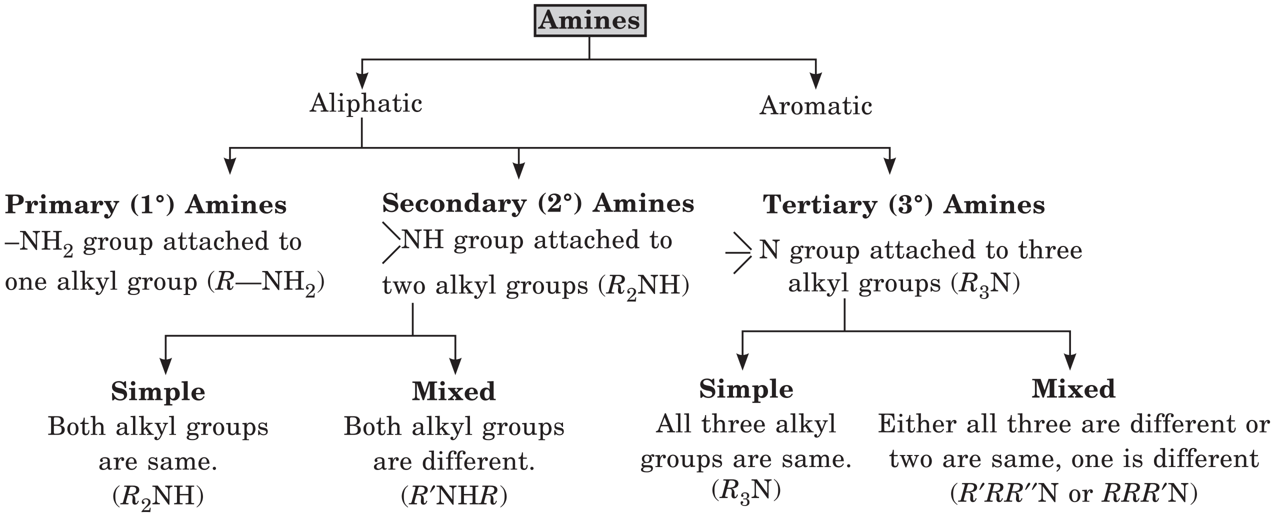
Amines

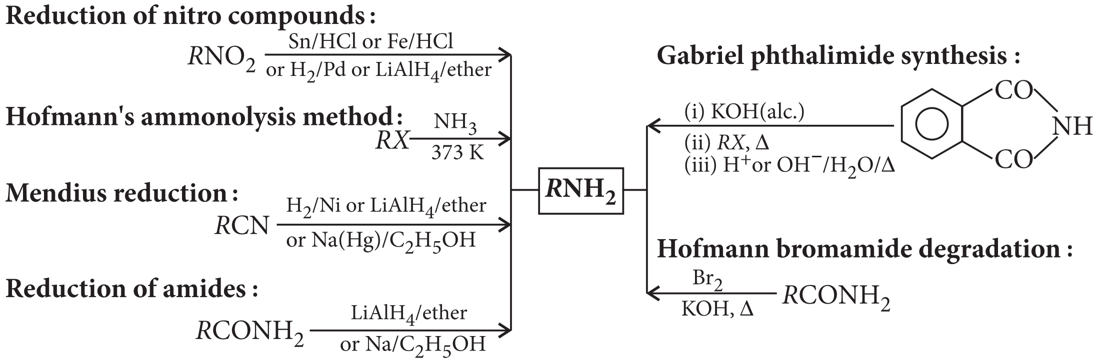
Recap Notes

AMINES

- **Amines :** These are alkyl or aryl derivatives of ammonia and are obtained by replacing one, two or three hydrogen atoms by alkyl/aryl groups.
- **Nomenclature :** In common system, an aliphatic amine is named by prefixing alkyl group to amine, *i.e.*, *alkylamine*. In IUPAC system, amines are named as *alkanamines*. In secondary and tertiary amines, when two or more groups are the same, the prefix *di* or *tri* is appended before the name of alkyl group.
- **Structure :** Nitrogen orbitals in amines are sp^3-hybridised and the geometry of amines is pyramidal. Due to the presence of unshared pair of electrons, the angle C—N—E, (where E is C or H) is less than 109.5 .
- **Classification :**



- **Preparation :**



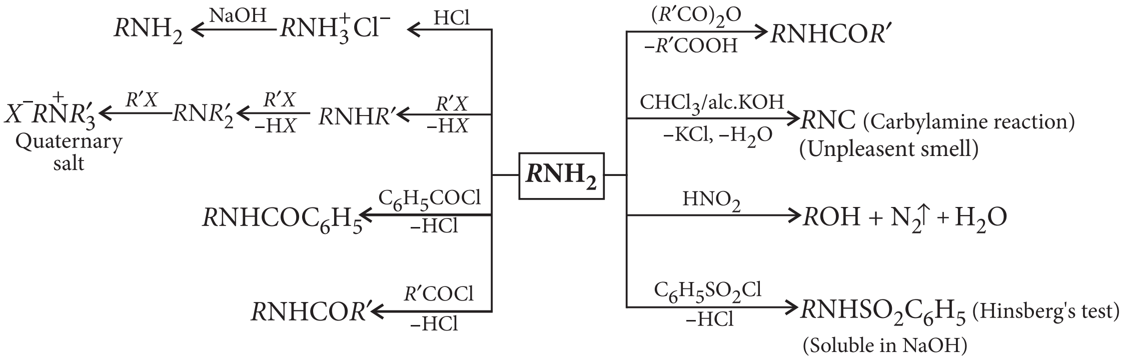
- **Limitations of Gabriel phthalimide synthesis :**
  - It is used for the preparation of only 1° amines. *tert*-Butylamine is a 1° amine, but cannot be prepared by this method. In this case, elimination takes place.
  - Aromatic amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution reaction with potassium phthalimide under mild conditions.

- **Physical properties :**
  - Lower amines are gases and liquids but higher amines are solids.
  - Primary and secondary amines have higher boiling points than other organic compounds due to hydrogen bonding.
  - Primary and secondary amines are soluble in water due to hydrogen bonding between $>NH_2$ and H_2O molecules.

- **Chemical properties :**
  - **Basic character of amines :**
    - Amines are basic in nature due to the presence of lone pair of electrons on nitrogen atom.
    - Aliphatic amines are stronger bases than ammonia due to *+I* effect of alkyl groups present in amines.
    - Aromatic amines are weaker bases than ammonia due to *–I* effect of aryl group.
    - Beside inductive effect, there are other effects like steric effect, solvation effect, resonance effect which affect the basic strength of amines.
    - In gaseous phase, the order of basicity of amines is 3° amine > 2° amine > 1° amine > NH_3.
    - In aqueous phase, despite of inductive effect, solvation effect and steric hindrance also play an important role. Thus, the order of basicity of amines is

$(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$ and $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

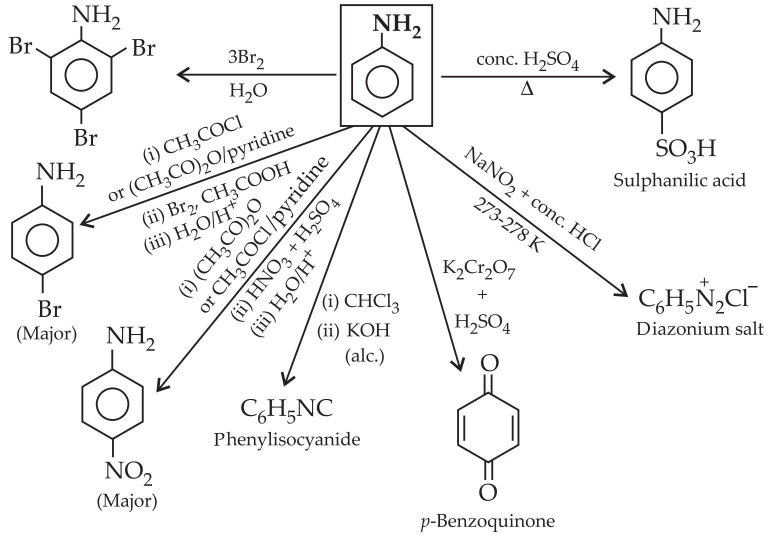
- **Chemical reactions :**



- **Identification of primary, secondary and tertiary amines :**

	Test	Primary amine	Secondary amine	Tertiary amine
1.	Reaction with nitrous acid.	Gives alcohol with effervescence of N_2 gas.	Gives oily nitrosoamine which gives Liebermann's nitrosoamine test.	Forms nitrite in cold which is soluble in water and on heating gives nitrosoamine.
2.	Reaction with benzene sulphonyl chloride (*Hinsberg's reagent*)	Gives *N*-alkylbenzene sulphonamide which is soluble in alkali.	Gives *N*, *N*-dialkylbenzene sulphonamide which is insoluble in alkali.	No reaction
3.	*Carbylamine test* : Reaction with chloroform and alcoholic KOH	Forms carbylamine or isocyanide (*R*NC) with characteristic unpleasant odour.	No reaction	No reaction

- **Electrophilic substitution reactions of arylamines :** Aniline undergoes electrophilic substitution reactions. $-NH_2$ group is *ortho*- and *para*-directing and a powerful activating group.



Practice Time

OBJECTIVE TYPE QUESTIONS

Multiple Choice Questions (MCQs)

1. Identify X, Y and Z in the given reaction :

$CH_2{=}CH_2 \xrightarrow[CCl_4]{Br_2} X \xrightarrow{NaCN} Y \xrightarrow{LiAlH_4} Z$

	X	Y	Z
(a)	$CH_2Br–CH_2Br$	$CH_3CH_2CH_2CN$	$CH_3CH_2CH_2CH_2NH_2$
(b)	$CH_2Br–CH_2Br$	CH_3CH_2CN	$CH_3CH_2CH_2NH_2$
(c)	CH_3CH_2Br	CH_3CH_2CN	$CH_3CH_2CH_2NH_2$
(d)	$CH_2Br–CH_2Br$	$NCCH_2CH_2CN$	$H_2NCH_2CH_2CH_2CH_2NH_2$

2. Benzoic acid is treated with $SOCl_2$ and the product (X) formed is reacted with ammonia to give (Y). (Y) on reaction with Br_2 and KOH gives (Z). (Z) in the reaction is

(a) aniline
(b) chlorobenzene
(c) benzamide
(d) benzoyl chloride.

