Methylamine

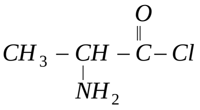
(c) Hydroxylamine (d) Ethylamine

3. Which of the following compounds is an amino acid [Manipal MEE 1995]

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

4. Nitro group in nitrobenzene is a [MNR 1986]

(a) Ortho director (b) Meta director

(c) Para director (d) Ortho and para director

5. The alkyl cyanides are

(a) Acidic (b) Basic

(c) Neutral (d) Amphoteric

6. 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

7. Aniline when treated with HNO_2 and HCl at 0^oC gives [CPMT 1982, 89; RPMT 2000]

(a) Phenol (b) Nitrobenzene

(c) A diazo compound (d) None of these

8. Nitrosobenzene can be isolated from nitrobenzene under [DPMT 1982]

(a) Metal and acid

(b) Zn dust and NH_4Cl

(c) Alkaline sodium arsenite

(d) Cannot be isolated

9. Alkyl cyanides when react with Grignard reagent, the product on hydrolysis found, is [MP PMT 1980]

(a) Aldehyde (b) Ketone

(c) Alcohol (d) Acid

10. The product formed when benzene is nitrated by fuming nitric acid is [MP PMT 1979]

(a) *m*-dinitrobenzene (b) Nitrobenzene

(c) *sym*-trinitrobenzene (d) None of these

11. Ethyl amine undergoes oxidation in the presence of $KMnO_4$ to form [CPMT 1985]

(a) An acid (b) An alcohol

(c) An aldehyde (d) A nitrogen oxide

12. Which of the following amines would undergo diazotisation

(a) Primary aliphatic amines (b) Primary aromatic amines

(c) Both (a) and (b) (d) None of these

13. Reaction of primary amines with aldehyde yields [NCERT 1984; Manipal MEE 1995]

(a) Amides (b) Aldimines

(c) Nitriles (d) Nitro compounds

14. When acetamide is treated with HNO_2, the gas is evolved [CPMT 1993]

(a) H_2 (b) O_2

(c) N_2 (d) CH_4

15. Nitrobenzene on nitration gives [NCERT 1982] [NCERT 1978; CPMT 1989]

(a) *o*-dinitrobenzene (b) *p*-dinitrobenzene

(c) *m*-dinitrobenzene (d) *o*- and *p*-nitrobenzene

16. Reduction of alkyl nitrites yields

(a) Alcohol (b) Base

(c) Amine (d) Acid

17. When primary amines are treated with HCl, the product obtained is

(a) An alcohol (b) A cyanide

(c) An amide (d) Ammonium salt

18. Which one is weakest base [BHU 1982; RPMT 2000]

(a) Ammonia (b) Methylamine

(c) Dimethylamine (d) Trimethylamine

19. Chloroform when treated with aniline and alcoholic KOH gives[CPMT 1986; EAM

MP PMT 1997; Pb. PMT 1999]

(a) Phenyl cyanide (b) Phenyl isocyanide
(c) Chlorobenzene (d) Phenol

20. Which of following do not react with HNO_2
(a) Primary nitroalkanes (b) Secondary nitroalkanes
(c) Tertiary nitroalkanes (d) All of these

21. Primary amines can be distinguished from secondary and tertiary amines by reacting with [CPMT 1983]
(a) Chloroform and alcoholic *KOH*
(b) Methyl iodide
(c) Chloroform alone
(d) Zinc dust

22. Which of following is not an usual method for preparation of primary amine
(a) Hofmann's method (b) Curtius reaction
(c) Schmidt reaction (d) Friedel-Craft's reaction

23. A solution of methyl amine
(a) Turns blue litmus red
(b) Turns red litmus blue
(c) Does not affect red or blue litmus
(d) Bleaches litmus

24. Mark the correct statement
[CPMT 1974; DPMT 1983; MP PMT 1994]
(a) Methyl amine is slightly acidic
(b) Methyl amine is less basic than NH_3
(c) Methyl amine is stronger base than NH_3
(d) Methyl amine forms salts with alkalies

25. The product of mustard oil reaction is
(a) Alkyl isothiocyanate (b) Dithio carbonamide
(c) Dithio ethylacetate (d) Thioether

26. Which of the following is azo- group
(a) $-N=$ (b) $-N=N-$
(c) $-NH-$ (d) $-CO-NH-$

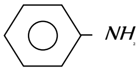
27. 'Oil of mirbane' is
(a) Aniline (b) Nitrobenzene
(c) *p*-nitroaniline (d) *p*-aminoazobenzene

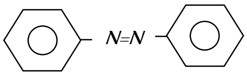
28. The maximum number of $-NO_2$ groups that can be introduced by nitration in benzene is usually
(a) 4 (b) 2
(c) 3 (d) 6

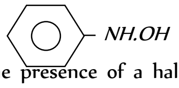
29. Nitrobenzene at room temperature is
(a) Gas (b) Liquid
(c) Solid (d) Solution

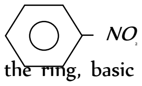
30. In the explosive amatol, TNT is mixed with [CPMT 1988]
(a) Ammonium citrate (b) Ammonium nitrate
(c) Ammonium oxalate (d) Ammonium sulphate

31. By reduction of nitrosobenzene which of the following is not obtained

(a) 

(b) 

(c) 

(d) 

32. By the presence of a halogen atom in the ring, basic properties of aniline is
(a) Increased (b) Decreased
(c) Unchanged (d) Doubled

33. In the mustard oil reaction, an amine is treated with
(a) Na / C_2H_5OH (b) Sn / HCl
(c) CS_2 (d) $K_2Cr_2O_7 / H_2SO_4$

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

35. Secondary nitro compounds when react with HNO_2 forms crystalline solids which one on treatment with *NaOH* gives
(a) Red solution (b) Blue solution
(c) White precipitate (d) Yellow colouration

36. Which of the following possess powerful mustard smell (and are called mustard oils)
(a) Alkyl isocyanates (b) Alkyl cyanates
(c) Alkyl isothiocyanates (d) Alkyl thiocyanates

37. On heating acetamide in presence of P_2O_5, which of the following is formed [MP PMT 1992; MP PET 1994; Kurukshetra CEE 1998]
(a) Ammonium acetate (b) Acetonitrile
(c) NH_3 (d) Methylamines

38. When chloroform reacts with ethyl amine in presence of alcoholic *KOH*, the compound formed is
[CPMT 1983; MP PMT 1993; CBSE PMT 1997; BHU 1999; AIEEE 2002]
(a) Ethyl cyanide (b) Ethyl isocyanide
(c) Formic acid (d) An amide

39. When methyl cyanide is hydrolysed in presence of alkali, the product is [MP PMT 1993; BCECE 2005]
(a) Acetamide (b) Methane
(c) $CO_2 + H_2O$ (d) Acetic acid

40. Hofmann's hypobromite reaction affords a method of
[MP PMT 1993]
(a) Preparing a tertiary amine
(b) Preparing a mixture of amines
(c) Stepping down a series
(d) Stepping up a series

41. The compound which on reaction with aqueous nitrous acid on HNO_2 at low temperature produces an oily nitrosoamine is[IIT 1981; CPMT 198
Kurukshetra CEE 1998; MP PMT 2001]
(a) Diethylamine (b) Ethylamine
(c) Aniline (d) Methylamine

42. Identify the product Z in the series

$$CH_3CN \xrightarrow{Na+C_2H_5OH} X \xrightarrow{HNO_2} Y \xrightarrow[H_2SO_4]{K_2Cr_2O_7} Z$$

[AIIMS 1983; JIPMER 2001]
(a) CH_3CHO (b) CH_3CONH_2
(c) CH_3COOH (d) CH_3CH_2NHOH

43. The end product of the reactions is

$$C_2H_5NH_2 \xrightarrow{HNO_2} A \xrightarrow{PCl_5} B \xrightarrow{H.NH_2} C$$

[CPMT 1988, 89, 93; DCE 1999; JIPMER 2000]
(a) Ethyl cyanide (b) Ethyl amine
(c) Methyl amine (d) Acetamide

44. Primary and secondary amines are distinguished by
[AMU 1988; MP PMT 1996]
(a) Br_2 / KOH (b) $HClO_4$
(c) HNO_2 (d) NH_3

45. Which one of the following will give a primary amine on hydrolysis
(a) Nitroparaffin (b) Alkyl cyanide
(c) Oxime (d) Alkyl isocyanide

46. Methyl amine reacts with HNO_2 giving [RPMT 1997]
(a) $CH_3O-N=O$ (b) CH_3-O-CH_3

(c) CH_3OH (d) (a) and (b) both

47. Nitrobenzene on reduction by zinc and NH_4Cl gives **[CPMT 1989, 94; BHU 1996; Pb. PMT 1999]**

(a) Aniline (b) Nitrosobenzene

(c) Hydrazobenzene (d) Phenylhydroxyl amine

48. The decreasing order of the basic character of the three amines and ammonia is **[MP PET/PMT 1988; KCET 1990]**

(a) $NH_3 > CH_3NH_2 > C_2H_5NH_2 > C_6H_5NH_2$

(b) $C_2H_5NH_2 > CH_3NH_2 > NH_3 > C_6H_5NH_2$

(c) $C_6H_5NH_2 > C_2H_5NH_2 > CH_3NH_2 > NH_3$

(d) $CH_3NH_2 > C_2H_5NH_2 > C_6H_5NH_2 > NH_3$

49. Correct order of increasing basicity is **[CBSE PMT 1992]**

(a) $NH_3 < C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2 < (C_2H_5)_3N$

(b) $C_6H_5NH_2 < NH_3 < (C_2H_5)_3N < (C_2H_5)_2NH < C_2H_5NH_2$

(c) $C_6H_5NH_2 < NH_3 < C_2H_5NH_2 < (C_2H_5)_3N < (C_2H_5)_2NH$

(d) $C_6H_5NH_2 < (C_2H_5)_3N < NH_3 < C_2H_5NH_2 < (C_2H_5)_2NH$

50. Among the following compounds nitrobenzene, benzene, aniline and phenol, the strongest basic behaviour in acid medium is exhibited by **[KCET 1993]**

(a) Phenol (b) Aniline

(c) Nitrobenzene (d) Benzene

51. Aniline on treatment with excess of bromine water gives **[AFMC 1990; MP PMT 1991; RPMT 1997]**

(a) Aniline bromide (b) *o*-bromoaniline

(c) *p*-bromoaniline (d) 2, 4, 6-tribromoaniline

52. Unpleasant smelling carbylamines are formed by heating alkali and chloroform with **[KCET 1987, 2000, 01]**

(a) Any amine (b) Any aliphatic amine

(c) Any aromatic amine (d) Any primary amine

53. When an organic compound was treated with sodium nitrite and hydrochloric acid in the ice cold, nitrogen gas was evolved copiously. The compound is **[KCET 1986]**

(a) A nitro compound

(b) A primary amine

(c) An aliphatic primary amine

(d) An aromatic primary amine

54. Aniline reacts with alkyl halide to give **[KCET 1984]**

(a) Amino compound

(b) Tertiary compound

(c) Quaternary ammonium compound

(d) Azomethane

55. Aniline on treatment with conc. HNO_3 + conc. H_2SO_4 mixture yields **[AIIMS 1992]**

(a) *o*- and p-nitroanilines (b) *m*-nitroanilines

(c) A black tarry matter (d) No reaction

56. Which statement is not correct **[MP PMT 1995]**

(a) Amines form hydrogen bond

(b) Ethyl amine has higher boiling point than propane

(c) Methyl amine is more basic than ammonia

(d) Dimethyl amine is less basic than methyl amine

57. Which of the following is not used as an explosive **[MP PET 1996]**

(a) Trinitrotoluene (b) Trinitrobenzene

(c) Picric acid (d) Nitrobenzene

58. Primary amines react with nitrous acid to yield

(a) Insoluble nitrite salts (b) Yellow oily layer

(c) Nitrogen gas (d) Azo dye

59. Which of the following has the smell of bitter almonds

(a) Nitromethane (b) Nitroethane

(c) Nitrobenzene (d) Aniline

60. The reaction of HNO_2 with '*A*' gives quaternary ammonium salt. A is **[MP PMT 1997]**

(a) Methyl amine (b) Dimethyl amine

(c) Trimethyl amine (d) Aniline

61. Reaction of nitrous acid with aliphatic primary amine in the cold gives **[MP PET/PMT 1998; CBSE PMT 1994]**

(a) A diazonium salt (b) An alcohol

(c) A nitrite (d) A dye

62. In presence of acid, hydrolysis of methyl cyanide gives **[MP PET/PMT 1998]**

(a) Acetic acid (b) Methylamine

(c) Methyl alcohol (d) Formic acid

63. The amine which does not react with acetyl chloride is **or** Which of the following cannot be acetylated **[MP PET 1999; MP PMT 1999]**

(a) CH_3NH_2 (b) $(CH_3)_2NH$

(c) $(CH_3)_3N$ (d) None of these

64. The fusion of sodium with amine gives mainly **[MP PMT 1999; CPMT 2002]**

(a) $NaCN$ (b) NaN_3

(c) $NaSCN$ (d) $NaNO_2$

65. Which of the following is most basic **[MP PMT 1999]**

(a) $C_6H_5NH_2$ (b) $(CH_3)_2NH$

(c) $(CH_3)_3N$ (d) NH_3

66. In reaction

$CH_3CN + 2H \xrightarrow[\text{Ether}]{HCl} X \xrightarrow{\text{Boiling} H_2O} Y$; the term *Y* is **[CBSE PMT 1999]**

(a) Acetone (b) Ethylamine

(c) Acetaldehyde (d) Dimethylamine

67. The following compound can be classified as *N-N* dimethyl propanamine, *N*-methyl aniline and aniline **[Bihar MEE 1996]**

(a) Primary, secondary, tertiary

(b) Primary, tertiary, secondary

(c) Secondary, tertiary, primary

(d) Tertiary, primary, secondary

(e) None of these

68. Which of the following compounds does not react with $NaNO_2$ and HCl **[KCET 1996]**

(a) C_6H_5OH (b) $C_6H_5NH_2$

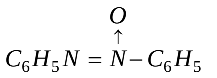
(c) $(CH_3)_3CNO_2$ (d) $(CH_3)_3CHNO_2$

69. In the reduction of nitrobenzene, which of the following is the intermediate **[CPMT 1999]**

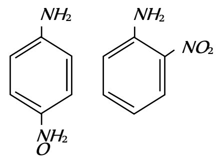
(a) $C_6H_5N = O$

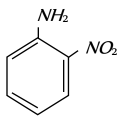
(b) $C_6H_5NH - NH - C_6H_5$

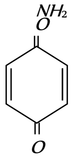
(c) $C_6H_5 - N = N - C_6H_5$

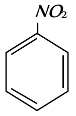
(d) 
$C_6H_5N = \overset{\overset{O}{\uparrow}}{N} - C_6H_5$

70. Aniline when treated with conc. HNO_3 gives **[KCET 1996]**

(a) 

(b) 

(c) 

(d) 

71. Which one of the following is not a base [EAMCET 1997]

(a) N_2H_4 (b) NH_2OH

(c) $(CH_3)_3N$ (d) HN_3

72. *p*-Nitrobromobenzene can be converted to *p*-nitroaniline by using $NaNH_2$. The reaction proceeds through the intermediate named[Orissa JEE 2005]

(a) Carbocation (b) Carbanion

(c) Benzyne (d) Dianion

73. If methyl is alkyl group, then which order of basicity is correct

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

(b) $R_2NH > R_3N > RNH_2 > NH_3$

(c) $RNH_2 > NH_3 > R_2NH > R_3N$

(d) $NH_3 > RNH_2 > R_2NH > R_3N$

74. Which of the following has the minimum heat of dissociation [Roorkee Qualifying 1998]

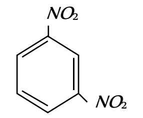
(a) $(CH_3)_3N \rightarrow BF_3$

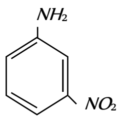
(b) $(CH_3)_3N \rightarrow B(CH_3)F_2$

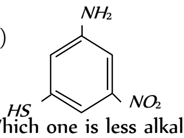
(c) $(CH_3)_3N \rightarrow B(CH_3)_2F$

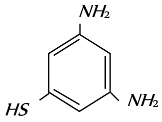
(d) $(CH_3)_3N \rightarrow B(CH_3)_3$

75. The major product (70% to 80%) of the reaction between *m*-dinitrobenzene with NH_4HS is [AIIMS 1997]

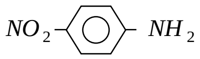
(a) 

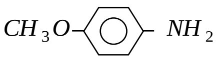
(b) 

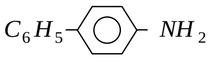
(c) 

(d) 

76. Which one is less alkaline [CPMT 1997]

(a) 
$NO_2-C_6H_4-NH_2$

(b) 
$CH_3O-C_6H_4-NH_2$

(c) 
$C_6H_5-C_6H_4-NH_2$

(d) All of these

77. In the diazotisation of aniline with sodium nitrite and hydrochloric acid, an excess of hydrochloric acid is used primarily to

(a) Suppress the concentration of free aniline available for coupling

(b) Suppress hydrolysis of phenol

(c) Insure a stoichiometric amount of nitrous acid

(d) Neutralize the base liberated

78. A primary amine can be converted to an alcohol by the action of

(a) Alkali (b) Nitrous acid

(c) Reducing agent (d) Oxidising agent

79. Arrange the following in increasing order of basicity $CH_3NH_2, (CH_3)_2NH, C_6H_5NH_2, (CH_3)_3N$ [AFMC 1997]

(a) $(CH_3)_3N < (CH_3)_2NH < CH_3NH_2 < C_6H_5NH_2$

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

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

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

80. In the reaction

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

The compound B is [KCET 1999]

(a) Acetic acid (b) Acetone

(c) Acetaldehyde (d) Ethyl alcohol

81. CH_3CN is known as acetonitrile because [AMU 1999]

(a) It contains an aceto group

(b) On hydrolysis it gives acetic acid

(c) Both (a) and (b)

(d) None of these

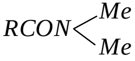
82. What is formed, when nitrobenzene is reduced using zinc and alkali [BHU 2000; AIIMS 2000; CBSE PMT 2000; MH CET 2003]

(a) Phenol (b) Aniline

(c) Nitrosobenzene (d) Hydrazobenzene

83. $RCOCl + 2Me_2NH \rightarrow A + Me_2\overset{+}{N}H_2Cl^-$

Here A is[RPMT 1997] [RPET 2000]

(a) 
$RCON\begin{matrix}Me\\Me\end{matrix}$ (b) $RCONH_2$

(c) $RCONHMe$ (d) $(RCO)_2NH$

84. Decreasing order of basicity is [RPET 2000]

(1) CH_3CONH_2 (2) $CH_3CH_2NH_2$

(3) Ph– CH_2CONH_2

(a) 1 > 2 > 3 (b) 2 > 1 > 3

(c) 3 > 2 > 1 (d) None of these

85. Among the following, the strongest base is [UPSEAT 2000; IIT-JEE (Screening) 2000]

(a) $C_6H_5NH_2$ (b) $p-NO_2C_6H_4NH_2$

(c) $m-NO_2-C_6H_4NH_2$ (d) $C_6H_5CH_2NH_2$

86. Aniline and methyl amine can be differentiated by [DPMT 2000]

(a) Reaction with chloroform and aqueous solution of KOH

(b) Diazotisation followed by coupling with phenol

(c) Reaction with HNO_2

(d) None of these

87. The amine which can react with $C_6H_5-SO_2-Cl$ to form a product insoluble in alkali shall be[AMU 2000]

(a) Primary amine

(b) Secondary amine

(c) Tertiary amine

(d) Both primary and secondary amines

88. A mixture of benzene and aniline can be separated by [KCET (Engg.) 2001]

(a) Hot water (b) dil. HCl

(c) dil. $NaOH$[Pb. PMT 1998] (d) Alcohol

89. Nitrobenzene on further excessive nitration gives [AFMC 2001]

(a) Trinitrobenzene (b) *m*-dinitrobenzene

(c) *p*-dinitrobenzene (d) All of these

90. The compound A with following sequence of reaction gave benzoic acid [CET Pune 1998]

$A \xrightarrow{NaNO_2/HCl} B \xrightarrow{KCN} C \xrightarrow{H_3O^+}$ benzoic acid. The compound A is [AMU 2001]

(a) Nitrobenzene (b) Aniline

(c) Benzaldehyde (d) Amides

91. Which of the following chemicals are used to manufacture methyl isocyanate that caused "Bhopal Tragedy"

(i) Methylamine (ii) Phosgene

(iii) Phosphine (iv) Dimethylamine

[AIIMS 2005]

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

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

92. An isocyanide on hydrolysis gives [AMU 2001]

(a) An amide

(b) A carboxylic acid and ammonia

(c) A N-substituted amide

(d) A 1-amine and formic acid

93. Methyl isocyanide on hydrolysis gives [UPSEAT 2001]

(a) CH_3NH_2 (b) $HCOOH$

(c) CH_3COOH (d) Both (a) and (b)

94. Pure aniline is a **[UPSEAT 2001]**

(a) Colourless solid

(b) Brown coloured solid

(c) Colourless liquid

(d) Brown coloured liquid

95. Reduction of methyl isocyanide gives **[RPMT 2002]**

(a) Ethylamine (b) Methylamine

(c) Dimethylamine (d) Trimethylamine

96. Reaction of aniline with benzaldehyde is **[RPMT 2002]**

(a) Polymerisation (b) Condensation

(c) Addition (d) Substitution

97. In the reaction $C_6H_5CHO + C_6H_5NH_2 \rightarrow$ $C_6H_5N = HCC_6H_5 + H_2O$, the compound $C_6H_5N = CHC_6H_5$ is known as

[RPMT 2000; AIIMS 2002; AMU 2001]

(a) Aldol (b) Schiff's reagent

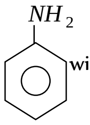
(c) Schiff's base (d) Benedict reagent

98. The unshared pair of electrons on a cyanide ion can acts as

[Kerala (Med.) 2002]

(a) Isocyanide centre (b) Amido centre

(c) Cationic centre (d) Nucleophilic centre

99. Electrophilic substitution of  with bromine gives

[Kerala (Med.) 2002]

(a) 1, 4, 6-tribromo aniline

(b) 2, 4, 6-tribromo aniline

(c) 4-bromo aniline

(d) 3-bromo aniline

100. Mustard gas is obtained by **[MP PET 2002]**

(a) The action of dilute acids on mustard seeds

(b) Treating ethylene with mustard oil

(c) Treating sulphur chloride with ethylene

(d) None of these

101. Which of the following is capable of forming a zwitter ion

[JIPMER 2002]

(a) $C_6H_5 - OH$ (b) $C_6H_4(NH_2)_2$

(c) $\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array}$ (d) $H_2N - CH_2 - COOH$

102. Which one of the following reducing agents is likely to be the most effective in bringing about the following change

$R - \overset{\overset{\displaystyle O}{\|}}{C}NH_2 \rightarrow RCH_2NH_2$ **[AMU 2002]**

(a) $H_2 - Ni$ (b) $NaBH_4$

(c) $LiAlH_4$ (d) *Na*-alcohol

103. During acetylation of amines what is replaced by acetyl groups

(a) Hydrogen atom attached to nitrogen atom

(b) One or more hydrogen atoms attached to carbon atom

(c) One or more hydrogen atoms attached to nitrogen atom

(d) Hydrogen atoms attached to either carbon atom or nitrogen atom

104. Hydrolysis of acetonitrile in acidic medium produces

[CPMT 2003; RPMT 2003]

(a) CH_3CH_2OH (b) CH_3COOH

(c) CH_3NC (d) CH_3COOCH_3

105. Which has a pyramidal structure **[UPSEAT 2003]**

(a) Trimethylamine (b) Methanol

(c) Acetylene (d) Water

106. Ethyl amine on acetylation gives **[BHU 2002; BVP 2003]**

(a) N-ethyl acetamide

(b) Acetamide

(c) Methyl acetamide

(d) None

107. The refluxing of $(CH_3)_2NCOCH_3$ with acid gives

[BHU 2002; BVP 2003]

(a) $(CH_3)_2NH + CH_3COOH$

(b) $(CH_3)_2NCOOH + CH_4$

(c) $2CH_3OH + CH_3CONH_2$

(d) $2CH_3NH_2 + CH_3COOH$

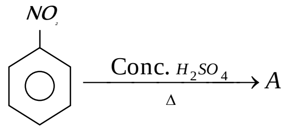
108. *p*-chloro aniline and anilinium hydrogen chloride can be distinguished by **[UPSEAT 2003]**

(a) Sandmaeyer reaction

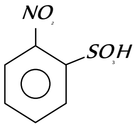
(b) Carbyl amine reaction

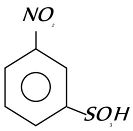
(c) Hinsberg's reaction

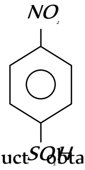
(d) $AgNO_3$

109. 

Product '*A*' in above reaction is **[RPMT 2003]**

(a) 

(b) 

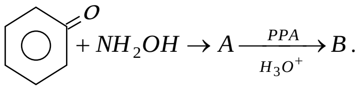
(c) 

(d) None of these

110. Product obtained by electrolytic reduction of nitrobenzene in presence of H_2SO_4 is **[RPMT 2003]**

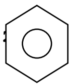
(a) *o*-amino phenol (b) *m*-amino phenol

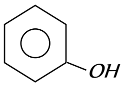
(c) *p*-amino phenol (d) None of these

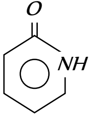
111. 

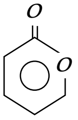
The product '*B*' is **[RPMT 2003]**

[UPSEAT

(a) 

(b) 

(c) 

(d) 

112. Identify the product *Z* in the following reaction

$C_6H_5NH_2 \xrightarrow{(AC)_2O} X \xrightarrow{Br_2/CCl_4} Y \xrightarrow{HOH} Z$

[Kerala (Med.) 2003]

(a) *p*-Bromoaniline (b) *p* -Bromoacetophenone

(c) *o*-Bromoacetophenone (d) *o*-Bromoacetonilide

113. Benzaldehyde condenses with *N, N*-dimethylaniline in presence of anhydrous $ZnCl_2$ to give **[Kerala (Med.) 2003]**

(a) Michler's ketone (b) Azo dye

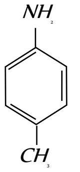
(c) Malachite green (d) Buffer yellow

114. The correct order of reactivity towards the electrophilic substitution of the compounds aniline (I) benzene (II) and nitrobenzene (III) is **[CBSE PMT 2003]**

(a) I > II > III (b) III > II > I

(c) II > III > I (d) I < II > III

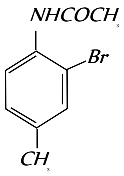
115. The final product *C*, obtained in this reaction



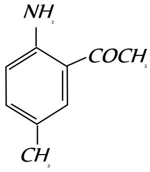
$\xrightarrow[CH_3COOH]{Ac_2O} A \xrightarrow{Br_2} B \xrightarrow[H^+]{H_2O} C$ would be

[CBSE PMT 2003]

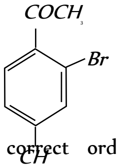
(a)



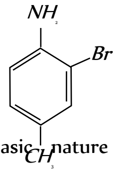
(b)



(c)



(d)



116. The correct order of increasing basic nature for the bases NH_3, CH_3NH_2 and $(CH_3)_2NH$ is **[AIEEE 2003]**

(a) $CH_3NH_2 < NH_3 < (CH_3)_2NH$

(b) $(CH_3)_2NH < NH_3 < CH_3NH_2$

(c) $NH_3 < CH_3NH_2 < (CH_3)_2NH$

(d) $CH_3NH_2 < (CH_3)_2NH < NH_3$

117. Nitrobenzene gives *N*-phenylhydroxylamine by **[AIIMS 2003]**

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

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

118. Among the following the weakest base is **[AIIMS 2003]**

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

(c) $O_2N\,CH_2NH_2$ (d) $CH_3NH\,CHO$

119. The correct order of basicity of amines in water is : **[Pb. CET 2003]**

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

120. Complete the following reaction : **[MHCET 2004]**

$R\ NH_2 + H_2SO_4 \rightarrow$

(a) $[R\ NH_3]^+HSO_4^-$ (b) $[R\ NH_3]_2^+SO_4^{2-}$

(c) $R\ NH_2.H_2SO_4$ (d) No reaction

121. Which of the following compound reacts with chloroform and a base to form phenyl isocyanide ? **[MHCET 2003]**

(a) Phenol (b) Aniline

(c) Benzene (d) Nitro benzene

122. Which one doesn't liberate NH_3 when undergoes hydrolysis

(a) Acetanilide (b) Acetonitrile

(c) Acetamide (d) Phenyl isocyanide

123. A nitrogen containing organic compound gave an oily liquid on heating with bromine and potassium hydroxide solution. On shaking the product with acetic anhydride, an antipyretic drug was obtained. The reactions indicate that the starting compound is

(a) Aniline (b) Benzamide

(c) Acetamide (d) Nitrobenzene

124. Benzamide on reaction with $POCl_3$ gives **[IIT-JEE 2004]**

(a) Aniline (b) Chlorobenzene

(c) Benzyl amine (d) Benzonitrile

125. Among the following which one does not act as an intermediate in Hofmann rearrangement **[AIIMS 2005]**

(a) $RNCO$ (b) $RCO\ddot{N}$

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

126. Aniline reacts with which of these to form Schiff base **[AFMC 2004]**

(a) Acetic acid (b) Benzaldehyde

(c) Acetone (d) NH_3

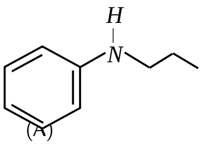
127. Which of the following does not reduce Tollen's reagent **[Kerala PMT 2004]**

(a) CH_3CHO (b) C_6H_5NHOH

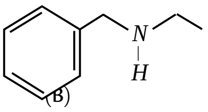
(c) $HCOOH$ (d) $C_6H_5NO_2$

(e) None of these

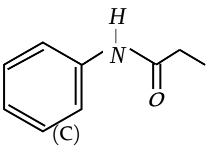
128. Which one of the following compound is most basic ? **[UPSEAT 2004]**



(A)



(B)



(C)

(a) (A) (b) (B)

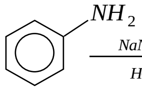
(c) (C) (d) All are equally basic

129. Which one of the following methods is neither meant for the synthesis nor for separation of amines **[AIEEE 2005]**

(a) Hinsberg method (b) Hofmann method

(c) Wurtz reaction (d) Curtius reaction

130. Aniline in a set of reactions yielded a product D.



$\xrightarrow[HCl]{NaNO_2} A \xrightarrow{CuCN} B \xrightarrow[Ni]{H_2} C \xrightarrow{HNO_2} D$

The structure of product D would be **[CBSE PMT 2005]**

(a) $C_6H_5CH_2NH_2$ (b) $C_6H_5NH\,CH_2CH_3$

(c) C_6H_5NHOH (d) $C_6H_5CH_2OH$

131. Electrolytic reduction of nitrobenzene in weakly acidic medium gives

(a) Aniline (b) Nitrosobenzene

(c) *N*-Phenylhydroxylamine (d) *p*-Hydroxylaniline

132. Among the following compounds $C_3H_7NH_2$, NH_3, CH_3NH_2, $C_2H_5NH_2$ and $C_6H_5NH_2$, the least basic compound is

(a) $C_3H_7NH_2$ (b) NH_3

(c) CH_3NH_2 (d) $C_6H_5NH_2$

(e) $C_2H_5NH_2$

133. The reduction of which of the following compound would yield secondary amine ? **[DCE 2004]**

(a) Alkyl nitrite
(b) Carbylamine
(c) Primary amine
(d) Secondary nitro compound

134. Azo dye is prepared by the coupling of phenol and : **[Pb. CET 2000]**

(a) Diazonium chloride
(b) *o*-nitro aniline
(c) Benzoic acid
(d) Chlorobenzene

135. $C_6H_5NH_2 \xrightarrow{NaNO_2 HCl} X \xrightarrow{Cu_2(CN)_2} Y \xrightarrow{H_2O / H^+} Z$

Z is identified as : **[Pb. PMT 2004]**

(a) $C_6H_5 - NH - CH_3$
(b) $C_6H_5 - COOH$
(c) $C_6H_5 - CH_2 - NH_2$
(d) $C_6H_5 - CH_2 - COOH$

136. When acetamide reacts with Br_2 and caustic soda, then we get :

(a) Acetic acid (b) Bromoacetic acid
(c) Methyl amine (d) Ethyl amine

137. In the reaction

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

the term Y is: **[BHU 2004]**

(a) Acetone (b) Ethyl amine
(c) Acetaldehyde (d) Dimethyl amine

138. Reaction of cyclohexanone with dimethylamine in the presence of catalytic amount of an acid forms a compounds if water during the reaction is continuously removed. The compound formed is generally known as **[AIEEE 2005]**

(a) A Schiff's base (b) An enamine
(c) An imine (d) An amine

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

In the given reaction what will be the product **[BHU 2005]**

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

140. Which of the following is secondary pollutant. **[BHU 2005]**

(a) CO_2 (b) NO_2
(c) PAN (d) SO_2

141. Nitration of aniline also gives *m*-nitro aniline, in strong acidic medium because **[Kerala CET 2005]**

(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 nucleophilic substitution reaction
(d) In strong acidic medium aniline present as anilinium ion
(e) Strong acid, gives nitrate anion, which attacks at *m*-position

142. Identify the product in following order

3,4,5-Tribromoaniline $\xrightarrow[\text{(ii)}H_3PO_2]{\text{(i)diazotizaton}}$? **[Kerala CET 2005]**

(a) 3, 4,5 –Tribromobenzene
(b) 1, 2, 3 – Tribromobenzene
(c) 2, 4, 6 – Tribromobenzene
(d) 3, 4, 5 – Tribromo nitro benzene
(e) 3, 4, 5 – Tribromo phenol

143. The correct order of basicity in amines

(i) $C_4H_5NH_2$ (ii) CH_3NH_2
(iii) $(CH_3)_2NH$ (iv) $(CH_3)_3N$

[Kerala CET 2005]

(a) (i) < (iv) < (ii) < (iii) (b) (iv) < (iii) < (ii) < (i)
(c) (i) < (ii) < (iii) < (iv) (d) (ii) < (iii) < (iv) < (i)
(e) (iv) < (iii) < (ii) < (i)

Tests for Nitrogen Containing Compounds

1. When acetamide reacts with Br_2 and caustic soda, then we get **[DPMT 1983; BHU 1997; Orissa JEE 2002; CPMT 1971, 78, 79, 81, 85, 2000, 03; MP PMT 1989; MP PET 1995, 2002]**

(a) Acetic acid (b) Bromoacetic acid
(c) Methyl amine (d) Ethane

2. In organic compounds, nitrogen is tested in Lassaigne's test as

(a) $NaNH_2$ (b) $NaCN$
(c) $NaNO_2$ **[CPMT 2004]** (d) $NaNO_3$

3. Liebermann's nitroso reaction is used for testing

(a) Primary amines (b) Secondary amines
(c) Tertiary amines (d) All the above

4. A nauseating smell in the carbylamine test for primary amines is due to the formation of **[MP PET 1993]**

(a) Isocyanide (b) Chloroform
(c) Cyanide (d) DDT

5. A positive carbylamine test is given by **[IIT-JEE 1999]**

(a) *N, N*-dimethylaniline
(b) 2, 4-dimethylaniline
(c) *N*-methyl-*o*-methylaniline
(d) *p*-methylbenzylamine