3. Amongst the given set of reactants, the most appropriate for preparing 2° amine is

(a) 2° R—Br + NH_3
(b) 2° R—Br + NaCN followed by H_2/Pt
(c) 1° R—NH_2 + RCHO followed by H_2/Pt
(d) 1° R—Br (2 moles) + potassium phthalimide followed by H_3O^+/heat.

4. Which of the following can exist as zwitter ion?

(a) p-Aminoacetophenone
(b) Sulphanilic acid
(c) p-Nitroaminobenzene
(d) p-Methoxyphenol

5. Which of the following amines will give carbylamine reaction?

(a) $(C_2H_5)_3N$
(b) $(C_2H_5)_2NH$
(c) $C_2H_5NH_2$
(d) $C_3H_7NHC_2H_5$

6. Among the compounds: $C_3H_7NH_2$, CH_3NH_2, $C_2H_5NH_2$ and $C_6H_5NH_2$. Which is the least basic compound?

(a) CH_3NH_2
(b) $C_2H_5NH_2$
(c) $C_3H_7NH_2$
(d) $C_6H_5NH_2$

7. The correct order of boiling points of the following isomeric amines is

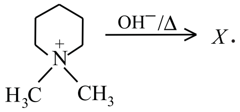
$C_4H_9NH_2$, $(C_2H_5)_2NH$, $C_2H_5N(CH_3)_2$

(a) $C_2H_5N(CH_3)_2 > (C_2H_5)_2NH > C_4H_9NH_2$
(b) $(C_2H_5)_2NH > C_2H_5N(CH_3)_2 > C_4H_9NH_2$
(c) $C_4H_9NH_2 > (C_2H_5)_2NH > C_2H_5N(CH_3)_2$
(d) $(C_2H_5)_2NH > C_4H_9NH_2 > C_2H_5N(CH_3)_2$

8. Tertiary amines have lowest boiling points amongst isomeric amines because

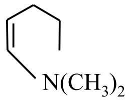
(a) they have highest molecular mass
(b) they do not form hydrogen bonds
(c) they are more polar in nature
(d) they are most basic in nature.

9. In the following reaction,



The organic product X has the structure

(a)


(b)


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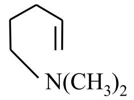

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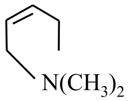


10. Amides may be converted into amines by a reaction named after

(a) Hoffmann
(b) Claisen
(c) Perkin
(d) Kekule.

11. The reaction of benzenesulphonyl chloride with ethylamine yields

(a) N-ethylbenzenesulphonamide, insoluble in alkali
(b) N, N-diethylbenzenesulphonamide, soluble in alkali
(c) N, N-diethylbenzenesulphonamide, insoluble in alkali
(d) N-ethylbenzenesulphonamide, soluble in alkali.

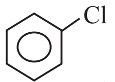
12. Basic strength of different alkyl amines depends upon

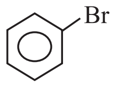
(a) $+I$ effect
(b) steric effect
(c) solvation effect
(d) all of these.

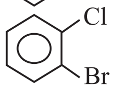
13. Which of the following amides will give ethylamine on reaction with sodium hypobromite?

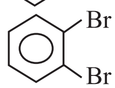
(a) Butanamide
(b) Propanamide
(c) Acetamide
(d) Benzamide

14. *o*-Chloroaniline is treated with a mixture of $NaNO_2$ and HCl and the product is reacted with cuprous bromide. The final product in the reaction will be

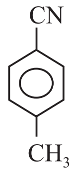
(a) 

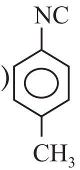
(b) 

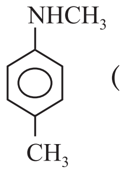
(c) 

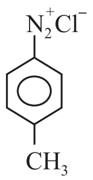
(d) 

15. When *p*-toluidine reacts with chloroform and alcoholic KOH, then the product is

(a) 

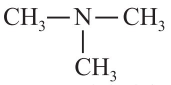
(b) 

(c) 

(d) 

16. Acetylation of a secondary amine in alkaline medium yields
(a) *N*, *N*-dialkyl acetamide
(b) *N*, *N*-dialkyl amine
(c) *N*, *N*-dialkyl amide
(d) acetyl dialkyl amine.

17. Amino group is *o, p*-directing for electrophilic substitution reaction. But, on nitration the major product is *m*-nitroaniline because
(a) aniline gets protonated with strong acids to give anilinium ion which is *m*-directing
(b) nitration requires nitric acid which oxidises $-NH_2$ to $-NO_2$ group
(c) electrophile NO_2^+ is a *m*-directing group
(d) benzene ring exerts $+I$ effect and deactivates the ring.

18. Which of the following is amphoteric in nature?
(a) CH_3NH_2 (b) CH_3NHCH_3
(c) CH_3CONH_2 (d) 
$CH_3-\underset{\underset{CH_3}{|}}{N}-CH_3$

19. The shape of $(CH_3)_3N$ is pyramidal because
(a) nitrogen forms three sp^3 hybridised sigma bonds with carbon atoms of methyl groups and there is one non-bonding electron pair
(b) nitrogen forms three sp^2 hybridised sigma bonds with carbon atoms of methyl groups and fourth orbital forms pi bond
(c) nitrogen has five valencies which are arranged in pyramidal shape.
(d) the unpaired electron present on nitrogen is delocalised.

20. Which of the following compounds will show Hoffmann bromamide degradation reaction?
(a) $C_6H_5NO_2$ (b) $C_6H_5CH_2NH_2$
(c) $C_6H_5CONH_2$ (d) $C_6H_5NHCH_3$

21. Which of the following statements is not true?
(a) In aqueous solution $(CH_3)_2NH$ is a stronger base than $(CH_3)_3N$.
(b) Secondary amines show carbylamine reaction.
(c) Nitrogen gas is evolved when ethylamine is treated with nitrous acid.
(d) Secondary amines can show metamerism.

22. Reduction of aromatic nitro compounds using Sn and HCl gives
(a) aromatic primary amines
(b) aromatic secondary amines
(c) aromatic tertiary amines
(d) aromatic amides.

23. Arrange the following compounds in increasing order of basicity : CH_3NH_2, $(CH_3)_2NH$, NH_3, $C_6H_5NH_2$
(a) $C_6H_5NH_2 < NH_3 < (CH_3)_2NH < CH_3NH_2$
(b) $CH_3NH_2 < (CH_3)_2NH < NH_3 < C_6H_5NH_2$
(c) $C_6H_5NH_2 < NH_3 < CH_3NH_2 < (CH_3)_2NH$
(d) $(CH_3)_2NH < CH_3NH_2 < NH_3 < C_6H_5NH_2$

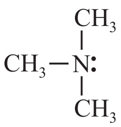
24. Primary amines react with benzoyl chloride to give
(a) benzamides (b) ethanamides
(c) imides (d) imines.

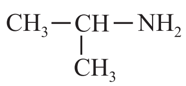
25. $CH_3CH_2Cl \xrightarrow{NaCN} X \xrightarrow{Ni/H_2} Y \xrightarrow[\text{anhydride}]{\text{Acetic}} Z$

Z in the above reaction is
(a) $CH_3CH_2CH_2NHCOCH_3$
(b) $CH_3CH_2CH_2NH_2$
(c) $CH_3CH_2CH_2CONHCH_3$
(d) $CH_3CH_2CH_2CONHCOCH_3$

26. Anilinium hydrogensulphate on heating with sulphuric acid at 453-473 K produces
(a) sulphanilic acid
(b) benzenesulphonic acid
(c) aniline
(d) anthranilic acid.

27. A compound *(X)* with molecular formula C_3H_9N reacts with $C_6H_5SO_2Cl$ to give a solid which is insoluble in alkali. *(X)* is

(a) $CH_3CH_2CH_2NH_2$ (b) 
$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N}}:$

(c) $CH_3-NH-CH_2CH_3$ (d) 
$CH_3-\underset{\underset{CH_3}{|}}{CH}-NH_2$

28. Electrophilic substitution of aniline with bromine- water at room temperature gives

(a) 2-bromoaniline
(b) 3-bromoaniline
(c) 2, 4, 6-tribromoaniline
(d) 3, 5, 6-tribromoaniline.

29. The decreasing order of boiling points of ethyldimethylamine, *n*-butylamine and diethylamine is

n-Butylamine > Diethylamine > Ethyldimethylamine.

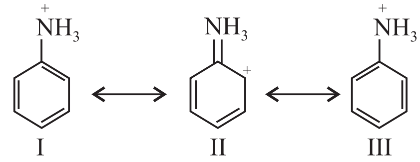
This trend of boiling point can be explained as

(a) boiling point increases with increase in molecular mass
(b) tertiary amines have highest boiling point due to highest basicity
(c) intermolecular hydrogen bonding is maximum in primary amines and absent in tertiary amines
(d) intramolecular hydrogen bonding is present in tertiary amines.

30. Which of the following is used as Hinsberg's reagent?

(a) $C_6H_5SO_2Cl$ (b) $C_6H_5SO_3H$
(c) $C_6H_5NHCH_3$ (d) $C_6H_5COCH_3$

31. Canonical structures of anilinium ion obtained by accepting a proton are given below. Choose the correct statements.



(a) Anilinium ion has two stable canonical structures I and III.
(b) II is not an acceptable structure because carbonium ion is less stable.
(c) Only I and III are acceptable aromatic canonical structures since II is non-aromatic.
(d) Anilinium ion has three stable canonical structures I, II and III.

32. Which of the following gas evolved when methylamine reacts with nitrous acid?

(a) CH_4 (b) Cl_2 (c) N_2 (d) H_2

33. What is obtained when benzoyl chloride reacts with aniline in the presence of sodium hydroxide?

(a) Benzoic acid (b) Benzanilide
(c) Acetanilide (d) Azobenzene

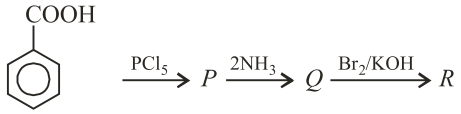
34. Aniline can be converted into benzylamine by which of the following processes in sequence?