6. The colour of *p*-amino azobenzene is **[BHU 1997]**

(a) Orange (b) Congo red
(c) Bismark brown (d) Indigo

7. When primary amine is heated with CS_2 in presence of excess mercuric chloride, it gives isothiocyanate. This reaction is called**[KCET 1998; CP**

(a) Hofmann bromide reaction
(b) Hofmann mustard oil reaction
(c) Carbylamine reaction
(d) Perkin reaction

8. Diazo-coupling is useful to prepare some **[CPMT 1999]**

(a) Dyes (b) Proteins
(c) Pesticides (d) Vitamins

9. Carbylamine test is used in the detection of **[DCE 1999]**

(a) Aliphatic 2° amine
(b) Aromatic 1°amine
(c) Aliphatic 1°amine
(d) Both aliphatic and aromatic 1°amines

10. Which of the following substance does not give iodoform test

(a) C_6H_5CN (b) RNH_2
(c) CH_3OH (d) All

11. Which one of the following compounds when heated with KOH and a primary amine gives carbylamine test **[Orissa JEE 2005]**

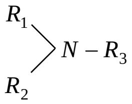
(a) $CHCl_3$ (b) CH_3Cl

(c) CH_3OH (d) CH_3CN

Critical Thinking

Objective Questions

1. The compound



forms nitroso amines when the substituents are

[Roorkee 1999]

(a) $R_1=CH_3, R_2=R_3=H$

(b) $R_1=R_2=H, R_3=C_2H_5$

(c) $R_1=H, R_2=R_3=CH_3$

(d) $R_1=CH_3, R_2=C_2H_5, R_3=H$

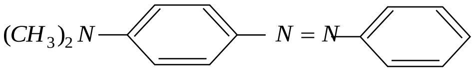
2. The action of nitrous acid on ethyl amine gives

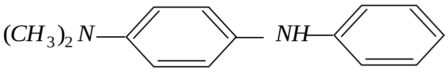
[DPMT 1982; CPMT 1971, 89, 94; MP PET 1993, 2001; RPMT 1997; Pb. PMT 1999]

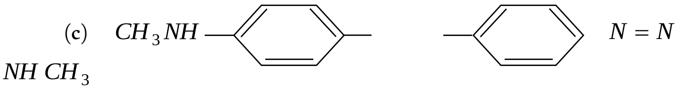
(a) Ethane (b) Ammonia

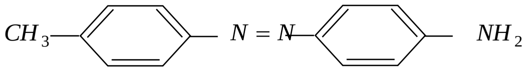
(c) Ethyl acohol (d) Nitroethane

3. Aniline when diazotized in cold and then treated with dimethyl aniline gives a coloured product. Its structure would be

(a) 

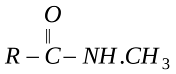
(b) 

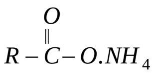
(c) 

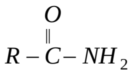
(d) 

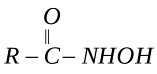
4. Indicate which nitrogen compound amongst the following would undergo Hofmann's reaction (i.e. reaction with Br_2 and strong KOH) to furnish the primary amine ($R-NH_2$)

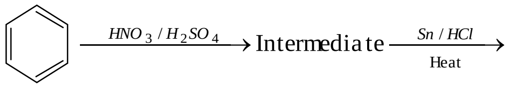
[CBSE PMT 1989]

(a) 
$R-\overset{O}{\overset{\|}{C}}-NH.CH_3$

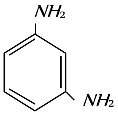
(b) 
$R-\overset{O}{\overset{\|}{C}}-O.NH_4$

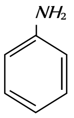
(c) 
$R-\overset{O}{\overset{\|}{C}}-NH_2$

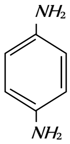
(d) 
$R-\overset{O}{\overset{\|}{C}}-NHOH$

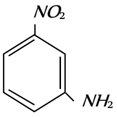
5. 

[BHU 1995]

(a) 

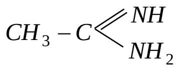
(b) 



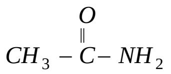


(c) (d)

6. The correct order of basicities of the following compounds is


$CH_3-C\begin{matrix}\nearrow NH \\ \searrow NH_2\end{matrix}$ $CH_3-CH_2-NH_2$ $(CH_3)_2NH$

1 2 3


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

4

[IIT-JEE (Screening) 2001]

(a) $2>1>3>4$ (b) $1>3>2>4$

(c) $3>1>2>4$ (d) $1>2>3>4$

7. Which of the following would be most reactive towards nitration[AMU 2000; UP

(a) Benzene (b) Nitro benzene

(c) Toluene (d) Chloro benzene

8. Aniline reacts with acetaldehyde to form

[MHCET 2004; AFMC 2004]

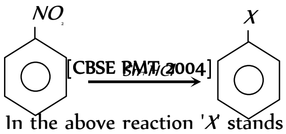
(a) Schiff's base (b) Carbylamine

(c) Immine (d) None of these

9. *p*-chloroaniline and anilinium hydrochloride can be distinguished by

(a) Sandmeyer reaction (b) $NaHCO_3$

(c) $AgNO_3$ (d) Carbylamine test

10. 

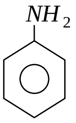
[CBSE PMT 2004]

In the above reaction 'X' stands for

[CPMT 1986, 2001; MP PET 1992; KCET (Engg./Med.) 2000]

(a) NH_2 (b) $SnCl_2$

(c) Cl (d) $NH_4^+Cl^-$

11. 

$+CHCl_3+KOH\rightarrow ?$

[BHU 2000; Pb. PMT 2000; Kerala 2003]

(a) Phenyl isocyanide (b) Benzyl amine

(c) Benzyl chloride (d) None of these

12. The order of basic strength among the following amines in benzene solution is [AIIMS 1991; RPMT 2002]

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

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

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

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

13. The refluxing of $(CH_3)_2NCOCH_3$ with acid gives

[KCET 1996]

(a) $2CH_3NH_2+CH_3COOH$

(b) $2CH_3OH+CH_3COOH$

(c) $(CH_3)_2NH+CH_3COOH$

(d) $(CH_3)_2NCOOH+CH_4$

14. Order of basicity of ethyl amines is [MP PMT/PET 1988]

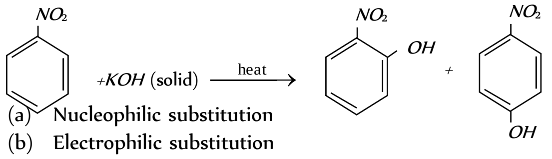
(a) Secondary > Primary > Tertiary

(b) Primary > Secondary > Tertiary

(c) Secondary > Tertiary > Primary

(d) Tertiary > Primary > Secondary

15. The following reaction is [KCET 1996]



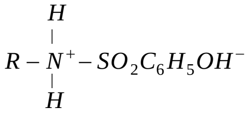
(a) Nucleophilic substitution

(b) Electrophilic substitution

(c) Free radical substitution

(d) None of these

16. RNH_2 reacts with $C_6H_5SO_2Cl$ in aqueous KOH to give a clear solution. On acidification a precipitate is obtained which is due to the formation of [Roorkee 2000]

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

(b) $R-N^-SO_2C_6H_5K^+$

(c) $R-NHSO_2C_6H_5$

(d) $C_6H_5SO_2NH_2$

17. If N and S are present in an organic compound during Lassaigne test, then both changes into [CPMT 1997]

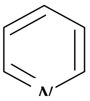
(a) Na_2S and $NaCN$

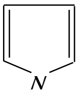
(b) $NaSCN$

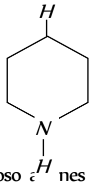
(c) Na_2SO_3 and $NaCN$

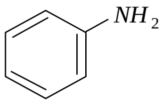
(d) Na_2S and $NaCNO$

18. The strongest base among the following is [AIIMS 2004; BHU 2004]

(a) 

(b) 

(c) 

(d) 

19. Nitroso amines $(R_2N-N=O)$ are soluble in water. On heating them with concentrated H_2SO_4 they give secondary amines. The reaction is called [AFMC 1998; AIIMS 1998; BHU 2002]

(a) Perkin's reaction

(b) Fittig's reaction

(c) Sandmeyer's reaction

(d) Liebermann's nitroso reaction

20. A primary amine is formed an amide by the treatment of bromine and alkali. The primary amine has : [BHU 2004]

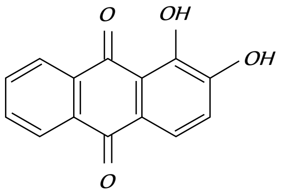
(a) 1 carbon atom less than amide

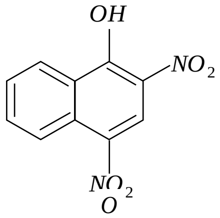
(b) 1 carbon atom more than amide

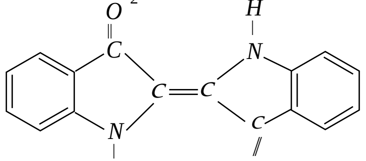
(c) 1 hydrogen atom less than amide

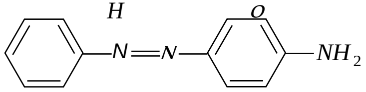
(d) 1 hydrogen atom more than amide

21. The structural formula of Indigo dye is : [DPMT 2004]

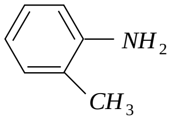
(a) 

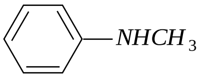
(b) 

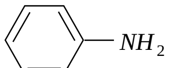
(c) 

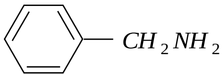
(d) 

22. Which of the following is the strongest base ? [AIEEE 2004]

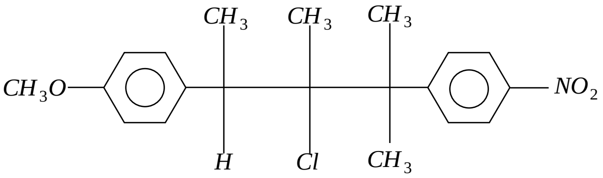
(a) 

(b) 

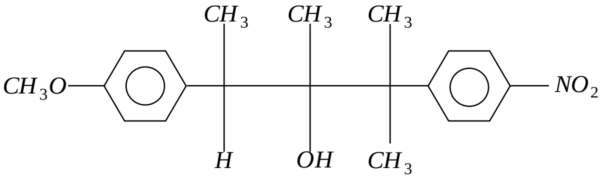
(c) 

(d) 

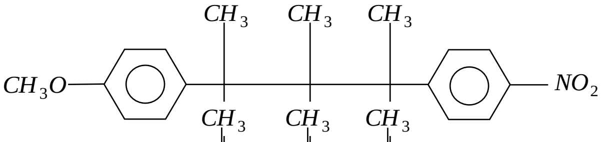
23. The following compound on hydrolysis in aqueous acetone will give



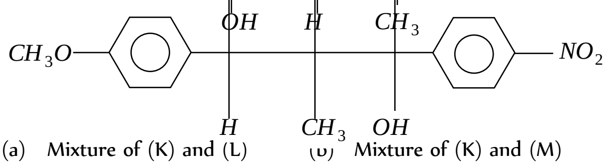
(K:)



(L:)



(M:)



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

(c) Only (M)
(d) Only (K)

Assertion & Reason

For AIIMS Aspirants

Read the assertion and reason carefully to mark the correct option out of the options given below :

(a) If both assertion and reason are true and the reason is the correct explanation of the assertion.
(b) If both assertion and reason are true but reason is not the correct explanation of the assertion.
(c) If assertion is true but reason is false.
(d) If the assertion and reason both are false.
(e) If assertion is false but reason is true.

1. Assertion : Benzene diazonium chloride does not give tests for nitrogen:
Reason : N_2 gas lose takes place during heating
[AIIMS 1999]

2. Assertion : Amines are basic in nature.
Reason : Presence of lone pair of electron on nitrogen atom. [AIIMS 1999]

3. Assertion : Methyl isocyanide reacts with ozone to form methyl isocyanate.
Reason : Methyl isocyanate was responsible for Bhopal tragedy.

4. Assertion : Alkyl cyanide can be prepared by carbylamine reaction
Reason : Ethyl amine when heated with chloroform in presence of alcoholic *KOH*, cyanide is formed.

5. Assertion : CN^- ion is an ambident nucleophile.
Reason : Nucleophiles are electron rich species.

6. Assertion : Sulphanilic acid exists as dipolar ion whereas *p*-aminobenzoic acid does not.
Reason : Carboxyl group being more acidic than $-SO_3H$ group can easily transfer a H^+ to the amino group.

7. Assertion : Nitrating mixture used for carrying 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.

8. Assertion : In order to convert *R–Cl* to pure *R–NH*, 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.

9. Assertion : Ammonolysis of alkyl halides involves the reaction between alkyl halides and alcoholic ammonia.
Reason : Reaction can be used to prepare only 2° amines.

10. Assertion : Nitroalkanes, but not nitroarenes can be distilled at normal atmospheric pressure.
Reason : Nitroalkanes are sparingly soluble in water while nitroarenes are insoluble.

11. Assertion : In Hofmann bromide reaction, the amine formed has one carbon atom less than the parent 1° amide.
Reason : *N*-methyl acetamide undergoes Hofmann bromamide reaction.

12. Assertion : Nitrobenzene does not undergo Friedel Craft alkylation.
Reason : Nitrobenzene is used as solvent in laboratory and industry.

13. Assertion : Ammonia is less basic than water.
Reason : Nitrogen is less electronegative than oxygen.

14. Assertion : The reaction between a diazo salt and an aromatic amine or a phenol, giving an aminoazo or hydroxyazo compounds is called coupling reaction.
Reason : Condensation of diazonium salt with phenol is carried out in weakly acidic medium.

15. Assertion : Carbylamine reaction involves the reaction between 1° amine and chloroform in basic medium.
Reason : In carbylamine reaction, $-NH_2$ group is converted into $-NC$ group.

16. Assertion : Me_3N reacts with BF_3 whereas Ph_3N does not.
Reason : The electron pair on nitrogen atom in Ph_3N is delocalised in the benzene ring and is not available to boron in BF_3

17. Assertion : *p*-Anisidine is weaker base than aniline.
Reason : $-OCH_3$ group in anisidine exerts $-R$ effect.

18. Assertion : Lower aldehydes and ketones are soluble in water but the solubility decreases as the molecular mass increases.
Reason : Distinction between aldehydes and ketones can be made by Tollen's test.
[AIIMS 1999]

19. Assertion : Aniline hydrogen sulphate on heating forms a mixture of ortho and para aminobenzene sulphonic acids.
Reason : The sulphonic acid group is electron withdrawing. [AIIMS 1996]

20. Assertion : $p-O_2N-C_6H_5COCH_3$ is prepared by Friedel Crafts acylation of nitrobenzene.
Reason : Nitrobenzene easily undergoes electrophilic substitution reaction. [AIIMS 2005]

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

Answers

Introduction of Nitrogen Containing Compounds

1	a	2	c	3	a	4	d	5	c
6	d	7	c	8	d	9	c	10	a
11	a	12	b	13	b	14	a	15	b

Preparation of Nitrogen Containing Compounds

1	c	2	d	3	b	4	b	5	b
6	b	7	c	8	a	9	c	10	a
11	d	12	d	13	b	14	b	15	d
16	c	17	a	18	b	19	a	20	c
21	b	22	a	23	a	24	a	25	b
26	b	27	c	28	d	29	c	30	a

31	a	32	a	33	a	34	d	35	c
36	c	37	b	38	a	39	d	40	b,c
41	d	42	b	43	c	44	c	45	c
46	b	47	b	48	a	49	c	50	a
51	c	52	a	53	c	54	a	55	b

Properties of Nitrogen Containing Compounds

1	d	2	d	3	b	4	b	5	a
6	c	7	c	8	d	9	b	10	c
11	c	12	b	13	b	14	c	15	c
16	a	17	d	18	a	19	b	20	c
21	a	22	d	23	b	24	c	25	a
26	b	27	b	28	c	29	b	30	b
31	d	32	a	33	c	34	a	35	b
36	c	37	b	38	b	39	d	40	c
41	a	42	c	43	b	44	c	45	d
46	d	47	d	48	b	49	d	50	b
51	d	52	d	53	c	54	c	55	c
56	d	57	d	58	c	59	c	60	c
61	b	62	a	63	c	64	a	65	b
66	c	67	e	68	c	69	a	70	c
71	d	72	c	73	a	74	b	75	b
76	a	77	a	78	b	79	c	80	b
81	b	82	d	83	a	84	b	85	d
86	b	87	b	88	b	89	b	90	b
91	c	92	d	93	d	94	c	95	c
96	b	97	c	98	c	99	b	100	c
101	d	102	a	103	c	104	b	105	a
106	a	107	a	108	d	109	b	110	c
111	c	112	a	113	c	114	a	115	d
116	c	117	d	118	b	119	a	120	b
121	b	122	d	123	b	124	d	125	d
126	b	127	d	128	b	129	c	130	d
131	a	132	d	133	b	134	a	135	b
136	c	137	c	138	b	139	b	140	c
141	d	142	b	143	a				

Tests for Nitrogen Containing Compounds

1	c	2	b	3	b	4	a	5	b
6	a	7	b	8	a	9	d	10	d
11	a								

Critical Thinking Questions

1	c	2	c	3	a	4	c	5	b
6	b	7	b	8	a	9	bc	10	a

11	a	12	b	13	c	14	a	15	a
16	c	17	b	18	c	19	d	20	a
21	c	22	d	23	a				

Assertion & Reason

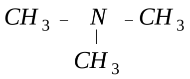
1	a	2	a	3	b	4	d	5	b
6	c	7	a	8	c	9	c	10	b
11	c	12	b	13	e	14	c	15	a
16	a	17	d	18	b	19	d	20	d
21	a								

Answers and Solutions

Introduction of Nitrogen Containing Compounds

4. (d) C_3H_9N can form all the 3 amines.

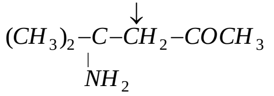
$\underset{1^o\text{ amine}}{CH_3CH_2CH_2-NH_2}$, $\underset{2^o\text{ amine}}{CH_3-CH_2-NH-CH_3}$



$CH_3-\underset{\displaystyle CH_3}{\underset{|}{N}}-CH_3$

3^o amine

5. (c) $(CH_3)_2C=O+H.CH_2-COCH_3+NH_3$

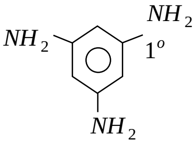


$$\downarrow$$
$$(CH_3)_2-\underset{\displaystyle NH_2}{\underset{|}{C}}-CH_2-COCH_3$$

diacetoneamine

8. (d) Allyl isocyanide. $CH_2=CH-CH_2-N\overset{\rightarrow}{=}C$

9. (c)



1^o amine

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

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

15. (b) Four 1^o amines are possible

$CH_3CH_2CH_2CH_2NH_2, (CH_3)_2CHCH_2NH_2,$

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

Preparation of Nitrogen Containing Compounds

1. (c) Hofmann's bromamide reaction

$\underset{\text{Acetamide}}{CH_3-CO-NH_2}+Br_2+4KOH\xrightarrow{H_2O}$

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

2. (d) $CH_3CONH_2\xrightarrow{NaOBr}CH_3NH_2$.

3. (b) $\underset{\text{Acetamide}}{CH_3CONH_2}+Br_2+4NaOH\rightarrow$

$\underset{\text{Methylamine}}{CH_3NH_2}+Na_2CO_3+2NaBr+2H_2O$

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

5. (b) $CH_3C\equiv N+4[H]\xrightarrow[\text{Reduction}]{Na+C_2H_5OH}CH_3CH_2NH_2$

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

$CH_3CH_2NH_2+K_2CO_3+2KBr+2H_2O$

7. (c) $C_2H_5I+NH_3\rightarrow HI+C_2H_5-NH_2$

$C_2H_5OH+NH_3\rightarrow H_2O+C_2H_5-NH_2$

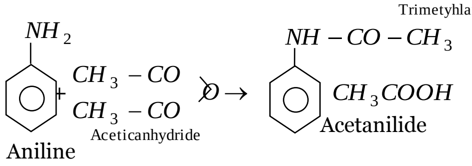
9. (c) $\underset{\text{Nitroethane}}{CH_3-CH_2-NO_2}+6[H]\xrightarrow{Sn\ /\ HCl}$

$\underset{\text{Ethyl amine}}{CH_3-CH_2-NH_2}+2H_2O$

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

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

12. (d)

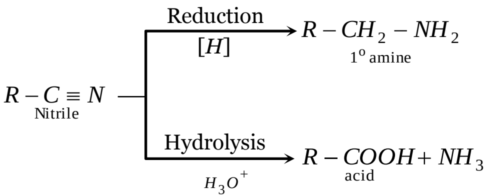


16. (c) $CH_3-N\overset{\rightarrow}{=}C+4[H]\xrightarrow{\text{Reduction}}\underset{2^o\text{ amine}}{CH_3-NH-CH_3}$

17. (a) $\underset{\text{Nitromethane}}{CH_3NO_2}+3Cl_2+3NaOH\rightarrow$

$\underset{\text{(chloropicrin)}}{CCl_3-NO_2}+3NaCl+3H_2O.$

18. (b)



19. (a) $C_2H_5OH+NH_3\xrightarrow[\text{alumina}]{H_3O^+}C_2H_5NH_2+H_2O$.

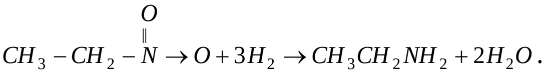
20. (c) $R-CN+H_2O\xrightarrow{H_2O\ /\ H^+}RCOOH+NH_3$

It yield amine when reduced as –

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

21. (b) $CH_3CONH_2\xrightarrow{P_2O_5}CH_3CN\xrightarrow{4H}CH_3CH_2NH_2$

22. (a)

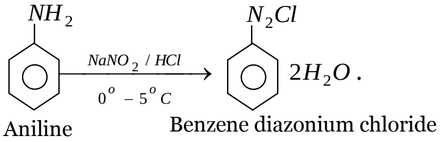


$CH_3-CH_2-\overset{\displaystyle O}{\overset{\|}{N}}\rightarrow O+3H_2\rightarrow CH_3CH_2NH_2+2H_2O$.

23. (a) $\underset{\text{Methyl amine}}{CH_3NH_2}\xrightarrow{NO_2}CH_3OH+N_2+H_2O$

24. (a) $\underset{1^o\text{-amine}}{R-NH_2}+CHCl_3+3KOH\rightarrow R-NC+3KCl+3HO$

25. (b)



26. (b) $CH_3CH_2COOH \xrightarrow{SOCl_2} CH_3CH_2COCl + SO_2 + HCl$

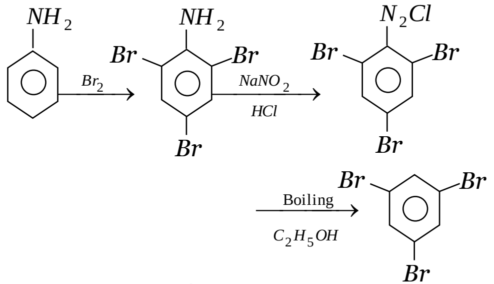
$CH_3CH_2COCl + NH_3 \rightarrow CH_3CH_2CONH_2 + HCl$

$CH_3CH_2CONH_2 + Br_2 / NaOH \rightarrow \underset{\text{Ethyl amine}}{CH_3CH_2NH_2} + CO_2$

27. (c) $CH_3COOH \xrightarrow{PCl_5} CH_3COCl \xrightarrow{NH_3} CH_3CONH_2$

$\xrightarrow{NaOBr} CH_3NH_2$

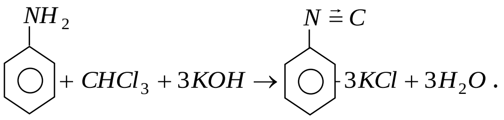
28. (d)



29. (c) $CH_3 - N \equiv C \xrightarrow{LiAlH_4} \underset{\text{sec. amine}}{CH_3 - NH - CH_3}$

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

33. (a)



$+ CHCl_3 + 3KOH \rightarrow$ $3KCl + 3H_2O$.

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

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

38. (a) $C_2H_5NH_2 + CS_2 + HgCl_2 \rightarrow C_2H_5NCS + 2HCl + HgS$.

39. (d) $C_6H_5NH_2 \xrightarrow[HCl]{NaNO_3} C_6H_5N_2Cl \xrightarrow{H_2O}$

$C_6H_5OH + N_2 + HCl$

41. (d) $\underset{\text{chlorobenzene}}{2C_6H_5Cl} + 2NH_3 \xrightarrow[\text{in xylene } 570^oK]{H_2O}$

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

44. (c) $C_6H_5NH_2 + HCl + NaNO_2 \rightarrow C_6H_5N_2Cl$

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

47. (b) $C_6H_5NH_2 \xrightarrow{NaNO_2 \ + \ HCl \ \ 0^o C} C_6H_5N_2Cl$

48. (a) $CH_3NO_2 + 6H \xrightarrow[HCl]{Sn} CH_3NH_2 + 2H_2O$

49. (c) $C_6H_5NH_2 \xrightarrow[0^oC - 5^oC]{NaNO_2 / HCl} \underset{\text{(X)}}{C_6H_5N_2^+Cl^-} \xrightarrow[H_2O]{HNO_2}$

$\underset{\text{(Y)}}{C_6H_5NO_2} + N_2 + HCl$

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

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

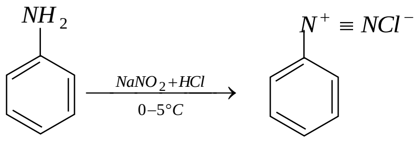
$ArCONH_2 \xrightarrow[-H_2O]{P_2O_5} ArCN$

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

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

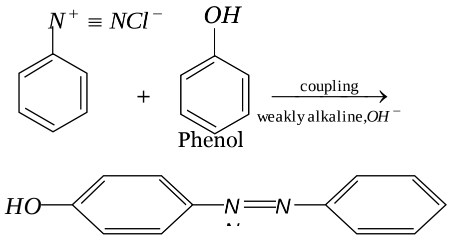
$(CH_3CH_2)_2 NH + HONO \rightarrow \underset{\text{oily}}{(CH_3CH_2)_2 N.NO} + H_2O$

52. (a) When aniline is treated with HNO_2 at 0–5°*C* then diazonium salt is formed and by the coupling of diazonium salt and phenol azo dyes are prepared.



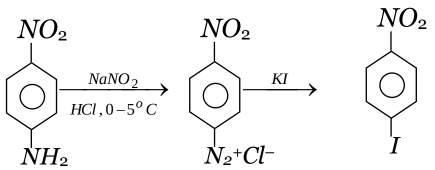
Aniline

Benzene diazonium chloride



Azo dye

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



p-nitroaniline

p-nitroiodobenzene

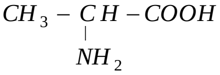
55. (b) $C_2H_5Br + KCN \xrightarrow{\text{alcohol}} C_2H_5CN + KBr$

Properties of Nitrogen Containing Compounds

1. (d) Tertiary amine does not react with nitrous acid because in it α-H atom is absent.

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

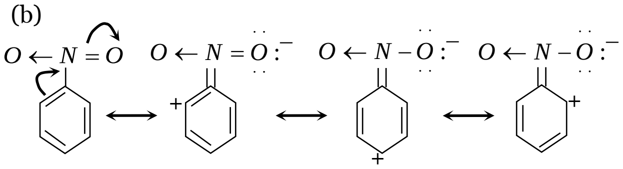
3. (b)



$CH_3 - \underset{\underset{NH_2}{|}}{CH} - COOH$

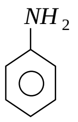
The compounds in which both amino $(-NH_2)$ as well as acidic (–*COOH*) group is present is called amino acid.

4. (b)



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

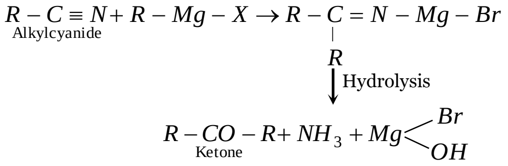
6. (c) $R - C \equiv N + 2H_2O \xrightarrow{\text{Hydrolysis}} R - COOH + NH_3$



Benzene diazonium

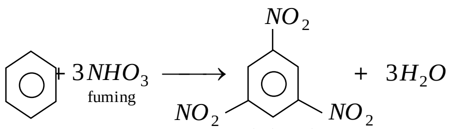
7. (c) $+\ HNO_2 + HCl \xrightarrow[\text{Diazotization}]{0^oC} \qquad + 2H_2O$

9. (b)



$$\underset{\text{Alkylcyanide}}{R-C\equiv N}+R-Mg-X\rightarrow R-\underset{\underset{R}{|}}{C}=N-Mg-Br$$
$$\downarrow \text{Hydrolysis}$$
$$\underset{\text{Ketone}}{R-CO-R}+NH_3+Mg{<}^{Br}_{OH}$$

10. (c)



sym-trinitro benzene

11. (c) $\underset{\text{Ethylamine}}{CH_3-CH_2-NH_2}\xrightarrow[{[O]}]{KMnO_4}\underset{\text{Aldimine}}{CH_3-CH=NH}$

$\xrightarrow{H_3O^+}\underset{\text{Acetaldehyde}}{CH_3-CHO}$

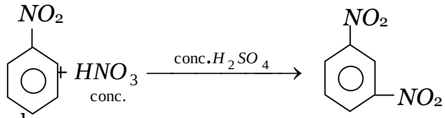
12. (b) Only primary aromatic amines can undergo diazotisation.

13. (b) $\underset{1^o\ \text{amine}}{R-CH_2-NH_2}+\underset{\text{aldehyde}}{O=CH-R}\rightarrow$

$\underset{\text{Aldimine}}{R-CH_2-N=CH-R}+H_2O$

14. (c) $\underset{\text{Acetamide}}{CH_3-CO-NH_2}+HNO_2\rightarrow \underset{\text{Acetic acid}}{CH_3COOH}+N_2\uparrow+H_2O$

15. (c)



Nitrobenzene m-dinitrobenzene

$-NO_2$ group is meta directing group.

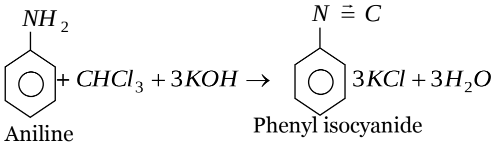
16. (a) $\underset{\text{Alkyl nitrite}}{R-O-N=O}+6[H]\xrightarrow{\text{Sn / HCl}}\underset{\text{Alcohol}}{ROH}+NH_3+H_2O$

17. (d) $CH_3-CH_2-NH_2+HCl\rightarrow \underset{\text{Ethyl ammonium chloride}}{CH_3CH_2-NH_3^+Cl^-}$

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

18. (a) $\underset{\substack{2^o\ \text{amine is}\\ \text{most basic}}}{(CH_3)_2NH}>\underset{1^o\ \text{amine}}{CH_3NH_2}>\underset{3^o\ \text{amine}}{(CH_3)_3N}>\underset{\substack{\text{Ammonia is}\\ \text{least basic}}}{\ddot{N}H_3}$

19. (b)



Aniline Phenyl isocyanide

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

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

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

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

This litmus paper test shows basic nature of amine.

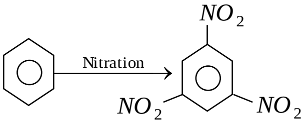
24. (c) Presence of alkyl group increases electron density on nitrogen atom due to +I effect. Thus basic nature increases.

25. (a) Mustard oil reaction

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

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

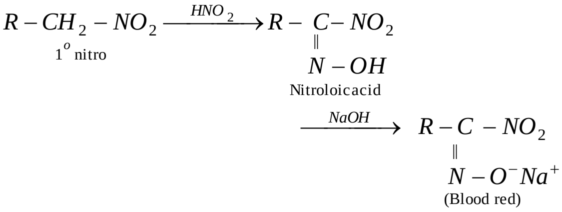
28. (c)



1, 3, 5-trinitrobenzene

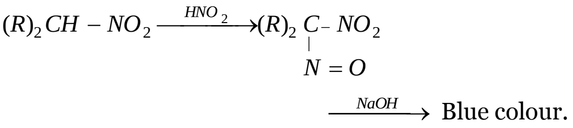
3- nitro group can be introduced.

34. (a)



$$\underset{1^o\ \text{nitro}}{R-CH_2-NO_2}\xrightarrow{HNO_2}\underset{\text{Nitroloic acid}}{R-\underset{\underset{N-OH}{\|}}{C}-NO_2}$$
$$\xrightarrow{NaOH}\underset{\text{(Blood red)}}{R-\underset{\underset{N-O^-Na^+}{\|}}{C}-NO_2}$$

35. (b)



$$(R)_2CH-NO_2\xrightarrow{HNO_2}(R)_2\underset{\underset{N=O}{|}}{C}-NO_2$$
$$\xrightarrow{NaOH}\text{Blue colour.}$$

37. (b) $\underset{\text{Acetamide}}{CH_3CONH_2}\xrightarrow{P_2O_5}\underset{\text{Acetonitrile}}{CH_3-C\equiv N}+H_2O$.

38. (b) $CHCl_3+C_2H_5NH_2+3KOH\rightarrow$

$\underset{\text{Ethyl isocyanide}}{C_2H_5N\overset{\rightarrow}{\equiv}C}+3KCl+3H_2O$

39. (d) $\underset{\text{Methyl cyanide}}{CH_3-C\equiv N}+2H_2O\rightarrow\underset{\text{Aceticacid}}{CH_3COOH}+NH_3$

40. (c) $\underset{(2c)}{CH_3CONH_2}+Br_2+4KOH\rightarrow$

$\underset{(1c)}{CH_3NH_2}+K_2CO_3+3KBr+2H_2O$

41. (a) $(C_2H_5)_2NH+(\text{aq.})HONO\rightarrow\underset{\text{Diethyl nitrosoamine}}{(C_2H_5)_2N-N=O}+H_2O$

42. (c) $CH_3-C\equiv N\xrightarrow[\text{Reduction}]{Na+EtOH}CH_3-CH_2-NH_2$

$\xrightarrow{HNO_2}CH_3CH_2-OH\xrightarrow[H_2SO_4]{K_2Cr_2O_7}CH_3COOH$

43. (b) $\underset{\text{Ethyl amine}}{C_2H_5NH_2}\xrightarrow{HNO_2}\underset{\text{Ethyl alcohol}}{C_2H_5OH}\xrightarrow{PCl_5}C_2H_5Cl$

$\xrightarrow{NH_3}\underset{\text{Ethyl amine}}{C_2H_5NH_2}$

44. (c) $\underset{1^o}{CH_3CH_2-NH_2}+HNO_2\rightarrow\underset{\text{Alcohol}}{CH_3CH_2-OH}+N_2+H_2O$

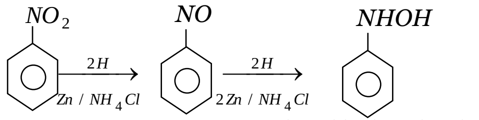
$\underset{2^o}{(CH_3CH_2)_2NH}+HNO_2\rightarrow\underset{\text{Nitroso amine}}{(CH_3CH_2)_2N-N=O}+H_2O$

45. (d) $\underset{\text{AlkylIsocyanide}}{RN\overset{\rightarrow}{\equiv}C}+2H_2O\xrightarrow{\text{Hydrolysis}}\underset{1^o\ \text{amine}}{RNH_2}+\underset{\text{Formic acid}}{HCOOH}$

46. (d) $CH_3NH_2 + 2HNO_2 \rightarrow CH_3-O-N=O+N_2+2H_2O$

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

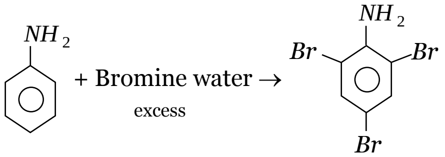
47. (d)



Phenyl hydroxyl amine

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

51. (d)

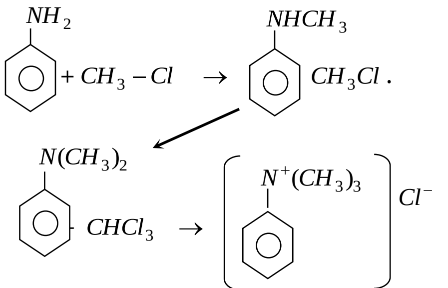


52. (d) $R-NH_2+CHCl_3+3NaOH \rightarrow RN \equiv C+3NaCl+3H_2O$

The unpleasant smell is due to the formation of isocyanide.