(a) $NaNO_2$ + HCl, CuCN, H_2/Ni
(b) Br_2/CCl_4, KCN, $LiAlH_4$
(c) HNO_2, $K_2Cr_2O_7/H^+$, Sn + HCl
(d) CH_3OH, $KMnO_4$, OH^-, H_3^+O

35. For a nitration of aniline, which of the following steps is followed?

(a) Direct nitration using nitrating mixture (conc. HNO_3 + conc. H_2SO_4) followed by oxidation.
(b) Using fuming HNO_3 carrying out reaction at 273 K followed by hydrolysis.
(c) Using $NaNO_2$ and HCl followed by reaction with conc. HNO_3 followed by hydrolysis.
(d) Acetylation followed by nitration and hydrolysis.

36. What is the end product in the following sequence of reactions?



(a) Aniline (b) Phenol
(c) Benzene
(d) Benzenediazonium chloride

37. Which of the following has highest pK_b value?

(a) $(CH_3)_3CNH_2$ (b) NH_3
(c) $(CH_3)_2NH$ (d) CH_3NH_2

38. Which of the following reactions is not correctly matched?

(a) Reaction used to convert amide into primary amine with one carbon atom less – Hoffmann bromamide reaction
(b) Reaction used to convert primary amines into isocyanides – Carbylamine reaction
(c) Reaction used to distinguish primary, secondary and tertiary amines – Hinsberg's reaction
(d) Preparation of primary amines using phthalimide – Victor Meyer's synthesis

39. Which of the following compounds cannot be identified by carbylamine test?

(a) $CH_3CH_2NH_2$ (b) $(CH_3)_2CHNH_2$
(c) $C_6H_5NH_2$ (d) $C_6H_5NHC_6H_5$

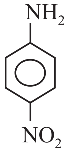
40. When excess of ethyl iodide is treated with ammonia, the product is

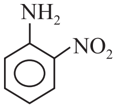
(a) ethylamine (b) diethylamine
(c) triethylamine
(d) tetraethylammonium iodide.

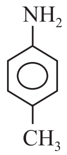
41. The amines are basic in nature, hence they form salts with hydrochloric acid. Which of the following will be insoluble in dil. HCl?

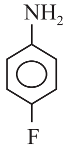
(a) $C_6H_5NH_2$ (b) $(C_6H_5)_3N$
(c) $C_2H_5NH_2$ (d) CH_3NHCH_3

42. The most basic amine among the following is

(a) 

(b) 

(c) 

(d) 

43. The end product Z of the reaction is

$$\text{Ethylamine} \xrightarrow{HNO_2} X \xrightarrow{PCl_5} Y \xrightarrow{KCN} Z$$

(a) propanenitrile (b) triethylamine
(c) diethylamine (d) propylamine.

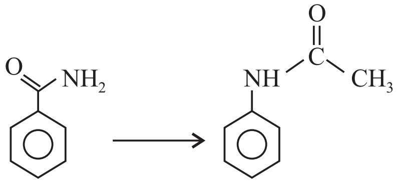
44. Secondary amines can be prepared by

(a) reduction of nitro compounds
(b) reduction of amides
(c) reduction of isonitriles
(d) reduction of nitriles.

45. Which of the following amines does not react with Hinsberg reagent?

(a) $CH_3CH_2—NH_2$ (b) $CH_3—NH—CH_3$
(c) $(CH_3CH_2)_3N$ (d) All of these

46. The reagent required to convert



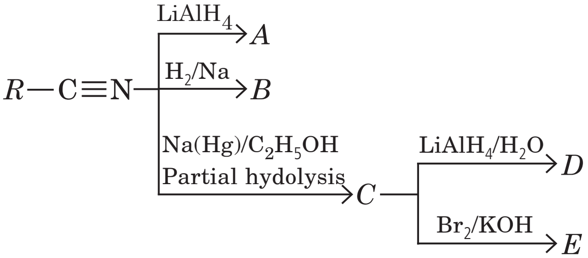
is

(a) KOH/Br_2, $LiAlH_4$ (b) $KOH/Br_2, CH_3COCl$
(c) HNO_2, $(CH_3CO)_2O$
(d) KOH/Br_2, CH_3OH/Na

47. Primary and secondary amines react with acid chloride or acid anhydride to form

(a) tertiaryamonium salts
(b) substituted amides
(c) diazonium salts
(d) nitro compounds

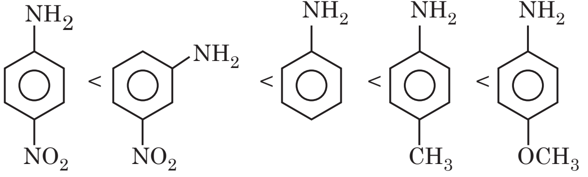
48. Read the given map carefully :



The correct statement about these products are

(a) A and B are chain isomers
(b) B and D are position isomers
(c) B and C are functional isomers
(d) D and E are members of same homologous series.

49. A basicity order is given below :



(5) (4) (3) (2) (1)

Which of the following cannot be predicted by the given order?

(a) $+R$ effect is more powerful than $+I$ effect.
(b) At m-position only $–I$ effect is applicable not R effect
(c) Electron donating groups increase the basicity of aniline.
(d) In (4), $–NO_2$ is showing $–R$ effect.

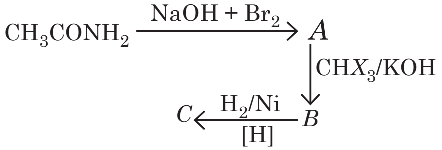
50. Science teacher Sunaina ask class – 12 students to write a sequence of two reactions for converting n-propylbromide to methyl propyl amine.

Four students written 4 different paths shown in all options, then which one is correct ?

(a) $\xrightarrow{KCN} \xrightarrow[H_2/Ni]{[H]}$ (b) $\xrightarrow{KCN} \xrightarrow{H_3O^+}$
(c) $\xrightarrow{AgCN} \xrightarrow[H_2/Ni]{[H]}$ (d) $\xrightarrow{AgCN} \xrightarrow{H_3O^+}$

51. In chemistry class various reactions of nitrogen containing compounds were taught, like preparation of amines and chemical reactions of amines.

Few reactions are shown here :



A and C can be differentiated by

(a) reaction with $C_6H_5SO_2Cl$
(b) treatment with diethyl oxalate
(c) both (a) and (b)
(d) A and C cannot be differenced as both are same.

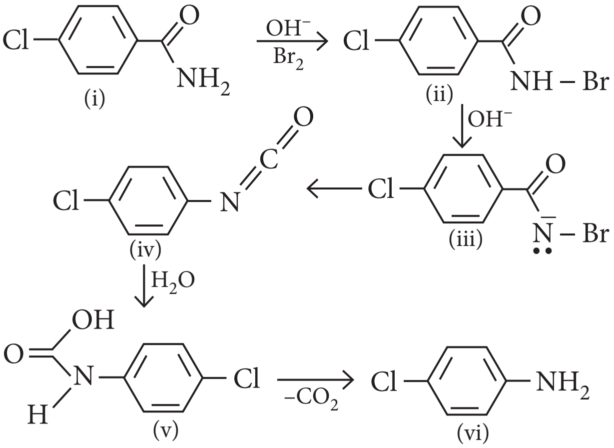
52. The correct order of basicity of the following amine in aqueous solution is

(a) $NH_3 < CH_3NH_2 < (CH_3)_2NH < (CH_3)_3N$
(b) $NH_3 < (CH_3)_2NH < CH_3NH_2 < (CH_3)_3N$
(c) $NH_3 < (CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$
(d) $NH_3 < CH_3NH_2 < (CH_3)_3N < (CH_3)_2N$

Case Based MCQs

Case I : Read the passage given below and answer the following questions from 53 to 56.

$RCONH_2$ is converted into RNH_2 by means of Hoffmann bromamide degradation. During the reaction amide is treated with Br_2 and alkali to get amine. This reaction is used to descend the series in which carbon atom is removed as carbonate ion (CO_3^{2-}). Hoffmann bromide degradation reaction can be written as :



53. Hoffmann bromamide degradation is used for the preparation of

(a) primary amines (b) secondary amines

(c) tertiary amines

(d) secondary aromatic amines.

54. Which is the rate determining step in Hoffmann bromamide degradation?

(a) Formation of (i) (b) Formation of (ii)

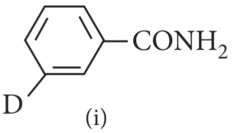
(c) Formation of (iii) (d) Formation of (iv)

55. Which of the following is used for the conversion of (i) to (ii)?

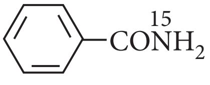
(a) KBr (b) KBr + CH_3ONa

(c) KBr + KOH (d) Br_2 + KOH

56. What are the constituent amines formed when the mixture of (i) and (ii) undergoes Hoffmann bromamide degradation?

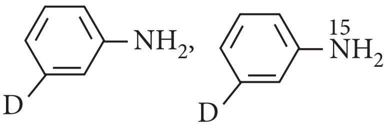


(i)

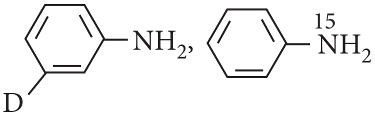


(ii)

(a)



(b)



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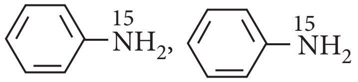
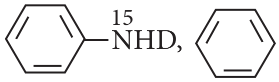


(d)



Case II : Read the passage given below and answer the following questions from 57 to 60.

The amines are basic in nature due to the presence of a lone pair of electron on N-atom of the $-NH_2$ group, which it can donate to electron deficient compounds. Aliphatic amines are stronger bases than NH_3 because of the $+I$ effect of the alkyl groups. Greater the number of alkyl groups attached to N-atom, higher is the electron density on it and more will be the basicity. Thus, the order of basic nature of amines is expected to be 3° > 2° > 1°, however the observed order is 2° > 1° > 3°. This is explained on the basis of crowding on N-atom of the amine by alkyl groups which hinders the approach and bonding by a proton, consequently, the electron pair which is present on N is unavailable for donation and hence 3° amines are the weakest bases.

Aromatic amines are weaker bases than ammonia and aliphatic amines. Electron-donating groups such as $-CH_3$, $-OCH_3$, etc. increase the basicity while electron-withdrawing substitutes such as $-NO_2$, –CN, halogens, etc. decrease the basicity of amines. The effect of these substituents is more at *p* than at *m*-positions.