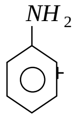
53. (c) $RNH_2+NaNO_2+HCl \rightarrow R-OH+NaCl+N_2+H_2O$

54. (c)



Quaternary ammonium salt

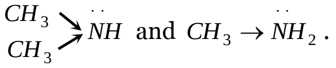
55. (c)



$+ HNO_3/H_2SO_4 \rightarrow$ A black mass.

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

56. (d)



$\overset{CH_3}{\underset{CH_3}{>}}\ddot{N}H$ and $CH_3 \rightarrow \ddot{N}H_2$.

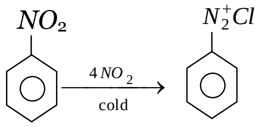
In methyl amine only one electron releasing group is present but in dimethyl amine two electron releasing groups are present which increase the basicity higher in dienethyl amine.

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

58. (c) $CH_3-NH_2+HNO_2 \rightarrow CH_3OH+N_2+H_2O$

60. (c) $R_3N+HONO \rightarrow R_3N.HONO$ called as Quaternary ammonium salt.

61. (b)



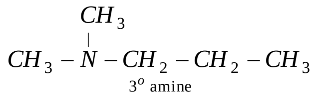
But $R-NH_2 \xrightarrow[\text{cold}]{4NO_2} R-OH+N_2+H_2O$

62. (a) $CH_3CN \xrightarrow{H_2O/H^+} CH_3COOH+NH_3$

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

67. (e) Because

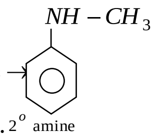
N-N dimethyl propanimine



$CH_3-\overset{\overset{CH_3}{|}}{N}-CH_2-CH_2-CH_3$

3^o amine

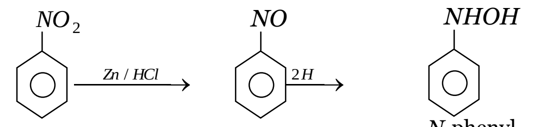
N-Methyl aniline →



aniline → 1^o amine.

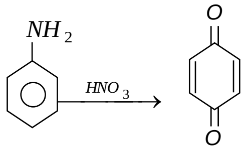
68. (c) Replacable H^- is absent.

69. (a)



Nitro benzene Nitro benzene N-phenyl hydroxylamine

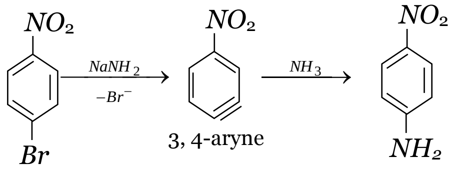
70. (c)



Because oxidation of aniline occur in absence of making effect.

P - Benzoquinone

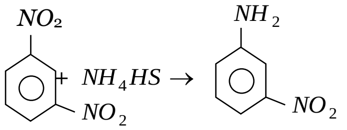
72. (c)



3, 4-aryne

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

75. (b)



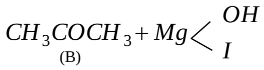
76. (a) Because of presence of electron withdrawing group -NO_2 .

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

78. (b) $R-NH_2+HNO_2 \rightarrow \underset{\text{alcohol}}{R-OH}+N_2+H_2O$.

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

80. (b) $CH_3CN + CH_3MgI \rightarrow \underset{(A)}{(CH_3)_2CNMgI} \xrightarrow[-NH_3]{H_2O/H^+}$



$\underset{(B)}{CH_3COCH_3} + Mg<^{OH}_{I}$

82. (d) $C_6H_5-NO_2 \xrightarrow[Zn/NaOH]{10[H]} \underset{\text{Hydrazo benzene}}{C_6H_5NH-NHC_6H_5}+4H_2O$

83. (a)

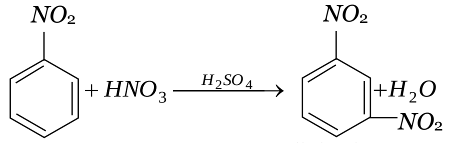
$RCOCl+2Me_2NH \rightarrow RCON<^{Me}_{Me}+Me_2+\overset{+}{N}H_2Cl^-$

Me = Methyl.

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

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

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

89. (b) 

m-dinitrobenzene

90. (b) $\underset{\text{Aniline}}{\underset{(A)}{C_6H_5NH_2}} \xrightarrow[0^oC]{NaNO_2 + HCl} \underset{(B)}{C_6H_5N_2Cl} \xrightarrow{KCN} \underset{(C)}{C_6H_5CN}$

$\downarrow H_3O$

$\underset{(D)}{C_6H_5COOH}$

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

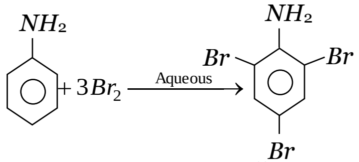
$CH_3NH_2 + COCl_2 \xrightarrow{-HCl} [CH_3NH - CO - Cl]$

$\xrightarrow[-HCl]{\Delta} \underset{\text{methyl}}{CH_3 - N = C = O}$

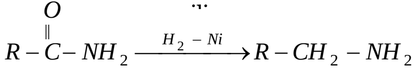
92. (d) $R - NC + 2H_2O \rightarrow RNH_2 + HCOOH$.

93. (d) $CH_3 - NC + 2H_2O \rightarrow CH_3NH_2 + HCOOH$

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

99. (b) 

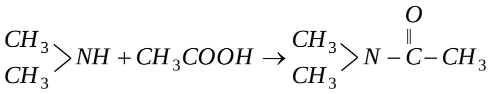
2, 4, 6 tribromo

102. (a) 

$R - \overset{O}{\overset{\|}{C}} - NH_2 \xrightarrow{H_2 - Ni} R - CH_2 - NH_2$

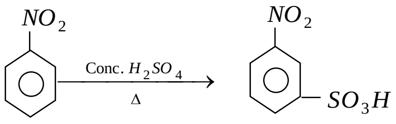
104. (b) $CH_3CN + 2H_2O \xrightarrow{HCl} CH_3COOH + NH_3$

106. (a) $CH_3CH_2NH_2 + CH_3COCl \rightarrow \underset{N\ \text{Ethylacetanilide}}{CH_3CH_2NHCOCH_3} + HCl$

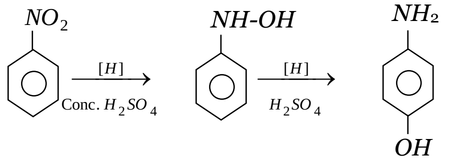
107. (a) 

$\begin{matrix} CH_3 \\ CH_3 \end{matrix} > NH + CH_3COOH \rightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix} > N - \overset{O}{\overset{\|}{C}} - CH_3$

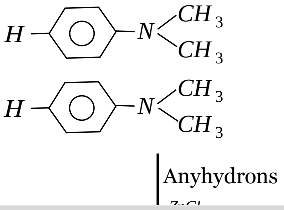
108. (d) Anilinium hydrogen chloride produces chloride ion which gives white precipitate with $AgNO_3$. In fact anilium chloride is a part of aniline.

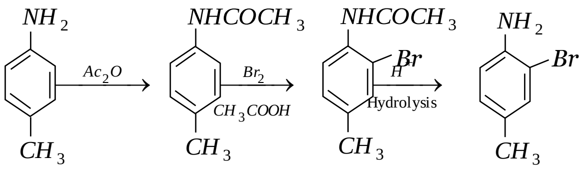
109. (b) 

(A)

110. (c) 

Nitrobenzene Phenyl hydroxyl amine *p*-amino phenol

113. (c) $C_6H_5CH = O +$ 

115. (d) 

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

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

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

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

121. (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.

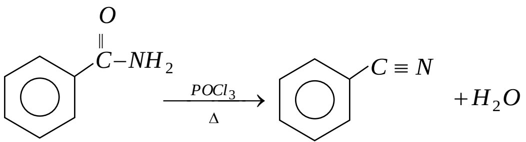
122. (d) Isocyanides on hydrolysis forms primary amines not ammonia

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

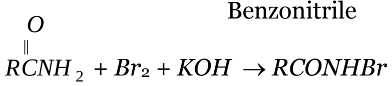
$\downarrow KOH$

$K_2CO_3 + C_6H_5NH_2 \xleftarrow[2KOH]{} C_6H_5NCO + KBr + H_2O$

$C_6H_5NH_2 + (CH_3CO)_2O \rightarrow \underset{\text{(antipyretic)}}{\underset{\text{Acetanilide}}{CH_3CONHC_6H_5}} + CH_3COOH$

124. (d) 

Benzonitrile

125. (d) (i) 

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

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

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

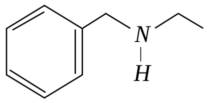
$RCONH_2 + Br_2 + 4KOH \rightarrow RNH_2 + 2KBr + K_2CO_3 + 2H_2O$

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

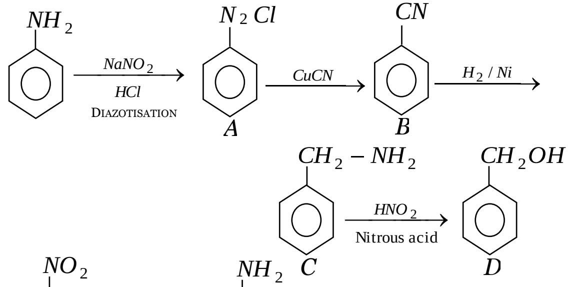
$C_6H_5 - NH_2 + O = CHC_6H_5 \xrightarrow[-H_2O]{\Delta} C_6H_5N = CHC_6H_5$

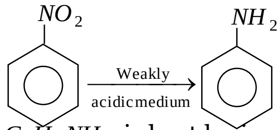
Benzylidine aniline

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

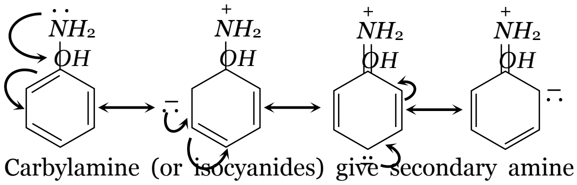
128. (b)


is most basic

130. (d)


131. (a)


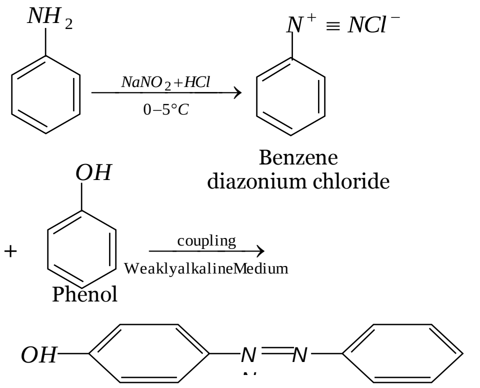
132. (d) $C_6H_5NH_2$ is least basic compound due to resonance by which the Lone pair of nitrogen takes part in resonance & due to unavailability of lone pair on N Aniline become less basic. The Lone pair of N is delocalized into benzene ring by resonance



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

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

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



p-hydroxyazobenzene

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

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

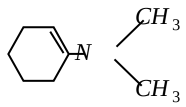
Thus product Z is identified as $C_6H_5 - COOH$

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

$CH_3CONH_2 \xrightarrow{Br_2 / KOH} CH_3NH_2$

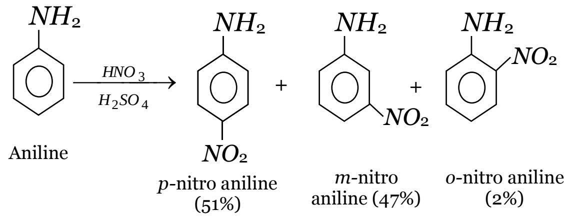
137. (c) $CH_3CN + 2H \xrightarrow[\text{Ether}]{HCl} HC \equiv CH$

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

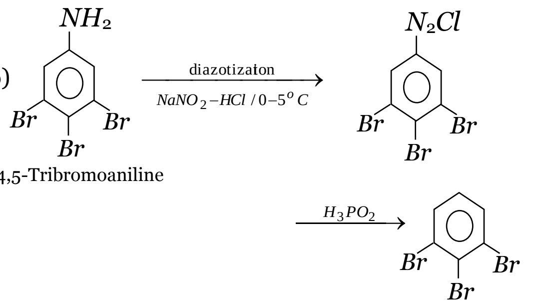
138. (b)


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

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

141. (d)


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.

142. (b)


143. (a) Basicity order is

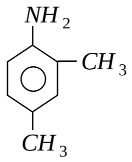
$C_4H_5NH_2 < (CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$

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

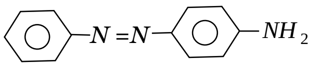
Tests for Nitrogen Containing Compounds

1. (c) $\underset{\text{Acetamide}}{CH_3CONH_2} + Br_2 + 4NaOH \to$

$\underset{\text{Methyl amine}}{CH_3NH_2} + Na_2CO_3 + 2NaBr + 2H_2O$

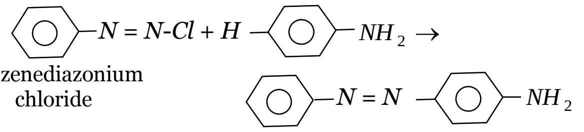
5. (b)


is a type of 1° amine and hence gives +ve carbyl test

6. (a)


Orange Colour

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



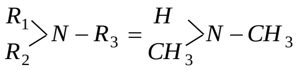
p-amino azo benzene (yellow dye)

11. (a) $CHCl_3$ gives carbylamine test.

$$RNH_2 + CHCl_3 + 3KOH(\text{alc.}) \xrightarrow{\Delta} \underset{\text{alkylisocyanide}}{RN \equiv C} + 3KCl + 3H_2O$$

Critical Thinking Questions

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

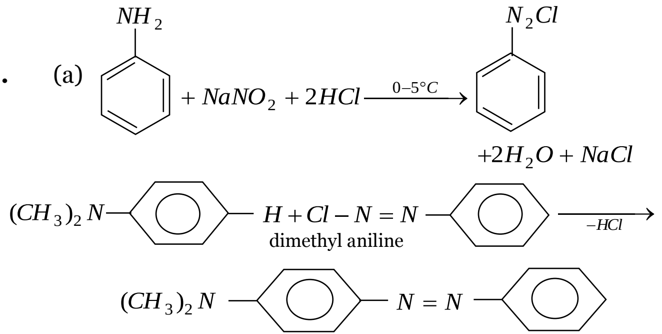


$$\begin{matrix}R_1\\R_2\end{matrix}\!>\!N - R_3 = \begin{matrix}H\\CH_3\end{matrix}\!>\!N - CH_3$$

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

2. (c) $\underset{\text{Ethylamine}}{CH_3CH_2NH_2} + HNO_2 \rightarrow \underset{\text{Ethylalcohol}}{CH_3CH_2OH} + N_2 + H_2O$

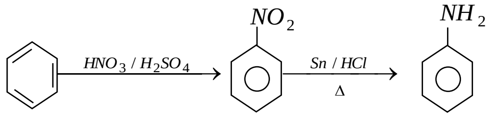
3. (a)



4. (c) Hofmann degradation of amide

$$R - CoNH_2 + Br_2 + 4KOH \longrightarrow \underset{\text{primary amine}}{R - NH_2} + 2KBr + K_2CO_3 + 2H_2O$$

5. (b)



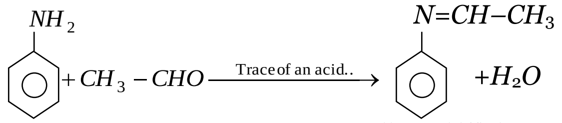
Nitrobenzene Aniline

6. (b) The relative basic charecter of $1^o, 2^o$ and 3^o amines also depends upon the nature of the alkyl group.

R	Relative basic strength
$-CH_3$	$R_2NH > R - NH_2 > R_3N > NH_3$
$-C_2H_5$	$R_2NH > R - NH_2 > NH_3 > R_3N$
$-CHMe_2$	$R - NH_2 > NH_3 > R_2NH > R_3N$
$-CMe_3$	$NH_3 > R - NH_2 > R_2NH > R_3N$

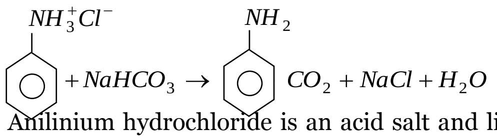
7. (b) The nitrogroup is very firmly linked to the benzene nucleus and does not undergo any displacement reaction. Nitro group deactivates the benzene nucleus.