57. Which one of the following is the strongest base in aqueous solution?

(a) Methyl amine

(b) Trimethyl amine

(c) Aniline

(d) Dimethyl amine

58. Which of the following order of basicity is correct?

(a) Aniline > *m*-toluidine > *o*-toluidine

(b) Aniline > *o*-toluidine > *m*-toluidine

(c) *o*-Toluidine > aniline > *m*-toluidine

(d) *o*-Toluidine < aniline < *m*-toluidine

59. What is the decreasing order of basicity of primary, secondary and tertiary ethylamines and NH_3?

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

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

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

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

60. The order of basic strength among the following amines in benzene solution is

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

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

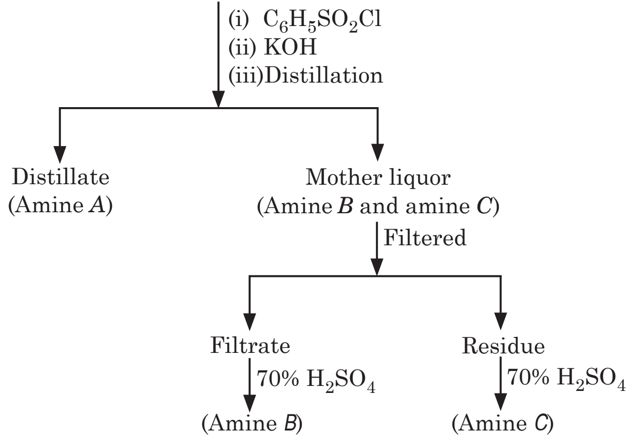
(c) $CH_3NH_2 > (CH_3)_2NH > (CH_3)_3N$

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

Case III : Read the passage given below and answer the following questions from 61 to 61.

When the mixture contains the three amine salts (1°, 2° and 3°) along with quaternary salt, it is distilled with KOH solution. The three amines distill, leaving the quaternary salt unchanged in the solution. Then the mixture of amines is separated by fractional distillation, Hinsberg's method and Hoffmann's method.

(1°, 2° and 3° amines in mixture)



61. Hinsberg reagent is

(a) aliphatic sulphonyl chloride

(b) phthalamide

(c) aromatic sulphonyl chloride

(d) anhydrous $ZnCl_2$ + conc. HCl.

62. Primary amine with Hinsberg's reagent forms

(a) *N*-alkyl benzene sulphonamide soluble in KOH solution

(b) *N*-alkyl benzene sulphonamide insoluble in KOH solution

(c) *N*,*N*-dialkyl benzene sulphonamide soluble in KOH solution

(d) *N*,*N*-dialkyl benzene sulphonamide insoluble in KOH solution.

63. To separate amines in a mixture, Hoffmann's method is used. The Hoffmann's reagent is

(a) benzenesulphonyl chloride

(b) diethyl oxalate

(c) benzeneisocyanide

(d) *p*-toulenesulphonic acid.

64. 3° amines with Hinsberg's reagent give

(a) no reaction

(b) product which is same as that of 1° amine

(c) product which is same as that of 2° amine

(d) products which is a quaternary salt.

Case IV : Read the passage given below and answer the following questions from 65 to 68.

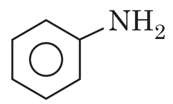
Amines are basic in nature. The basic strength of amines can be expressed by their dissociation constant, K_b or pK_b.

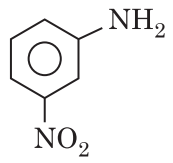
$$RNH_2 + H_2O \rightleftharpoons RNH_3^+ + OH^-$$

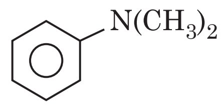
$$K_b = \frac{[RNH_3^+][OH^-]}{[RNH_2]} \text{ and } pK_b = -\log K_b$$

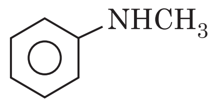
Greater the K_b value or smaller the pK_b value, more is the basic strength of amine. Aryl amines such as aniline are less basic than aliphatic amines due to the involvement of lone pair of electrons on N-atom with the resonance in benzene. In derivatives of aniline, the electron releasing groups increase the basic strength while electron withdrawing groups decrease the basic strength. The base weakening effect of electron withdrawing group and base strengthening effect of electron releasing group is more marked at *p*-position than at *m*-position. *o*-Substituted aniline is less basic than aniline due to ortho effect and is probable due to combination of electronic and steric effect.

65. Which of the following has lowest pK_b value?

(a) 

(b) 

(c) 

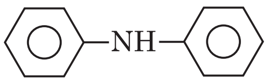
(d) 

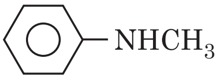
66. The strongest base among the following is

(a) $C_6H_5NH_2$ (b) p-$NO_2 - C_6H_4NH_2$

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

67. Which among the following shoes maximum pK_b value ?

(a) 

(b) 

(c) $(CH_3CH_2)_2NH$ (d) $(CH_3)_2NH$

68. Which of the following statements is not correct?

(a) Methylamine is more basic than NH_3.

(b) Primary amines form hydrogen bonds.

(c) Ethylamine has higher boiling point than propane.

(d) Dimethylamine is less basic than methylamine.

Assertion & Reasoning Based MCQs

For question numbers 69-80, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

(c) Assertion is correct statement but reason is wrong statement.

(d) Assertion is wrong statement but reason is correct statement.

69. Assertion : *Ortho* substituted anilines are usually weaker bases than anilines.
Reason : This is due to *ortho* effect.

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

71. Assertion : In strongly acidic solutions, aniline becomes more reactive towards electrophilic reagents.
Reason : The amino group being completely protonated in strongly acidic solution, the lone pair of electrons on the nitrogen is no longer available for resonance.

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

73. 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 for boron in BF_3.

74. Assertion : Aniline is a weaker base than cyclohexylamine.
Reason : Aniline undergoes halogenation even in the absence of a catalyst.

75. Assertion : Controlled nitration of aniline at low temperature mainly gives m-nitroaniline.
Reason : In acidic medium, $-NH_2$ group gets converted into m-directing group.

76. Assertion : Ammonolysis of alkyl halides involves the reaction between alkyl halides and alcoholic ammonia.
Reason : Reaction can be used to prepare 1°, 2°, 3° amines and finally quaternary ammonium salts.

77. Assertion : Aniline does not undergo Friedel-Crafts reaction.
Reason : $-NH_2$ group of aniline reacts with $AlCl_3$.

78. Assertion : Boiling point of amines are lower than those of alcohols and carboxylic acids.
Reason : Amines are much more soluble in water than less polar solvents like alcohol, ether, etc.

79. Assertion : Nitration of aniline can be done conveniently by protecting the amino group by acetylation.
Reason : Acetylation increases the electron density in the benzene ring.

80. Assertion : Aniline hydrogen sulphate, on heating, forms p-aminosulphonic acid.
Reason : The sulphonic acid group is electron-withdrawing.

SUBJECTIVE TYPE QUESTIONS

Very Short Answer Type Questions (VSA)

1. Write chemical equations for the following conversion :
Benzyl chloride to 2-phenylethanamine.

2. What carbylamine reaction ?

3. Rearrange the following in an increasing order of their basic strengths :
$C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_6H_5)_2NH$ and CH_3NH_2

4. Write IUPAC name of the following compound: $(CH_3CH_2)_2NCH_3$

5. Propanamine and *N*, *N*-dimethylmethanamine contain the same number of carbon atoms, even though propanamine has higher boiling point than *N*, *N*-dimethylmethanamine. Why?

6. Arrange the following compounds in increasing order of solubility in water :
$C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_2H_5NH_2$

7. Write the structure for *N*-ethylmethylamine.

8. How will you convert the following :
Aniline into *N*-phenylethanamide
(Write the chemical equations involved.)

9. Why primary aromatic amines cannot be prepared by Gabriel phthalimide synthesis?

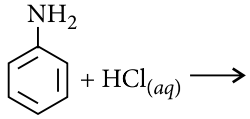
10. Draw the structure of *N*, *N*-diethylethanamine.

Short Answer Type Questions (SA-I)

11. How are the following conversions carried out?
(i) CH_3CH_2Cl to $CH_3CH_2CH_2NH_2$
(ii) Benzene to aniline

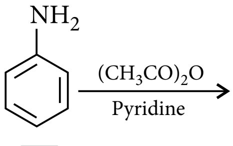
12. Account for the following :
(i) Tertiary amines do not undergo acylation reaction.
(ii) Amines are more basic than comparable alcohols.

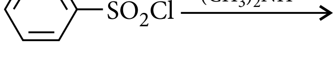
13. Complete the following reactions :
(i) $CH_3CH_2NH_2 + CHCl_3 + \text{alc. KOH} \xrightarrow{\text{Heat}}$

(ii) 

14. Acetamide is less basic than ethanamine. Why?

15. Write the structures of the main products of the following reactions :

(i) 

(ii) 

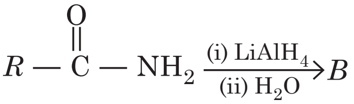
16. Give the structures of *A*, *B* and *C* in the following reactions :
(i) $C_6H_5NO_2 \xrightarrow{Sn + HCl} A \xrightarrow[273\text{ K}]{NaNO_2 + HCl} B \xrightarrow{H_2O} C$
(ii) $CH_3CN \xrightarrow{H_2O/H^+} A \xrightarrow[\Delta]{NH_3} B \xrightarrow{Br_2 + KOH} C$

17. Give the chemical tests to distinguish between the following pairs of compounds :
(i) Methylamine and dimethylamine
(ii) Aniline and *N*-methylaniline

18. How would you account for the following :
(i) Aniline is a weaker base than cyclohexylamine.
(ii) Methylamine in aqueous medium gives reddish-brown precipitate with $FeCl_3$.

19. How will you convert the following :
(i) Nitrobenzene into aniline
(ii) Ethanoic acid into methanamine

20. Give the structure of of products *A* and *B* in the given sequence of reactions.
(i) $R - C \equiv N \xrightarrow[Na(Hg)/C_2H_5OH]{H_2/Ni} A$

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

Short Answer Type Questions (SA-II)

21. How are the following reactions carried out? Write the equations and conditions.

(i) Acetic acid to ethylamine

(ii) Bromocyclohexane to cyclohexanamine.

(iii) Methylamine to dimethylamine.