8. (a)



Anil or Schiff's base

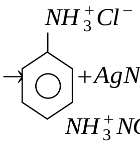
9. (bc) (1) With $NaHCO_3 \rightarrow$



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

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

(2) With $AgNO_3 \rightarrow$

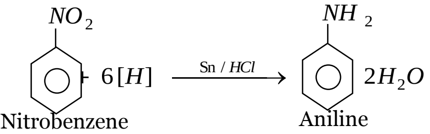


$+AgNO_3 \rightarrow$

$NH_3^+NO_2^- + AgCl \downarrow$ (White ppt)

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

10. (a)



Nitrobenzene Aniline

11. (a) $C_6H_5 - NH_2 + CHCl_3 + 3KOH \rightarrow \underset{\text{Phenyl Isocyanide}}{C_6H_5NC} + 3KCl + 3H_2O$

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

$K_b = 5.4 \times 10^{-4}$ 4.5×10^{-4} 0.6×10^{-4}

13. (c) $(CH_3)_2NCOCH_3 + HCl / H_2O$

$\downarrow$

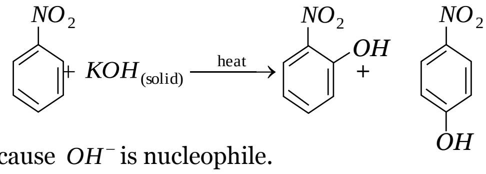
$(CH_3)_2NH + CH_3COOH$

14. (a) Order of basicity of amines

(i) $2^o > 1^o > 3^o$

(ii) $R_2NH > RNH_2 > ArCH_2 - NH_2 > NH_3 > ArNH - R > ArNH_2 > ArNH - Ar$

15. (a)



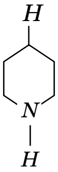
Because OH^- is nucleophile.

16. (c) $C_6H_5SO_2Cl + RNH_2 \rightarrow RNHSO_2C_6H_5 \xrightarrow{KOH} \underset{\text{soluble in } KOH}{RNKSO_2C_6H_5}$

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

$$3NaCNS + FeCl_3 \rightarrow \underset{\substack{\text{Ferric sulpho cyanide}\\\text{(Blood red colour)}}}{Fe(CNS)_3} + 3NaCl$$

18. (c)



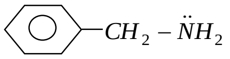
does not have aromaticity by which the Lone pair of electron of Nitrogen does not delocalised in benzene ring so it will be strong base on other hand rest 3 have aromaticity *i.e.,* they follow the huckel rule so the electron pair of Nitrogen delocalised in ring by resonance & resulting they become less basic.

19. (d) Liebermann's Nitroso reaction.

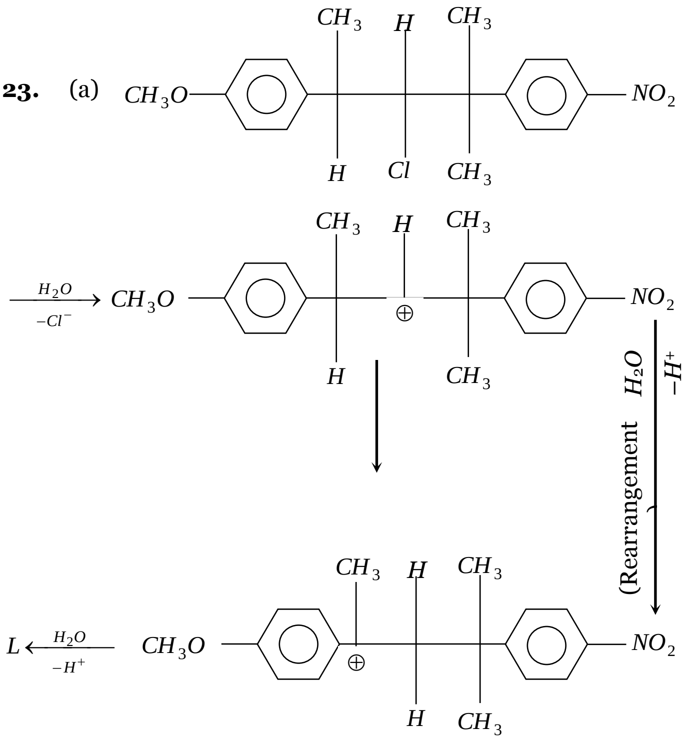
20. (a) $$\underset{\text{(Acetamide)}}{CH_3CONH_2} + Br_2 + 4KOH \xrightarrow[-2H_2O]{} \underset{\text{(Methyl amine)}}{CH_3NH_2} + 2KBr + 2K_2CO_3$$

21. (c) The class of Indigo dye is Indigoid or vat dye. Indigo dyes are insoluble in water.

22. (d) Lone pair of $\ddot{N}$ are not taking part in conjugation whereas in other parts lone pairs are taking part in conjugation



23. (a)



Assertion and Reason

1. (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.

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

3. (b) The reason being that the terminal carbon atom in isocyanide has electron-deficient carbon having a sexlet of electrons and hence undergoes addition reactions with ozone.

4. (d) When primary amines are heated with chloroform in the presence of alcoholic KOH, isocyanides are formed. This reaction is known as carbylamine reaction. eg. ethyl amine gives ethyl isocyanide on treatment with $CHCl_3$ and alcoholic KOH.

$$\underset{\text{Ethylamine}}{C_2H_5 - NH_2} + \underset{\text{Chloroform}}{CHCl_3} + 3KOH(\text{alc}) \xrightarrow{\Delta} C_2H_5 - N \overset{\rightarrow}{=} C + 3KCl + 3H_2O$$

5. (b) Nucleophilic species which have more than one site of reaction are called ambident nucleophiles.

$$:\overline{C} = N : \Leftrightarrow : C = \overline{N} :$$

6. (c) $-SO_3H$ group being more acidic than $-CO_2H$ group can easily transfer a proton to the amino group.

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

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

9. (c) Reaction can be used to prepare 1°, 2°, 3° amines and finally quarternary ammonium salts.

10. (b) Nitroarene cannot be distilled under normal atmospheric pressure. This is because either they decompose or they explode on strong heating.

11. (c) Only 1° amines undergo Hofmann bromamide reaction. Since $CH_3CONHCH_3$ is a 2° amine therefore, it does not undergo Hofmann bromamide reaction.

12. (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.

13. (e) Ammonia is more basic than water. It is because nitrogen being less electronegative than oxygen has a greater tendency to donate electrons.

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

15. (a) $$RNH_2 + CHCl_3 + 3KOH(alc) \rightarrow R - N \overset{\rightarrow}{=} C + 3KCl + 3H_2O$$

17. (d) *p*-Anisidine is a stronger base than aniline.

$-OCH_3$ group in anisidine exerts $+R-$ effect.

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

20. (d) The nitro group strongly deactivates the benzene ring towards electrophilic substitution.

Nitrobenzene does not undergo Friedel-Craft acylation reaction.

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

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

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

SET Self Evaluation Test - 29

1. Melting points are normally the highest for [AIIMS 2004]

(a) Tertiary amides (b) Secondary amides

(c) Primary amides (d) Amines

2. Amines behave as [Karnataka (Med.) 1999]

(a) Lewis acids

(b) Lewis bases

(c) Aprotic acids

(d) Amphoteric compounds

3. Which of the following compound gives dye test

[MP PET/PMT 1998]

(a) Aniline

(b) Methylamine

(c) Diphenylamine

(d) Ethylamine

4. In hydrolysis of aniline, the reagent used is [AFMC 1995]

(a) Dil. HCl (b) Acetyl chloride

(c) CH_3OH (d) None of these

5. A nitrogen containing organic compound on heating with chloroform and alcoholic KOH, evolved very unpleasant smelling vapour. The compound could be

[BHU 2002; BVP 2003]

(a) *N, N*-dimethyl amine

(b) Nitrobenzene

(c) Aniline

(d) Benzamide

6. The reaction between a primary amine, chloroform and few drops of alcoholic KOH is known as

[MNR 1987; MP PMT 1994; Bihar MEE 1996;
AIIMS 1998; MP PET 2002]

(a) Cannizzaro reaction

(b) Carbylamine reaction

(c) Wurtz's reaction

(d) Reimer-Tiemann reaction

7. Nitrolim is [BVP 2004]

(a) $CaC_2 + N_2$ (b) $CaCN_2 + C$

(c) $Ca(CN)_2 + C$ (d) $Ca(CN)_2 + NH_4CN$

8. Phenyl isocyanides are prepared from which of the following reactions [CBSE PMT 1999]

(a) Rosenmund's reaction

(b) Carbylamine reaction

(c) Reimer-Tiemann reaction

(d) Wurtz reaction

9. On strong heating, ammonium acetate gives [MNR 1995]

(a) Acetamide

(b) Methyl cyanide

(c) Urea

(d) Formamide

10. Aniline is separated from a mixture by [UPSEAT 2000, 01]

(a) Fractional crystallization

(b) Fractional distillation

(c) Vacuum distillation

(d) Steam distillation

11. Molecular formula of chloropicrin is [MH CET 2003]

(a) $CHCl_3NO_2$ (b) CCl_3NO_3

(c) CCl_2NO_2 (d) CCl_3NO_2

12. In amines, the hybridisation state of *N* is [CPMT 1999]

(a) sp (b) sp^2

(c) sp^3 (d) sp^2d

13. Foul smelling compound formed, during carbyl amine reaction is :

(a) Alcohol

(b) Aldehyde

(c) Alkyl isocyanide

(d) Carboxylic acid

14. The end product of the reaction [Kerala PMT 2004]

$\text{ethylamine} \xrightarrow{HNO_2} A \xrightarrow{PCl_5} B \xrightarrow{KCN} C$ is

(a) Ethyl amine

(b) Diethyl amine

(c) Propane nitrite

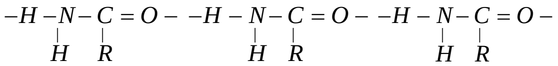
(d) Triethyl amine

(e) Methyl amine

AS Answers and Solutions

(SET -29)

1. (c) The higher boiling points of amide is because of Intermolecular hydrogen bonding



$$-\underset{H}{N}-\underset{R}{C}=O-\;-H-\underset{H}{N}-\underset{R}{C}=O-\;-H-\underset{H}{N}-\underset{R}{C}=O-$$

Due to intermolecular hydrogen bonding they have high boiling point than amine and amongst amide the order of Boiling point are

Primary > Sec > Tertiary

This is because of alkyl group by which the carbonyl oxygen do not form the hydrogen bond (other molecule) so primary amide have high boiling point and Tertiary amides does not have to form bond with O of other amide and have least B.P

2. (b) In amines nitrogen has a love pair of e^-. It can donate a election pair. So amines behaves as a lewis base.

3. (a) Basically all the Azo dye are derivatives of aniline.

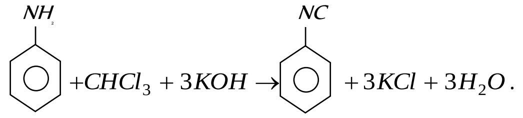
4. (a) All amines react with mineral acids such as HCl, H_2SO_4, HNO_3 etc. to form salts which are soluble in water.

5. (c) $C_6H_5NH_2 + CHCl_3 + \underset{\text{(Alc)}}{3KOH} \rightarrow C_6H_5NC + 3KCl + 3H_2O$

6. (b) $CH_3NH_2 + CHCl_3 + 3KOH \rightarrow \underset{\text{Isocyanide}}{R\overset{\oplus}{N} \equiv \overset{\ominus}{C}} + 3KCl + 3H_2O$

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

8. (b)



$+CHCl_3 + 3KOH \rightarrow \;\; + 3KCl + 3H_2O.$

Carbyl amine reaction.

***

9. (b) $CH_3COONH_4 \xrightarrow{\Delta} CH_3CONH_2 \xrightarrow{\Delta} CH_3CN + H_2O$

10. (d) Steam distellation is used for separation of aniline from mixture. Aniline is insoluble in water but it is steam soluble.

11. (d) Molecular formula of chloropicrin is CCl_3NO_2

12. (c) It is similar that of NH_3 except H- is replaced by $-R$ group.

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

13. (c) On heating $CHCl_3$ with ethanolic KOH and primary amine, isocyanide is formed and is readily detected by its offensive odour. This is called as carbyl amine test.

$$\underset{\text{Chloroform}}{CHCl_3} + \underset{\text{Potassium hydroxide}}{3\,KOH} + \underset{\text{Primary amine}}{RNH_2}$$

$$\xrightarrow{\Delta} \underset{\text{Alkyl Isocyanide (Foul smell)}}{RNC} + \underset{\text{Potassium chloride}}{3\,KCl} + \underset{\text{Water}}{H_2O_2}$$

14. (c) $C_2H_5NH_2 + HNO_2 \rightarrow \underset{(A)}{C_2H_5OH} + N_2 + H_2O$

$C_2H_5OH + PCl_5 \rightarrow \underset{(B)}{C_2H_5Cl} + POCl_3 + HCl$

$C_2H_5Cl + KCN \rightarrow \underset{(C)\text{Propane nitrile}}{C_2H_5CN} + KCl$

Assertion & Reason

1	a	2	a	3	b	4	d	5	b
6	c	7	a	8	c	9	c	10	b
11	c	12	b	13	e	14	c	15	a
16	a	17	d	18	b	19	d	20	d
21	a								

Answers and Solutions

Introduction of Nitrogen Containing Compounds

4. (d) C_3H_9N can form all the 3 amines.

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

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

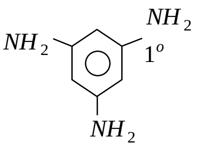
5. (c) $(CH_3)_2C=O + H.CH_2-COCH_3 + NH_3$

$$\downarrow$$

$$\underset{\text{diacetoneamine}}{(CH_3)_2-\underset{\underset{NH_2}{|}}{C}-CH_2-COCH_3}$$

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

9. (c)



1^o amine

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

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

15. (b) Four 1^o amines are possible

$CH_3CH_2CH_2CH_2NH_2, (CH_3)_2CHCH_2NH_2,$

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

Preparation of Nitrogen Containing Compounds

1. (c) Hofmann's bromamide reaction

$$\underset{\text{Acetamide}}{CH_3-CO-NH_2} + Br_2 + 4KOH \xrightarrow{H_2O}$$

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

2. (d) $CH_3CONH_2 \xrightarrow{NaOBr} CH_3NH_2.$

3. (b) $\underset{\text{Acetamide}}{CH_3CONH_2} + Br_2 + 4NaOH \rightarrow$

$$\underset{\text{Methylamine}}{CH_3NH_2} + Na_2CO_3 + 2NaBr + 2H_2O$$

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

5. (b) $CH_3C\equiv N + 4[H] \xrightarrow[\text{Reduction}]{Na+C_2H_5OH} CH_3CH_2NH_2$

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

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

7. (c) $C_2H_5I + NH_3 \rightarrow HI + C_2H_5-NH_2$

$C_2H_5OH + NH_3 \rightarrow H_2O + C_2H_5-NH_2$

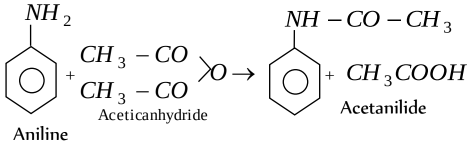
9. (c) $\underset{\text{Nitroethane}}{CH_3-CH_2-NO_2} + 6[H] \xrightarrow{\text{Sn / HCl}}$

$$\underset{\text{Ethyl amine}}{CH_3-CH_2-NH_2} + 2H_2O$$

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

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

12. (d)

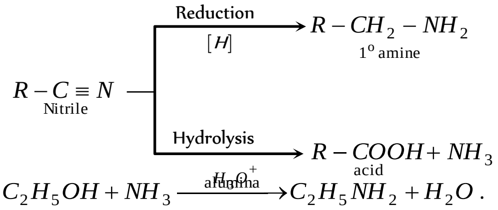


16. (c) $CH_3-N \overset{\rightarrow}{\equiv} C + 4[H] \xrightarrow{\text{Reduction}} \underset{2^o \text{ amine}}{CH_3-NH-CH_3}$

17. (a) $\underset{\text{Nitromethane}}{CH_3NO_2} + 3Cl_2 + 3NaOH \rightarrow$

$$\underset{\text{(chloropicrin)}}{CCl_3-NO_2} + 3NaCl + 3H_2O.$$

18. (b)



19. (a) $C_2H_5OH + NH_3 \xrightarrow{\text{alumina}} C_2H_5NH_2 + H_2O.$

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

It yield amine when reduced as –

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

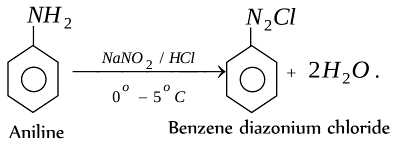
21. (b) $CH_3CONH_2 \xrightarrow{P_2O_5} CH_3CN \xrightarrow{4H} CH_3CH_2NH_2$

22. (a) $CH_3-CH_2-\overset{\overset{O}{\|}}{N} \rightarrow O + 3H_2 \rightarrow CH_3CH_2NH_2 + 2H_2O.$

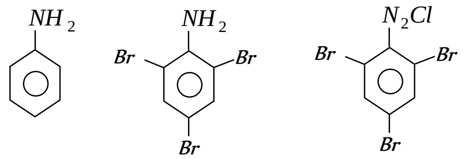
23. (a) $\underset{\text{Methyl amine}}{CH_3NH_2} \xrightarrow{NO_2} CH_3OH + N_2 + H_2O$

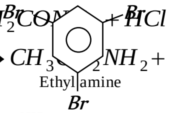
24. (a) $\underset{1^o\text{–amine}}{R-NH_2} + CHCl_3 + 3KOH \rightarrow R-NC + 3KCl + 3HO$

25. (b)



26. (b) $CH_3CH_2COOH \xrightarrow{SOCl_2} CH_3CH_2COCl + SO_2 + HCl$



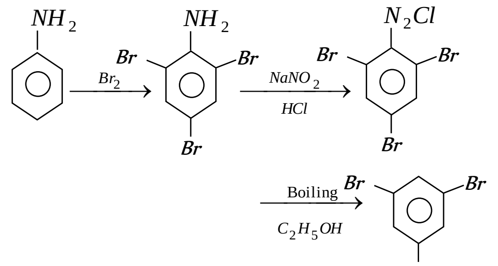


$CH_3CH_2COCl + NH_3 \rightarrow CH_3CH_2CONH_2 + HCl$

$CH_3CH_2CONH_2 + Br_2 / NaOH \rightarrow \underset{\text{Ethyl amine}}{CH_3CH_2NH_2} + CO_2$

27. (c) $CH_3COOH \xrightarrow{PCl_5} CH_3COCl \xrightarrow{NH_3} CH_3CONH_2 \xrightarrow{NaOBr} CH_3NH_2$

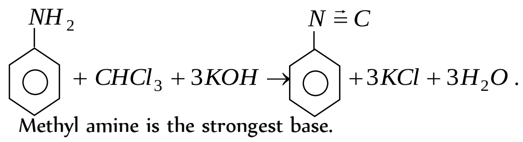
28. (d)



29. (c) $CH_3 - N \equiv C \xrightarrow{LiAlH_4} \underset{\text{sec. amine}}{CH_3 - NH - CH_3}$

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

33. (a)



$C_6H_5NH_2 + CHCl_3 + 3KOH \rightarrow C_6H_5N \equiv C + 3KCl + 3H_2O$.