22. Which amine in each of the following pairs is a stronger base? Give reason.

(i) 

$CH_3-CH(NH_2)-CH_3$ and $CH_3-CH(NH_2)-COOCH_3$

(ii) $CH_3CH_2CH_2NH_2$ and $CH_3NHCH_2CH_3$

23. Write the structures of main products when aniline reacts with the following reagents :

(i) Br_2 water

(ii) HCl

(iii) $(CH_3CO)_2O$/pyridine

24. A compound X (C_7H_7Br) reacts with KCN to give Y (C_8H_7N). Reduction of Y with $LiAlH_4$ yields Z ($C_8H_{11}N$). Z gives carbylamine reaction, reacts with Hinsberg's reagent in the presence of aq. KOH to give a clear solution. With $NaNO_2$ and HCl at 0°C (Z) gives a neutral compound which gives red colour with ammonium cerric nitrate. What are X, Y and Z ?

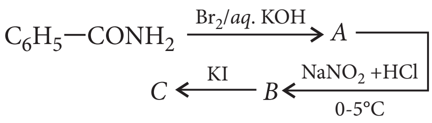
25. (a) Give one chemical test to distinguish between the compounds of the following pairs:

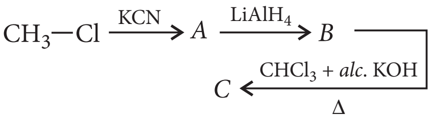
(i) CH_3NH_2 and $(CH_3)_2NH$

(ii) $(C_2H_5)_2NH$ and $(C_2H_5)_3N$

(b) Why aniline does not undergo Friedel–Crafts reaction?

26. Write the structures of A, B and C in the following sequence of reactions :

(i) 

(ii) 

27. Write the structure of
2, 4-dinitrochlorobenzene.

28. Write the structure of *N*-methylethanamine.

29. Write the structure of 2-aminotoluene.

30. Amit wants to manufacture aniline for the synthesis of dye stuff. For this he has selected tin and hydrochloric acid as reducing agent for the reduction of nitrobenzene. But his friend suggested to use iron scrap and hydrochloric acid as the reducing agent.

Now answer the following questions :

(i) Write the chemical equation for the reduction of nitrobenzene to aniline.

(ii) Why Amit's friends has suggested to use scrap iron and HCl in place of tin and HCl?

31. (a) Give a simple chemical test to distinguish between aniline and *N*, *N*-dimethylaniline.

(b) Arrange the following in the increasing order of their boiling point :

$C_2H_5NH_2$, C_2H_5OH, $(CH_3)_3N$

32. Write the chemical equations for the following conversions :

(i) Ethyl isocyanide to ethylamine.

(ii) Aniline to benzonitrile

(iii) Aniline to *p*-nitroaniline.

33. An aromatic compound '*A*' on treatment with aqueous ammonia and heating forms compound '*B*' which on heating with Br_2 and KOH forms a compound '*C*' of molecular formula C_6H_7N. Write the structures and IUPAC names of compounds *A*, *B* and *C*.

34. Account for the fact that although *N*, *N*-dimethyl aniline is only slightly more basic than aniline, 2, 6-dimethyl *N*, *N*-dimethyl aniline is much more basic than 2, 6-dimethyl aniline.

35. Give reasons :

(i) Acetylation of aniline reduces its activation effect.

(ii) CH_3NH_2 is more basic than $C_6H_5NH_2$.

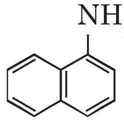
(iii) Although $—NH_2$ is *o*/*p* directing group, yet aniline on nitration gives a significant amount of *m*-nitroaniline.

Long Answer Type Questions (LA)

36. (a) Write structures of different isomers corresponding to the molecular formula, C_3H_9N. Write IUPAC name of the isomers which will liberate nitrogen gas on treatment with nitrous acid.

(b) Classify the following amines as primary, secondary and tertiary :

(i)



(ii)

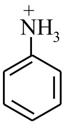
(iii) $(C_2H_5)_2CHNH_2$ (iv) $(C_2H_5)_2NH$

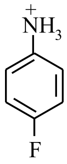
37. (a)

$$\underset{\text{optically active}}{C_5H_{13}N(X)} \xrightarrow[-N_2]{NaNO_2/HCl} Y \text{ (tertiary alcohol) + other products}$$

Find X and Y. Is Y optically active? Write the intermediate steps.

(b) Which of the following is more acidic and why?





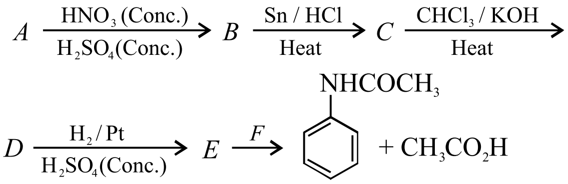
38. (a) Write the reactions of (i) aromatic and (ii) aliphatic primary amines with nitrous acid.

(b) Write the chemical equations for the following conversions

(i) Chlorobenzene to *p*-chloroaniline

(ii) Aniline to *p*-bromoaniline

39. Write the structure of the reagents/organic compounds A to F in the following sequence of reactions :



40. Give plausible explanation for each of the following :

(i) Why are amines less acidic than alcohols of comparable molecular masses?

(ii) Why do primary amines have higher boiling point than tertiary amines?

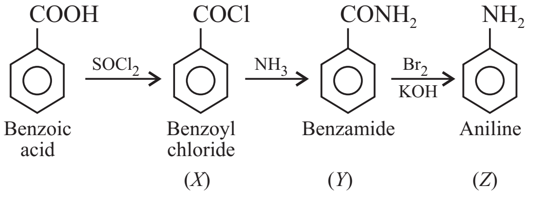
(iii) Why are aliphatic amines stronger bases than aromatic amines?

ANSWERS

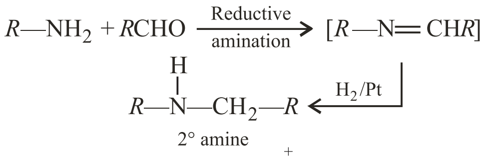
OBJECTIVE TYPE QUESTIONS

1. **(d) :** $CH_2{=}CH_2 \xrightarrow[CCl_4]{Br_2} \underset{(X)}{CH_2Br-CH_2Br} \xrightarrow{NaCN} \underset{(Y)}{NCCH_2CH_2CN} \xrightarrow{LiAlH_4} \underset{\substack{(1,\,4\text{-Diaminobutane})\\(Z)}}{H_2NCH_2CH_2CH_2CH_2NH_2}$

2. **(a) :**

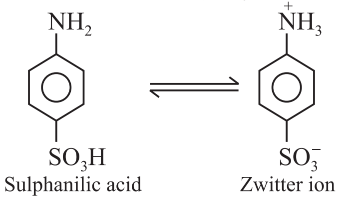


3. **(c) :**



$$R{-}NH_2 + RCHO \xrightarrow[\text{amination}]{\text{Reductive}} [R{-}N{=}CHR] \xrightarrow{H_2/Pt} \underset{2^\circ\text{ amine}}{R{-}\overset{H}{\underset{|}{N}}{-}CH_2{-}R}$$

4. **(b) :**



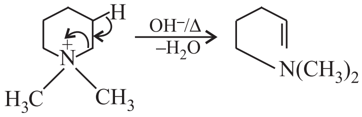
5. **(c) :** Only primary amines will give carbylamine reaction.

6. **(d) :** Aryl amines are less basic than alkyl amines because phenyl group exerts –*I* effect and one pair of electrons on nitrogen is in conjugation resulting in decrease in electron density on nitrogen atom for protonation.

7. **(c) :** The boiling points of amines vary in the order of primary > secondary > tertiary.

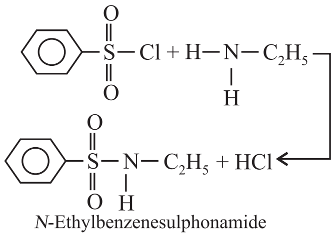
8. **(b) :** Primary and secondary amines can form hydrogen bonds whereas tertiary amines fail to do so. Hence, their boiling points are lowest.

9. **(c) :**



10. **(a)**

11. **(d) :**

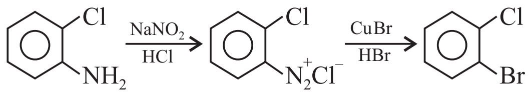


N-Ethylbenzenesulphonamide
(soluble in alkali)

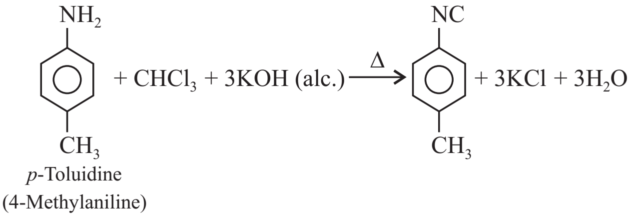
12. (d)

13. (b) : $\underset{\text{Propanamide}}{CH_3CH_2CONH_2} \xrightarrow[\text{(NaOBr)}]{Br_2/NaOH}$

$$CH_3CH_2NH_2 + NaBr + Na_2CO_3 + H_2O$$

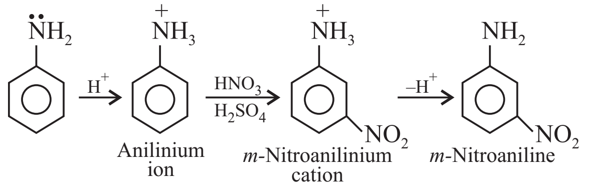
14. (c) : 

15. (b) :



16. (a) : $\underset{\substack{\text{Secondary}\\ \text{amine}}}{R_2NH} + \underset{\substack{\text{Acetyl}\\ \text{chloride}}}{CH_3COCl} \longrightarrow \underset{\substack{N,\,N\text{-dialkyl acetamide}\\ \text{or dialkylethanamide}}}{R_2NCOCH_3}$

17. (a) : Anilinium ion formed by protonation of aniline deactivates *o*- and *p*-positions hence, substitution takes place at *m*-position.



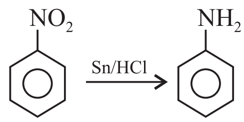
18. (c) : Amines are basic in nature while amides are amphoteric in nature.