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

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

38. (a) $C_2H_5NH_2 + CS_2 + HgCl_2 \rightarrow C_2H_5NCS + 2HCl + HgS$.

39. (d) $C_6H_5NH_2 \xrightarrow[HCl]{NaNO_3} C_6H_5N_2Cl \xrightarrow{H_2O} C_6H_5OH + N_2 + HCl$

41. (d) $\underset{\text{chlorobenzene}}{2C_6H_5Cl} + 2NH_3 \xrightarrow[\text{in xylene } 570^oK]{H_2O} \underset{\text{(Aniline)}}{C_6H_5NH_2} + Cu_2Cl_2 + H_2O$

44. (c) $C_6H_5NH_2 + HCl + NaNO_2 \rightarrow C_6H_5N_2Cl$

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

47. (b) $C_6H_5NH_2 \xrightarrow{NaNO_2 + HCl \; 0^oC} C_6H_5N_2Cl$

48. (a) $CH_3NO_2 + 6H \xrightarrow[HCl]{Sn} CH_3NH_2 + 2H_2O$

49. (c) $C_6H_5NH_2 \xrightarrow[0^oC - 5^oC]{NaNO_2 / HCl} \underset{\text{(X)}}{C_6H_5N_2^+Cl^-} \xrightarrow[H_2O]{HNO_2} \underset{\text{(Y)}}{C_6H_5NO_2} + N_2 + HCl$

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

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

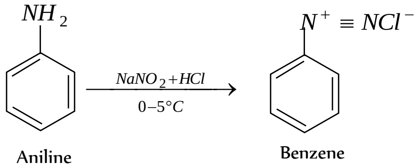
$ArCONH_2 \xrightarrow[-H_2O]{P_2O_5} ArCN$

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

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

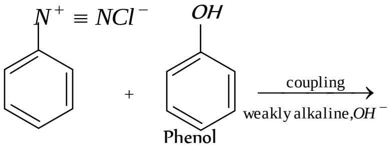
$(CH_3CH_2)_2NH + HONO \rightarrow \underset{\text{oily}}{(CH_3CH_2)_2N.NO} + H_2O$

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

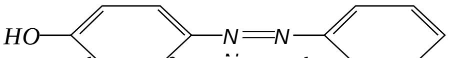


Aniline

Benzene diazonium chloride

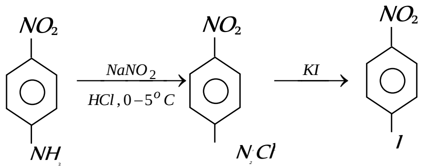


Phenol



Azo dye

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



p-nitroaniline

p-nitroiodobenzene

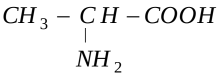
55. (b) $C_2H_5Br + KCN \xrightarrow{\text{alcohol}} C_2H_5CN + KBr$

Properties of Nitrogen Containing Compounds

1. (d) Tertiary amine does not react with nitrous acid because in it α-H atom is absent.

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

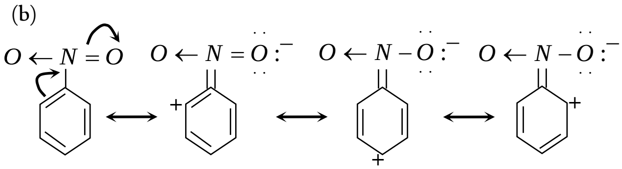
3. (b)



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

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

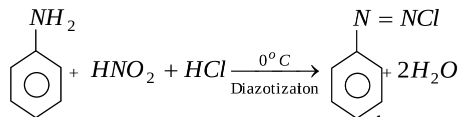
4. (b)



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

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

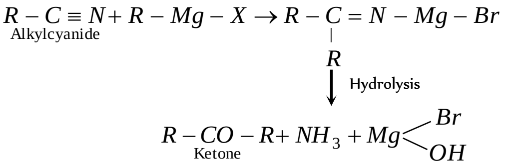
7. (c)



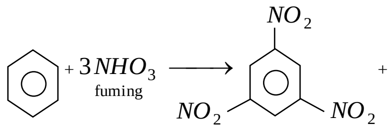
Aniline

Benzene diazonium chloride

9. (b)



$\underset{\text{Alkylcyanide}}{R - C \equiv N} + R - Mg - X \rightarrow R - \underset{\displaystyle R}{\underset{|}{C}} = N - Mg - Br \xrightarrow{\text{Hydrolysis}} \underset{\text{Ketone}}{R - CO - R} + NH_3 + Mg\begin{matrix} Br \\ OH \end{matrix}$

10. (c) 

sym-trinitro benzene

11. (c) $\underset{\text{Ethylamine}}{CH_3-CH_2-NH_2}\xrightarrow[{[O]}]{KMnO_4}\underset{\text{Aldimine}}{CH_3-CH=NH}$

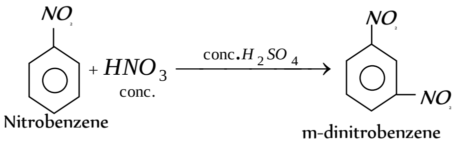
$\xrightarrow{H_3O^+}\underset{\text{Acetaldehyde}}{CH_3-CHO}$

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

13. (b) $\underset{1^o\text{ amine}}{R-CH_2-NH_2}+\underset{\text{aldehyde}}{O=CH-R}\rightarrow$

$\underset{\text{Aldimine}}{R-CH_2-N=CH-R}+H_2O$

14. (c) $\underset{\text{Acetamide}}{CH_3-CO-NH_2}+HNO_2\rightarrow\underset{\text{Acetic acid}}{CH_3COOH}+N_2\uparrow+H_2O$

15. (c) 

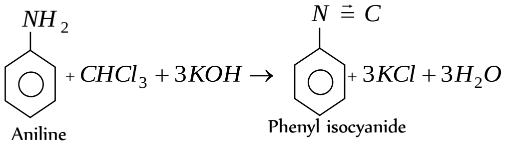
$-NO_2$ group is meta directing group.

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

17. (d) $CH_3-CH_2-NH_2+HCl\rightarrow\underset{\text{Ethyl ammonium chloride}}{CH_3CH_2-NH_3^+Cl^-}$

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

18. (a) $\underset{\substack{2^o\text{ amine is}\\ \text{most basic}}}{(CH_3)_2NH}>\underset{1^o\text{ amine}}{CH_3NH_2}>\underset{3^o\text{ amine}}{(CH_3)_3N}>\underset{\substack{\text{Ammonia is}\\ \text{least basic}}}{\ddot{N}H_3}$

19. (b) 

Aniline Phenyl isocyanide

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

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

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

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

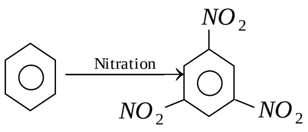
This litmus paper test shows basic nature of amine.

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

25. (a) Mustard oil reaction

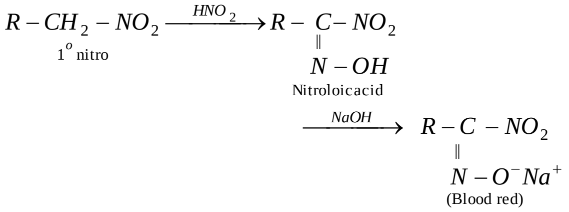
$\underset{\text{Ethyl amine}}{CH_3-CH_2-NH_2}+CS_2\xrightarrow{HgCl_2}$

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

28. (c) 

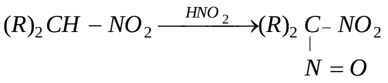
1, 3, 5-trinitrobenzene

3- nitro group can be introduced.

34. (a) 

$$\underset{1^o\text{ nitro}}{R-CH_2-NO_2}\xrightarrow{HNO_2}\underset{\text{Nitroloicacid}}{R-\underset{\substack{\|\\ N-OH}}{C}-NO_2}$$

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

35. (b) 

$$(R)_2CH-NO_2\xrightarrow{HNO_2}(R)_2\underset{\substack{|\\ N=O}}{C}-NO_2$$

$\xrightarrow{NaOH}$ Blue colour.

37. (b) $\underset{\text{Acetamide}}{CH_3CONH_2}\xrightarrow{P_2O_5}\underset{\text{Acetonitrile}}{CH_3-C\equiv N}+H_2O.$

38. (b) $CHCl_3+C_2H_5NH_2+3KOH\rightarrow$

$\underset{\text{Ethyl isocyanide}}{C_2H_5N\equiv C}+3KCl+3H_2O$

39. (d) $\underset{\text{Methyl cyanide}}{CH_3-C\equiv N}+2H_2O\rightarrow\underset{\text{Aceticacid}}{CH_3COOH}+NH_3$

40. (c) $\underset{(2c)}{CH_3CONH_2}+Br_2+4KOH\rightarrow$

$\underset{(1c)}{CH_3NH_2}+K_2CO_3+3KBr+2H_2O$

41. (a) $(C_2H_5)_2NH+(\text{aq.})HONO\rightarrow\underset{\text{Diethyl nitrosoamine}}{(C_2H_5)_2N-N=O}+H_2O$

42. (c) $CH_3-C\equiv N\xrightarrow[\text{Reduction}]{Na+EtOH}CH_3-CH_2-NH_2$

$\xrightarrow{HNO_2}CH_3CH_2-OH\xrightarrow[H_2SO_4]{K_2Cr_2O_7}CH_3COOH$

43. (b) $\underset{\text{Ethyl amine}}{C_2H_5NH_2}\xrightarrow{HNO_2}\underset{\text{Ethyl alcohol}}{C_2H_5OH}\xrightarrow{PCl_5}C_2H_5Cl$

$\xrightarrow{NH_3}\underset{\text{Ethyl amine}}{C_2H_5NH_2}$

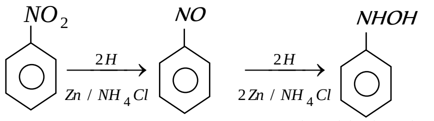
44. (c) $\underset{1^o}{CH_3CH_2-NH_2}+HNO_2\rightarrow\underset{\text{Alcohol}}{CH_3CH_2-OH}+N_2+H_2O$

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

45. (d) $\underset{\text{AlkylIsocyanide}}{RN\equiv C}+2H_2O\xrightarrow{\text{Hydrolysis}}\underset{1^o\text{ amine}}{RNH_2}+\underset{\text{Formic acid}}{HCOOH}$

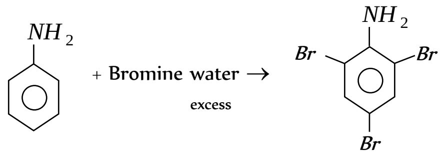
46. (d) $CH_3NH_2+2HNO_2\rightarrow CH_3-O-N=O+N_2+2H_2O$

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

47. (d) 

Phenyl hydroxyl amine

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

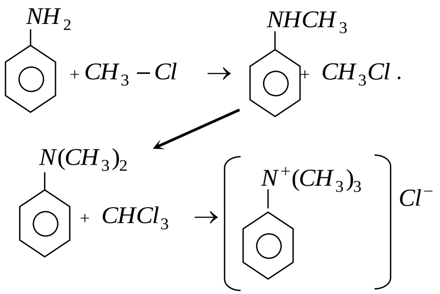
51. (d) 

52. (d) $R-NH_2+CHCl_3+3NaOH\rightarrow RN\equiv C+3NaCl+3H_2O$

The unpleasant smell is due to the formation of isocyanide.

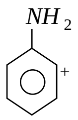
53. (c) $RNH_2 + NaNO_2 + HCl \rightarrow R-OH + NaCl + N_2 + H_2O$

54. (c)



Quaternary ammonium salt

55. (c)



$+ HNO_3 / H_2SO_4 \rightarrow$A black mass.

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

56. (d) $\begin{matrix}CH_3\\CH_3\end{matrix}\!> \overset{\cdot\cdot}{N}H$ and $CH_3 \rightarrow \overset{\cdot\cdot}{N}H_2$.

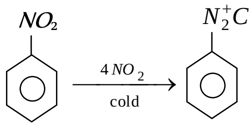
In methyl amine only one electron releasing group is present but in dimethyl amine two electron releasing groups are present which increase the basicity higher in dienethyl amine.

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

58. (c) $CH_3-NH_2 + HNO_2 \rightarrow CH_3OH + N_2 + H_2O$

60. (c) $R_3N + HONO \rightarrow R_3N.HONO$ called as Quaternary ammonium salt.

61. (b)



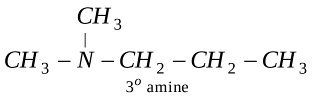
But $R-NH_2 \xrightarrow[\text{cold}]{4\,NO_2} R-OH + N_2 + H_2O$

62. (a) $CH_3CN \xrightarrow{H_2O/H^+} CH_3COOH + NH_3$

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

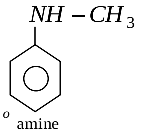
67. (e) Because

N-N dimethyl propanimine



$$\underset{3^o\text{ amine}}{CH_3-\overset{\overset{CH_3}{|}}{N}-CH_2-CH_2-CH_3}$$

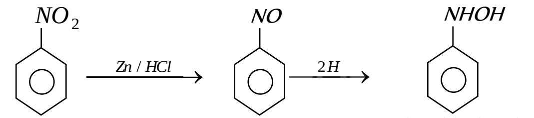
N-Methyl aniline →



aniline → 1^o amine. 2^o amine

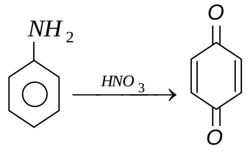
68. (c) Replacable H^- is absent.

69. (a)



Nitro benzene Nitro benzene *N*-phenyl hydroxylamine

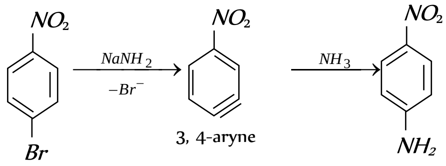
70. (c)



Because oxidation of aniline occur in absence of making effect.

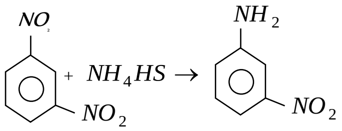
P - Benzoquinone

72. (c)



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

75. (b)



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

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

78. (b) $R-NH_2 + HNO_2 \rightarrow \underset{\text{alcohol}}{R-OH} + N_2 + H_2O$.

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

80. (b) $CH_3CN + CH_3MgI \rightarrow \underset{\text{(A)}}{(CH_3)_2CNMgI} \xrightarrow[-NH_3]{H_2O/H^+}$

$$\underset{\text{(B)}}{CH_3COCH_3} + Mg\begin{matrix}\diagup OH\\ \diagdown I\end{matrix}$$

82. (d) $C_6H_5-NO_2 \xrightarrow[Zn/NaOH]{10[H]} \underset{\text{Hydrazo benzene}}{C_6H_5NH-NHC_6H_5} + 4H_2O$

83. (a) $RCOCl + 2Me_2NH \rightarrow RCON\begin{matrix}\diagup Me\\ \diagdown Me\end{matrix} + Me_2 + \overset{+}{N}H_2Cl^-$

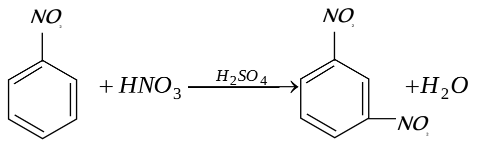
Me = Methyl.

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

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

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

89. (b)



m-dinitrobenzene

90. (b) $\underset{\substack{\text{(A)}\\ \text{Aniline}}}{C_6H_5NH_2} \xrightarrow[0^oC]{NaNO_2 + HCl} \underset{\text{(B)}}{C_6H_5N_2Cl} \xrightarrow{KCN} \underset{\text{(C)}}{C_6H_5CN}$

$$\downarrow H_3O$$

$$\underset{\text{(D)}}{C_6H_5COOH}$$

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

$CH_3NH_2 + COCl_2 \xrightarrow{-HCl} [CH_3NH-CO-Cl]$

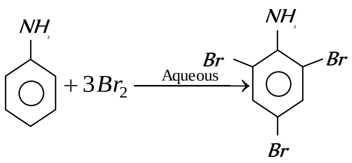
$\xrightarrow[-HCl]{\Delta} \underset{\text{methyl isocyanate}}{CH_3-N=C=O}$

92. (d) $R-NC + 2H_2O \rightarrow RNH_2 + HCOOH$.

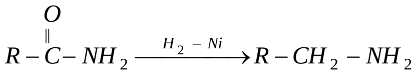
93. (d) $CH_3-NC + 2H_2O \rightarrow CH_3NH_2 + HCOOH$

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

99. (b)

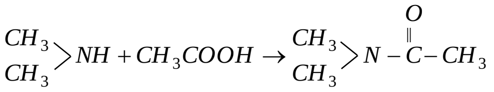


2, 4, 6 tribromo aniline

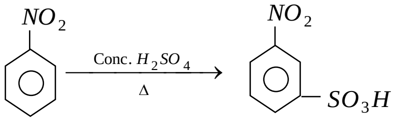
102. (a) 
$R-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow{H_2-Ni} R-CH_2-NH_2$

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

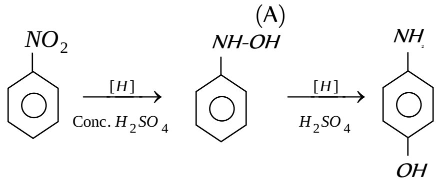
106. (a) $CH_3CH_2NH_2 + CH_3COCl \rightarrow \underset{N\ \text{Ethylacetanilide}}{CH_3CH_2NHCOCH_3} + HCl$

107. (a) 
$\begin{matrix}CH_3\\CH_3\end{matrix}\!>NH + CH_3COOH \rightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!>N-\overset{\overset{O}{\|}}{C}-CH_3$

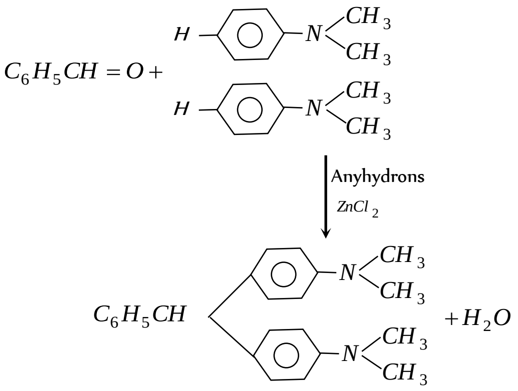
108. (d) Anilinium hydrogen chloride produces chloride ion which gives white precipitate with $AgNO_3$. In fact anilium chloride is a part of aniline.

109. (b) 

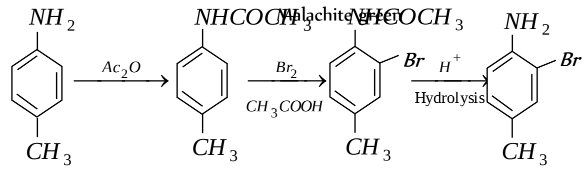
(A)

110. (c) 

Nitrobenzene
Phenyl hydroxyl amine
p-amino phenol

113. (c) 

Malachite green

115. (d) 

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

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

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

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

121. (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.

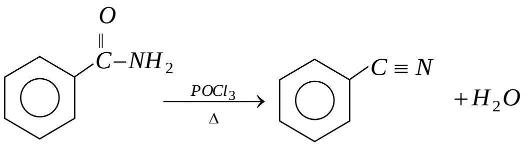
122. (d) Isocyanides on hydrolysis forms primary amines not ammonia

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

$\downarrow KOH$

$K_2CO_3 + C_6H_5NH_2 \xleftarrow{2KOH} C_6H_5NCO + KBr + H_2O$

$C_6H_5NH_2 + (CH_3CO)_2O \rightarrow \underset{\substack{\text{Acetanilide}\\ \text{(antipyretic)}}}{CH_3CONHC_6H_5} + CH_3COOH$

124. (d) 

Benzonitrile

125. (d) (i) 
$R\overset{\overset{O}{\|}}{C}NH_2 + Br_2 + KOH \rightarrow RCONHBr + KBr + H_2O$

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

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

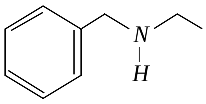
$RCONH_2 + Br_2 + 4KOH \rightarrow RNH_2 + 2KBr + K_2CO_3 + 2H_2O$

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

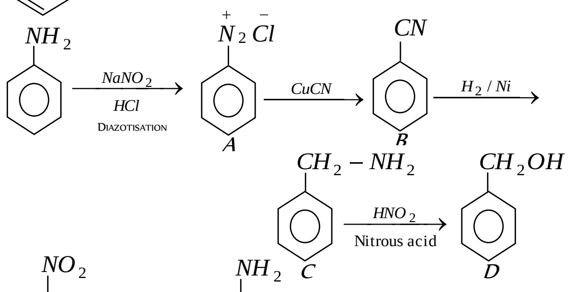
$$C_6H_5-NH_2 + O=CHC_6H_5 \xrightarrow[-H_2O]{\Delta} \underset{\text{Benzylidine aniline}}{C_6H_5N=CHC_6H_5}$$

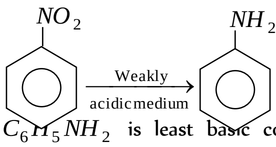
127. (d) $\underset{\text{Acetamide}}{CH_3CONH_2} + Br_2 + 4KOH \xrightarrow[-2H_2O]{}$

$$\underset{\text{(Methyl amine)}}{CH_3NH_2} + 2KBr + 2K_2CO_3$$

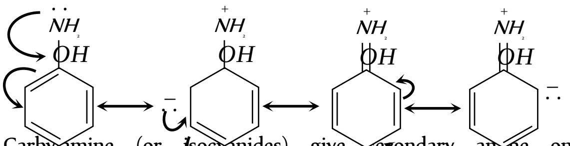
128. (b) 

is most basic

130. (d) 

131. (a) 

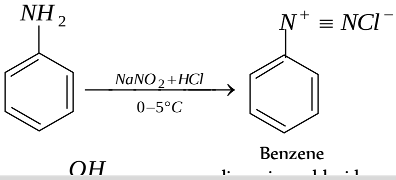
132. (d) $C_6H_5NH_2$ is least basic compound due to resonance by which the Lone pair of nitrogen takes part in resonance & due to unavailability of lone pair on *N* Aniline become less basic. The Lone pair of *N* is delocalized into benzene ring by resonance



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

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

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



Benzene

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

$\xrightarrow{Cu_2(CN)_2} \underset{(Y)}{C_6H_5CN} \xrightarrow{H_2O/H^+} \underset{\text{Benzoic acid}(Z)}{C_6H_5 - COOH}$

Thus product Z is identified as $C_6H_5 - COOH$

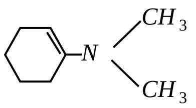
136. (c) This is Hofman-bromide reaction. In this reaction one carbon less amines are formed from amides.

$CH_3CONH_2 \xrightarrow{Br_2 / KOH} CH_3NH_2$

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

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

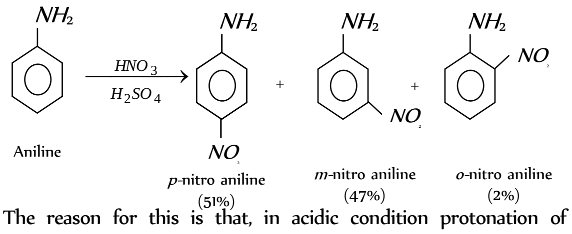
138. (b)



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

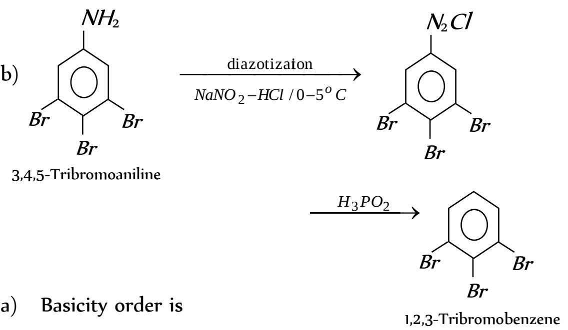
140. (c) Pollutants which are formed by reaction amongst the primary pollutants (persist in the environment in the form they are passed into it) are called as secondary pollutants. e.g. peroxyacyl nitrates (PAN) are formed through reaction between nitrogen oxides and hydrocarbons in the presence of sunlight.

141. (d)



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.

142. (b)



143. (a) Basicity order is

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

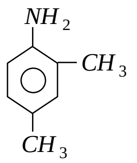
$(CH_3)_3N$ is less basic due to steric effect while $C_4H_5NH_2$ is less basic due to resonance.

Tests for Nitrogen Containing Compounds

1. (c) $\underset{\text{Acetamide}}{CH_3CONH_2} + Br_2 + 4NaOH \rightarrow$

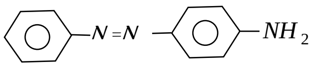
$\underset{\text{Methyl amine}}{CH_3NH_2} + Na_2CO_3 + 2NaBr + 2H_2O$

5. (b)



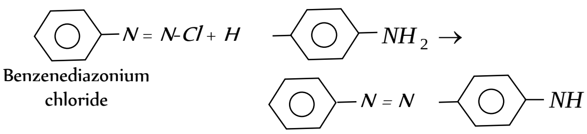
is a type of 1^o amine and hence gives +ve carbyl test

6. (a)



Orange Colour

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



p-amino azo benzene (yellow dye)

11. (a) $CHCl_3$ gives carbylamine test.

$RNH_2 + CHCl_3 + 3KOH(\text{alc.}) \xrightarrow{\Delta}$

$\underset{\text{alkylisocyanide}}{RN \rightleftharpoons C} + 3KCl + 3H_2O$

Critical Thinking Questions

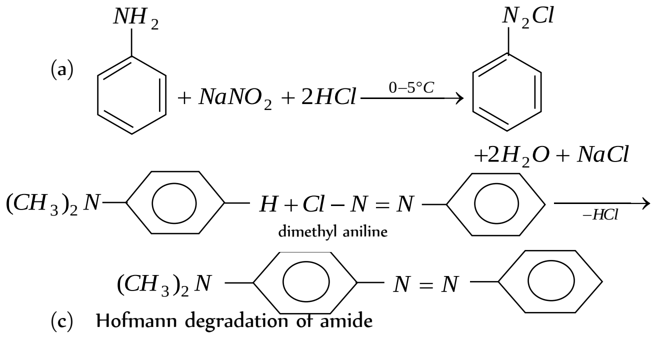
1. (c) $R_1 = H$ and $R_2 = R_3 = CH_3$

$$\begin{matrix} R_1 \\ R_2 \end{matrix}\!\!> N - R_3 = \begin{matrix} H \\ CH_3 \end{matrix}\!\!> N - CH_3$$

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

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

3. (a)

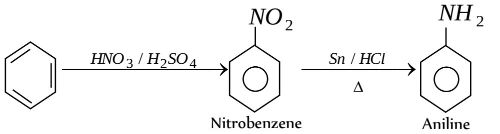


4. (c) Hofmann degradation of amide

$R - CoNH_2 + Br_2 + 4KOH \longrightarrow$

$\underset{\text{primary amine}}{R - NH_2} + 2KBr + K_2CO_3 + 2H_2O$

5. (b)

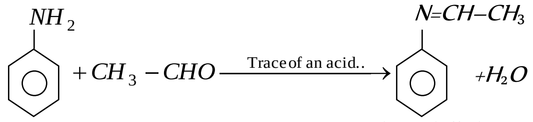


6. (b) The relative basic charecter of $1^o, 2^o$ and 3^o amines also depends upon the nature of the alkyl group.

R	Relative basic strength
$-CH_3$	$R_2NH > R-NH_2 > R_3N > NH_3$
$-C_2H_5$	$R_2NH > R-NH_2 > NH_3 > R_3N$
$-CHMe_2$	$R-NH_2 > NH_3 > R_2NH > R_3N$
$-CMe_3$	$NH_3 > R-NH_2 > R_2NH > R_3N$

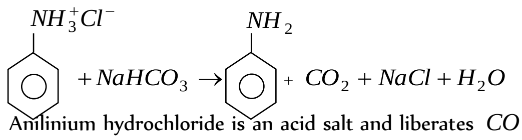
7. (b) The nitrogroup is very firmly linked to the benzene nucleus and does not undergo any displacement reaction. Nitro group deactivates the benzene nucleus.

8. (a)



Anil or Schiff's base

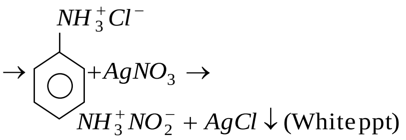
9. (bc) (1) With $NaHCO_3 \rightarrow$



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

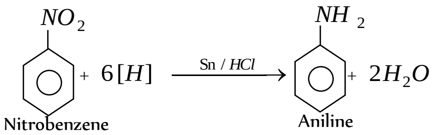
But p-chloro aniline is basic not acidic it does not liberate CO_2.

(2) With $AgNO_3 \rightarrow$



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

10. (a)



11. (a) $C_6H_5-NH_2 + CHCl_3 + 3KOH \rightarrow$

$$\underset{\text{Phenyl Isocyanide}}{C_6H_5NC} + 3KCl + 3H_2O$$

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

$K_b = 5.4\times10^{-4}$ $\quad 4.5\times10^{-4}$ $\quad 0.6\times10^{-4}$

13. (c) $(CH_3)_2NCOCH_3 + HCl/H_2O$

$$\downarrow$$

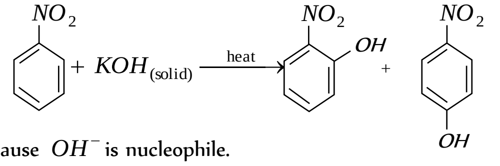
$$(CH_3)_2NH + CH_3COOH$$

14. (a) Order of basicity of amines

(i) $2^o > 1^o > 3^o$

(ii) $R_2NH > RNH_2 > ArCH_2-NH_2 > NH_3 > ArNH-R > ArNH_2 > ArNH-Ar$

15. (a)



Because OH^- is nucleophile.

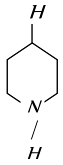
16. (c) $C_6H_5SO_2Cl + RNH_2 \rightarrow RNHSO_2C_6H_5 \xrightarrow{KOH}$

$$\underset{\text{soluble in } KOH}{RNKSO_2C_6H_5}$$

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

$$3NaCNS + FeCl_3 \rightarrow \underset{\substack{\text{Ferric sulpho cyanide}\\ \text{(Blood red colour)}}}{Fe(CNS)_3} + 3NaCl$$

18. (c)



does not have aromaticity by which the Lone pair of electron of Nitrogen does not delocalised in benzene ring so it will be strong base on other hand rest 3 have aromaticity *i.e.,* they follow the huckel rule so the electron pair of Nitrogen delocalised in ring by resonance & resulting they become less basic.

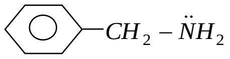
19. (d) Liebermann's Nitroso reaction.

20. (a) $\underset{\text{(Acetamide)}}{CH_3CONH_2} + Br_2 + 4KOH \xrightarrow[-2H_2O]{}$

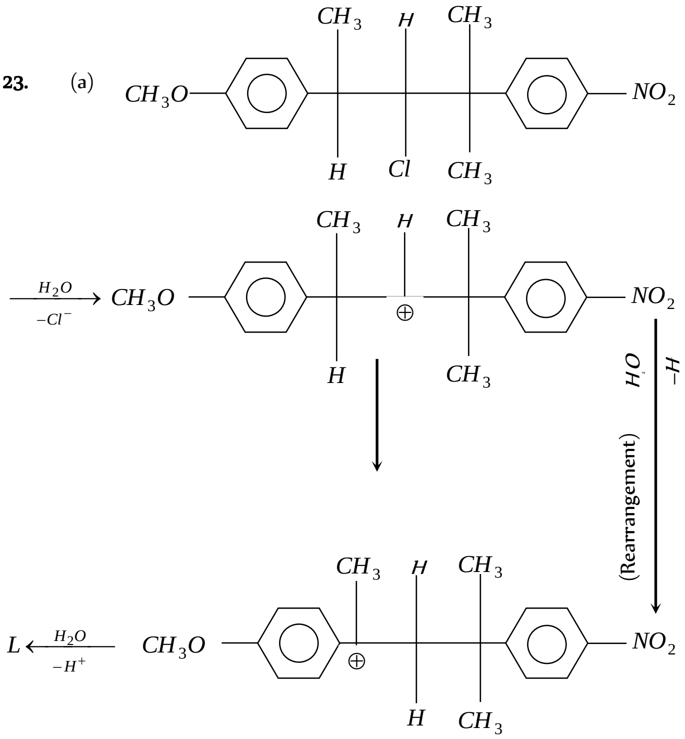
$$\underset{\text{(Methyl amine)}}{CH_3NH_2} + 2KBr + 2K_2CO_3$$

21. (c) The class of Indigo dye is Indigoid or vat dye. Indigo dyes are insoluble in water.

22. (d) Lone pair of $\ddot{N}$ are not taking part in conjugation whereas in other parts lone pairs are taking part in conjugation



23. (a)



Assertion and Reason

1. (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.

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

3. (b) The reason being that the terminal carbon atom in isocyanide has electron-deficient carbon having a sexlet of electrons and hence undergoes addition reactions with ozone.

4. (d) When primary amines are heated with chloroform in the presence of alcoholic *KOH*, isocyanides are formed. This reaction is known as carbylamine reaction. eg. ethyl amine gives ethyl isocyanide on treatment with $CHCl_3$ and alcoholic *KOH*.

$$\underset{\text{Ethylamine}}{C_2H_5 - NH_2} + \underset{\text{Chloroform}}{CHCl_3} + 3KOH(\text{alc}) \xrightarrow{\Delta}$$

$$C_2H_5 - N \overset{\rightarrow}{=} C + 3KCl + 3H_2O$$

5. (b) Nucleophilic species which have more than one site of reaction are called ambident nucleophiles.

$$:\overline{C} = N: \leftrightarrow :C = \overline{N}:$$

6. (c) $-SO_3H$ group being more acidic than $-CO_2H$ group can easily transfer a proton to the amino group.

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

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

9. (c) Reaction can be used to prepare 1°, 2°, 3° amines and finally quarternary ammonium salts.

10. (b) Nitroarene cannot be distilled under normal atmospheric pressure. This is because either they decompose or they explode on strong heating.

11. (c) Only 1° amines undergo Hofmann bromamide reaction. Since $CH_3CONHCH_3$ is a 2° amine therefore, it does not undergo Hofmann bromamide reaction.

12. (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.

13. (e) Ammonia is more basic than water. It is because nitrogen being less electronegative than oxygen has a greater tendency to donate electrons.

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

15. (a) $RNH_2 + CHCl_3 + 3KOH(alc) \rightarrow R-N \overset{\rightarrow}{=} C + 3KCl + 3H_2O$

17. (d) *p*-Anisidine is a stronger base than aniline.

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

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

20. (d) The nitro group strongly deactivates the benzene ring towards electrophilic substitution.

Nitrobenzene does not undergo Friedel-Craft acylation reaction.

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

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

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