19. (a) : Nitrogen forms three sp^3 hybridised sigma bonds with carbon atoms of methyl groups and has a non-bonding electron pair in fourth sp^3 orbital. Thus $(CH_3)_3N$ has pyramidal shape.

20. (c) : Amides on reaction with Br_2 and KOH will give amine containing one carbon atom less. This reaction is called Hoffmann bromamide degradation.

$$C_6H_5CONH_2 + Br_2 + 4KOH \xrightarrow{\Delta} C_6H_5NH_2 + 2KBr + K_2CO_3 + 2H_2O$$

21. (b) : Only primary amines show carbylamine reaction.

22. (a) : 

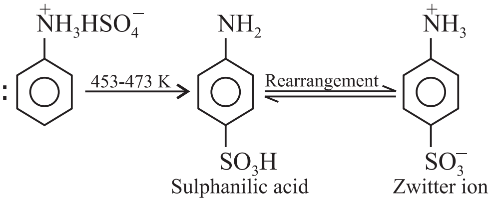
23. (c) : $C_6H_5NH_2 < NH_3 < CH_3NH_2 < (CH_3)_2NH$

24. (a) : Primary amines react with benzoyl chloride to give benzamides and the reaction is known as benzoylation.

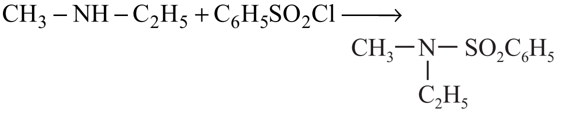
$$\underset{\text{Methanamine}}{CH_3NH_2} + \underset{\text{Benzoyl chloride}}{C_6H_5COCl} \longrightarrow \underset{N\text{-Methylbenzamide}}{CH_3NHCOC_6H_5} + HCl$$

25. (a) : $CH_3CH_2Cl \xrightarrow{NaCN} \underset{(X)}{CH_3CH_2CN} \xrightarrow{Ni/H_2}$

$$\underset{(Y)}{CH_3CH_2CH_2NH_2} \xrightarrow{(CH_3CO)_2O} \underset{(Z)}{CH_3CH_2CH_2NHCOCH_3}$$

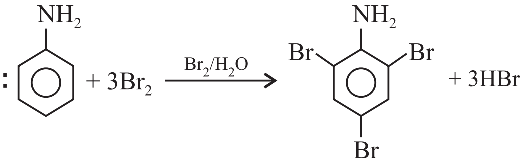
26. (a) : 

27. (c) : Since the compound reacts with benzenesulphonyl chloride to give a product which is insoluble in alkali, it shows there is no H attached to N in the product. Hence, the compound *X* is a secondary amine.



$$CH_3-NH-C_2H_5 + C_6H_5SO_2Cl \longrightarrow CH_3-\underset{\substack{|\\ C_2H_5}}{N}-SO_2C_6H_5$$

N-Ethyl-*N*-methylbenzene sulphonamide

28. (c) : 

2, 4, 6-Tribromoaniline

29. (c) : The trend in boiling point can be explained on the basis of intermolecular hydrogen bonding which is maximum in primary amines.

30. (a) : Benzenesulphonyl chloride ($C_6H_5SO_2Cl$) acts as Hinsberg's reagent.

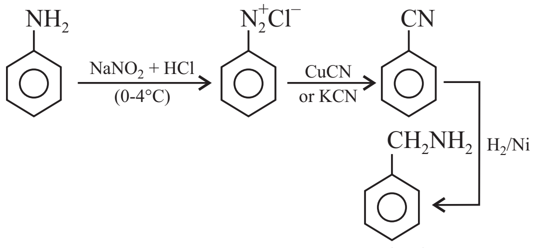
31. (a) : II is not an acceptable canonical structure because nitrogen has 10 valence electrons in the structure. Anilinium ion exists in two canonical structures only which are I and III.

32. (c) : $CH_3-NH_2 + HNO_2 \xrightarrow{NaNO_2 + HCl} [CH_3\overset{+}{N}_2\overset{-}{Cl}]$

$$\xrightarrow{H_2O} HCl + N_2 + CH_3OH$$

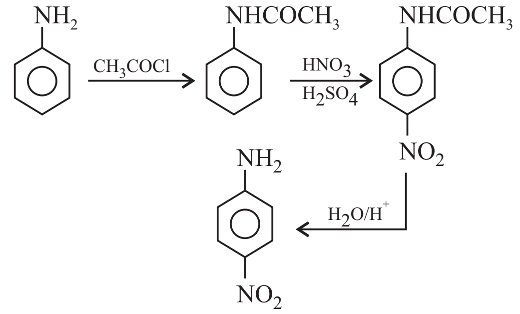
33. (b) : $\underset{\text{Aniline}}{C_6H_5NH_2} + \underset{\text{Benzoyl chloride}}{ClCOC_6H_5} + NaOH \rightarrow$

$$\underset{\text{Benzanilide}}{C_6H_5NH-COC_6H_5} + NaCl + H_2O$$

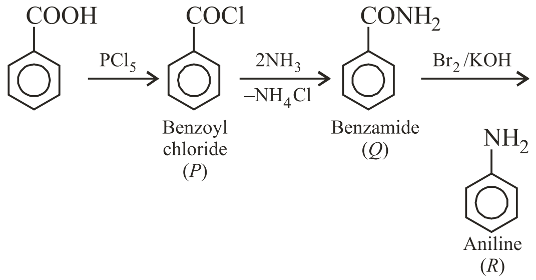
34. (a) : 

Benzylamine

35. (d) : $-NH_2$ group is oxidised on direct nitration hence $-NH_2$ group is blocked by acetylation and then nitration is carried out.



36. (a) :



37. (b) : Higher the basicity lower is the pK_b value. Since NH_3 is the weakest base, hence it has highest pK_b value.

38. (d) : The synthesis of primary amines from phthalimide is known as Gabriel phthalimide synthesis.

39. (d) : Secondary amines do not give carbylamine test.

40. (d) : $\underset{\text{(Excess)}}{NH_3 + C_2H_5I} \longrightarrow \underset{\text{Quaternary salt}}{[(C_2H_5)_4N^+]I^-}$

41. (b) : There is no free hydrogen in tertiary amines hence they do not form salts and are not soluble in acids.

42. (c) : Only $-CH_3$ group is electron donating group hence it increases the electron density on nitrogen making it most basic.

43. (a) :

$$\begin{tikzcd}
C_2H_5NH_2 \arrow[r, "HNO_2"] & \underset{(X)}{C_2H_5OH} \arrow[r, "PCl_5"] & \underset{(Y)}{C_2H_5Cl} \arrow[d, "KCN"] \\
 & & \underset{(Z)}{\underset{\text{Propanenitrile}}{C_2H_5CN}}
\end{tikzcd}$$

44. (c) : $RN \equiv C \xrightarrow{4H} RNHCH_3$

Other compounds give primary amines.

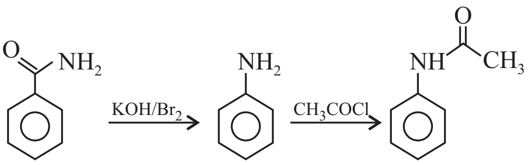
$$RNO_2 \xrightarrow{6H} RNH_2 + 2H_2O$$

$$RCONH_2 \xrightarrow{4H} RCH_2NH_2 + H_2O$$

$$RCN \xrightarrow{4H} RCH_2NH_2$$

45. (c) : 3° amines do not react with Hinsberg reagent.

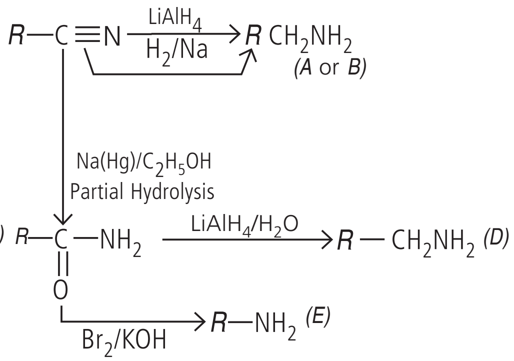
46. (b) :



47. (b) : $RNH_2 + RCOCl \longrightarrow RNHCOR + HCl$

$$RNH_2 + (RCO)_2O \longrightarrow \underset{\text{Substituted amides}}{RNHCOR} + RCOOH$$

48. (d) :



49. (d) : At meta position $-NO_2$ shows $-I$ effect while at *o* – and *p* – positions it shows $-R$ effect.

50. (c) :

$$\begin{tikzcd}
CH_3CH_2CH_2Br \arrow[r, "KCN"] & CH_3CH_2CH_2CN \arrow[r, "{[H]}", "H_2/Ni"'] \arrow[d, "H_3O+"] & \underset{n\text{-Butylamine}}{CH_3CH_2CH_2CH_2NH_2} \\
 & CH_3CH_2CH_2COOH &
\end{tikzcd}$$

$$\begin{tikzcd}
CH_3CH_2CH_2Br \arrow[r, "AgCN"] & CH_3CH_2CH_2NC \arrow[d, "H_3O+"] \arrow[dr, "{[H]}\ H_2/Ni"] & \\
 & CH_3CH_2CH_2NH_2 + HCOOH & \underset{\text{Methyl propyl amine}}{CH_3CH_2CH_2NH—CH_3}
\end{tikzcd}$$

51. (c) :

$$\begin{tikzcd}
CH_3CONH_2 \arrow[rr, "NaOH + Br_2"] & & \underset{\text{(Primary Amine)}}{CH_3NH_2\ (A)} \arrow[d, "CHX_3/KOH"] \\
\underset{\text{Secondary Amine}}{\underset{(C)}{CH_3NHCH_3}} & & \underset{(B)}{CH_3N \equiv C} \arrow[ll, "H_2/Ni", "{[H]}"']
\end{tikzcd}$$

52. (c) : The value of *pK_b* describes the relative strength of the bases.

	NH_3	CH_3NH_2	$(CH_3)_2NH$	$(CH_3)_3N$
pK_b	4.7	3.38	3.27	4.22

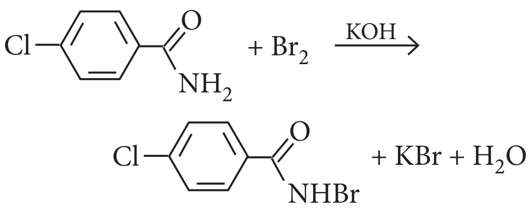
So, the correct order of basicity in aqueous medium is :

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

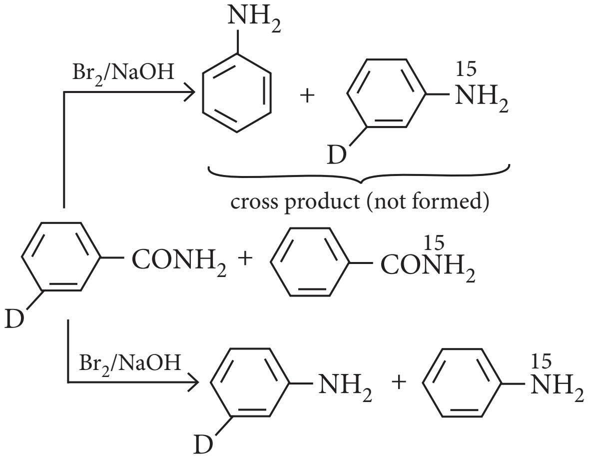
53. (a)

54. (d) : The rate determining step is probably loss of Br^- to form isocyanate as this is the slowest step.

55. (d) :



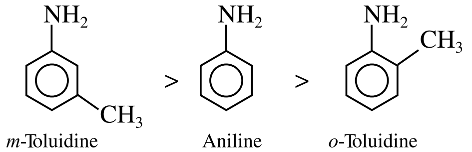
56. (b) : Since, the overall reaction is intermolecular, hence there will be no effect on product formation.



57. (d) : The increasing order of basicity of the given compounds is $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > C_6H_5NH_2$. Due to the $+I$ effect of alkyl groups, the electron density on nitrogen increases and thus, the availability of the lone pair of electrons to proton increases and hence, the basicity of amines also increases. So, aliphatic amines are more basic than aniline. In case of tertiary amine $(CH_3)_3N$, the covering of alkyl groups over nitrogen atom from all sides makes the approach and bonding by a proton relatively difficult, hence the basicity decreases. Electron withdrawing groups decrease electron density on nitrogen atom and thereby decreasing basicity.

58. (d) : In general, electron donating ($+R$) group which when present on benzene ring ($-NH_2$, $-OR$, $-R$, etc.) at the para position increases the basicity of aniline.

Ortho substituted anilines are weaker bases than aniline due to *ortho* effect.



59. (d) : In case of ethylamines, the combined effect of inductive effect, steric effect and solvation effect gives the order of basic strength as

$$\underset{(2^\circ)}{(C_2H_5)_2NH} > \underset{(3^\circ)}{(C_2H_5)_3N} > \underset{(1^\circ)}{C_2H_5NH_2} > NH_3$$

60. (b) : In non-aqueous solvents the basic strength of alkyl amines follows the order :

tertiary amines > secondary amines > primary amines.

61. (c)

62. (a) : A primary amine forms *N*-alkylbenzene sulphonamide with Hinsberg's reasent because of the presence of an acidic hydrogen on the N-atom, dissolves in aqueous KOH.

63. (b)

64. (a) : Tertiary amine does not contain a replaceable hydrogen on the nitrogen atom. So, 3° amine does not react with Hinsberg's reagent.

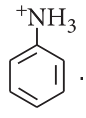
65. (c)

66. (d) **67. (a)**

68. (d) : Dimethylamine is more basic than methylamine.

69. (a) : *Ortho* effect is a consequence of steric and electronic factors.

70. (c) : Only primary amines can be prepared from amides ($RCONH_2$) by treating with Br_2 and KOH. Thus, *N*-methyl acetamide *i.e.*, $CH_3CONHCH_3$ does not undergo Hoffmann bromamide reaction.

71. (d) : In strongly acidic medium, aniline gets protonated and so the lone pair of electrons is not available to produce $+E$ or $+M$ effects. On the other hand, the $-\overset{+}{N}H_3$ group exerts strong $-I$ effect and thus it causes the deactivation of the ring  .

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

73. (a)

74. (b) : Aniline exists as resonance hybrid. As a result of resonance, the lone pair of electrons on nitrogen gets delocalized over the benzene ring and thus, is less easily available for protonation than in case of cyclohexylamine where no such resonance takes place.

75. (a) : Under acidic condition, aniline gets protonated to anilinium ion ($-NH_3^+$ group). This is deactivating and *m*-directing group. Thus, controlled nitration of aniline mainly gives *m*-nitroaniline.

76. (b) **77. (a)**

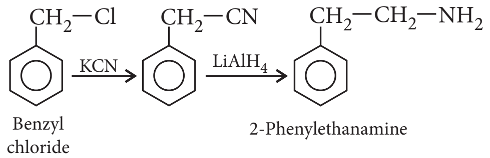
78. (b) : It is because hydrogen bonding is less pronounced in primary and secondary amines than that in alcohols or carboxylic acids and nitrogen is less electronegative than oxygen.

79. (c) : Acetylation decreases the electron density in the benzene ring and deactivate the ring hence control the reaction.

80. (b) : $-NH_2$ being *o*, *p*-directing group directs $-SO_3H$ group to less hindered *p*-position.

SUBJECTIVE TYPE QUESTIONS

1.



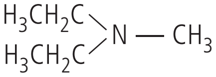
2. Carbylamine reaction is the reaction in which 1° amines produce a bad smelling compound when treated with chloroform in the presence of alkali.

$RNH_2 + CHCl_3 + 3KOH \xrightarrow{Heat} R—N \rightleftarrows C + 3KCl + 3H_2O$

It is the test for primary amines.

3. $(C_6H_5)_2NH < C_6H_5NH_2 < C_6H_5N(CH_3)_2 < CH_3NH_2$

4.



$(H_3CH_2C)_2N—CH_3$

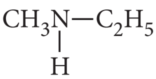
IUPAC name : *N*-Ethyl-*N*-methylethanamine

5. Primary amines $(R-NH_2)$ have two hydrogen atoms on nitrogen which can undergo intermolecular hydrogen bonding whereas no such hydrogen bonding is present in tertiary amines (R_3N). So, primary amines boil at a higher temperature than tertiary amines.

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

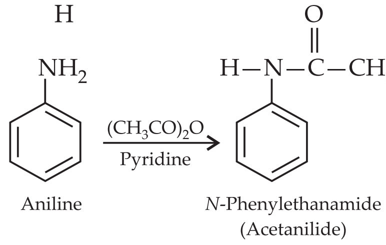
1° amines are more soluble in water than 2° amines. Aniline due to large hydrophobic benzene ring is least soluble.

7.



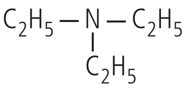
$CH_3N(H)—C_2H_5$ (*N*-ethylmethylamine)

8.



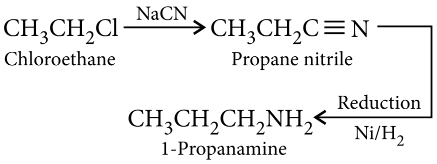
9. Aromatic amines cannot be prepared by Gabriel phthalimide synthesis because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

10.

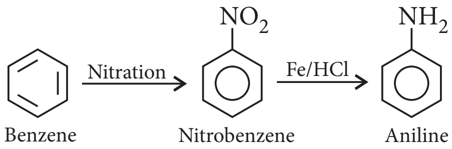


$C_2H_5—N(C_2H_5)—C_2H_5$

11. (i)



(ii)

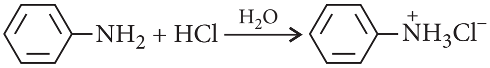


12. (i) In tertiary amines there are no acidic hydrogen due to which they do not undergo acylation reaction.

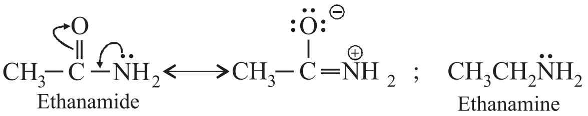
(ii) N being less electronegative than O gives lone pair of electron more easily than O atom. Therefore amines are more basic than alcohols.

13. (i) $CH_3—CH_2—NH_2 + CHCl_3 + alc\ 3KOH \xrightarrow{Heat} CH_3—CH_2—NC + 3KCl + 3H_2O$

(ii)

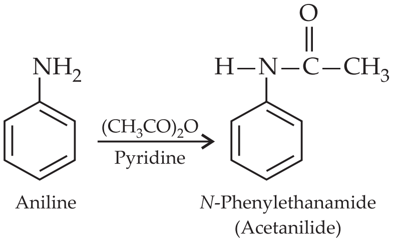


14.

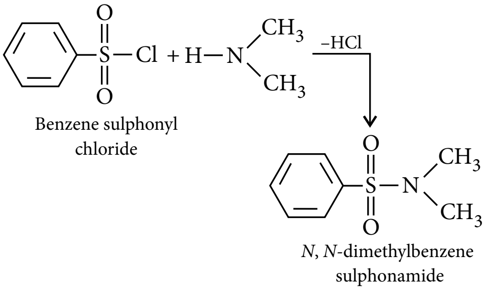


In acetamide, lone pair on nitrogen atom is involved in resonance and hence is not free for donation as in the case of ethanamine.

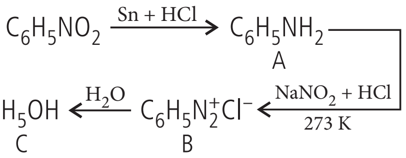
15. (i)



(ii)

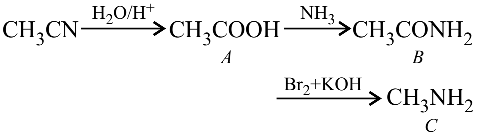


16. (i)



$C_6H_5NO_2 \xrightarrow{Sn + HCl} \underset{A}{C_6H_5NH_2} \xrightarrow[273\ K]{NaNO_2 + HCl} \underset{B}{C_6H_5N_2^+Cl^-} \xrightarrow{H_2O} \underset{C}{C_6H_5OH}$

(ii)

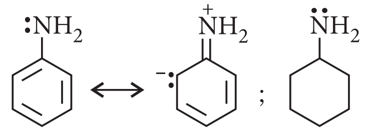


$CH_3CN \xrightarrow{H_2O/H^+} \underset{A}{CH_3COOH} \xrightarrow{NH_3} \underset{B}{CH_3CONH_2} \xrightarrow{Br_2+KOH} \underset{C}{CH_3NH_2}$

17. (i) Methylamine gives carbylamine test, *i.e.*, on treatment with alc. KOH and chloroform, followed by heating it gives offensive odour of methyl isocyanide. Dimethylamine does not give this test.

(ii) Aniline gives carbylamine test, *i.e.*, on treatment with alc. KOH and chloroform followed by heating it gives offensive odour of phenylisocyanide but *N*-methylaniline being secondary amine, does not show this test.

18. (i) Aniline is weaker base than cyclohexylamine because of resonance. Due to electromeric effect, the lone pair on nitrogen is attracted by benzene ring. Hence, donor tendency of $-\ddot{N}H_2$ group decreases. There is no resonance in cyclohexylamine. Electron repelling nature of cyclohexyl group further increases the donor property of NH_2 group. So, cyclohexylamine is a stronger base.



Aniline
(Resonance structures)

Cyclohexylamine
(No resonance)

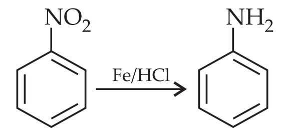
(ii) Methylamine forms hydroxide ions when dissolved in water due to the following acid - base equilibrium.

$CH_3-NH_2 + H_2O \rightleftharpoons CH_3-\overset{+}{N}H_3 + OH^-$

These OH^- ions react with Fe^{3+} ions to form ferric hydroxide.

$2Fe + 6OH^- \longrightarrow 2Fe(OH)_3$

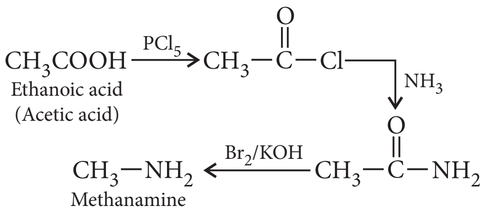
19. (i)



Nitrobenzene

Aniline

(ii)



$$CH_3COOH \xrightarrow{PCl_5} CH_3-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{NH_3} CH_3-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{Br_2/KOH} CH_3-NH_2$$

Ethanoic acid (Acetic acid); Methanamine

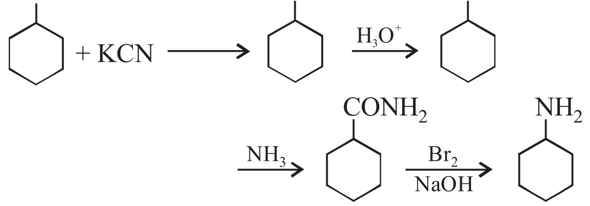
20. (i) $R-C\equiv N \xrightarrow[Na(Hg)/C_2H_5OH]{H_2/Ni} R-CH_2-NH_2$

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

21. (i) $\underset{\text{Acetic acid}}{CH_3COOH} + NH_3 \longrightarrow \underset{\text{Acetamide}}{CH_3CONH_2}$

$\xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4} \underset{\text{Ethylamine}}{CH_3CH_2NH_2}$

(ii)



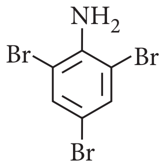
(iii) $CH_3NH_2 + CHCl_3 + KOH \xrightarrow{\Delta} CH_3NC$

$\xrightarrow[Na/C_2H_5OH]{H_2} CH_3NHCH_3$

22. (i) $CH_3-\overset{NH_2}{\overset{|}{C}H}-CH_3$ is more basic than $CH_3-\underset{NH_2}{\underset{|}{C}H}-COOCH_3$ because $-COOCH_3$ is an electron withdrawing group which decrease the electron density on nitrogen atom.

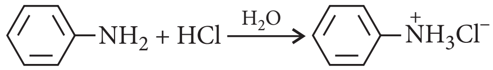
(ii) 2° amines are more basic than 1° amines, because in 2° amine there are two electron releasing groups and in 1° amine only one electron releasing group is present, so, $CH_3NHCH_2CH_3$ is more basic than $CH_3CH_2CH_2NH_2$.

23. (i) $C_6H_5NH_2 + Br_{2(aq)} \longrightarrow$

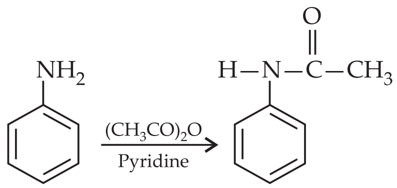


$+ 3HBr$

(ii)



(iii)

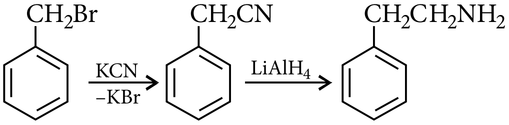


Aniline

N-Phenylethanamide
(Acetanilide)

24. $\underset{(X)}{C_7H_7Br} \xrightarrow[-KBr]{KCN} \underset{(Y)}{C_8H_7N} \xrightarrow{LiAlH_4} \underset{(Z)}{C_8H_{11}N}$

or

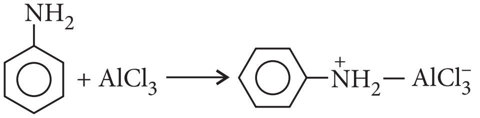


(X) (Y) (Z)

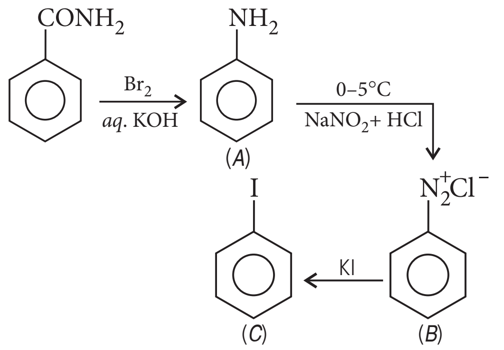
25. (a) (i) Methylamine gives carbylamine test, *i.e.*, on treatment with alc. KOH and chloroform, followed by heating it gives offensive odour of methyl isocyanide. Dimethylamine does not give this test.

(ii) $(C_2H_5)_2NH$ and $(C_2H_5)_3N$ can be distinguish by Hinsberg's reagent.

(b) (i) In Friedel Crafts reaction, $AlCl_3$ is added as a catalyst which is a Lewis acid. It forms a salt with aniline due to which the nitrogen of aniline acquires positive charge. This positively charged nitrogen acts as a strong deactivating group, hence aniline does not undergo Friedel Crafts reaction.



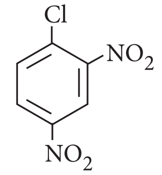
26. (i)



(ii)

$$CH_3{-}Cl \xrightarrow{KCN} \underset{(A)}{CH_3CN} \xrightarrow{LiAlH_4} \underset{(B)}{CH_3CH_2NH_2} \xrightarrow[\Delta]{CHCl_3 + alc.\ KOH} \underset{(C)}{CH_3CH_2NC}$$

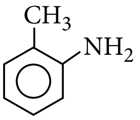
27.



2, 4-Dinitrochlorobenzene

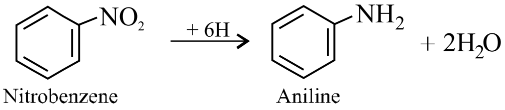
28. $CH_3CH_2NHCH_3$

29.



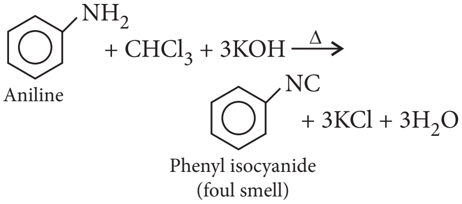
2-Aminotoluene

30. (i) $[Fe + 2HCl \longrightarrow FeCl_2 + 2H] \times 3$



(ii) Amit's friend has suggested to use scrap iron and hydrochloric acid because in this reaction $FeCl_2$ formed gets hydrolysed to release HCl during the reaction. Thus only small amount of HCl is required to initiate the reaction and scrap iron is also cheaper.

31. (a) Aniline undergoes isocyanide test (carbylamine reaction) whereas, *N*, *N* – dimethylaniline does not.



(b) Increasing order of boiling points :

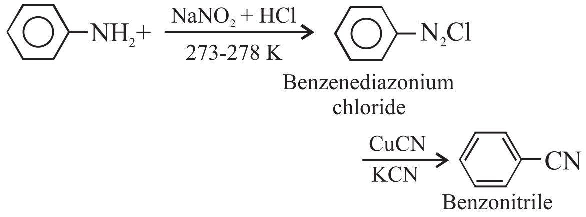
$(CH_3)_3N < C_2H_5NH_2 < C_2H_5OH$

Tertiary amine does not have hydrogen to form hydrogen bonding and hydrogen bonding in alcohol is stronger than that of amines because oxygen is more electronegative than nitrogen.

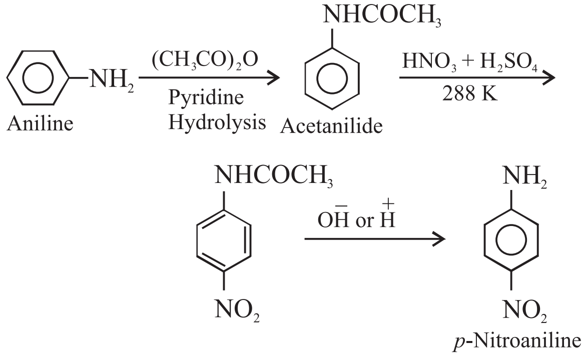
32. (i)

$$\underset{\text{Ethyl isocyanide}}{C_2H_5 - N \equiv C} + 2HOH \xrightarrow[\text{Hydrolysis}]{H^+} \underset{\text{Ethylamine}}{C_2H_5NH_2} + HCOOH$$

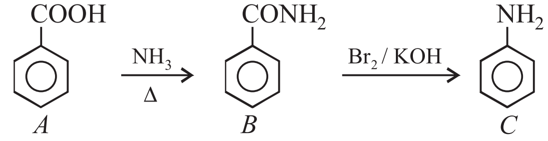
(ii)



(iii)



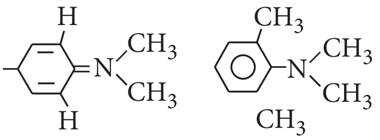
33. Formula of the compound '*C*' indicates it to be an amine. Since it is obtained by the reaction of Br_2 and KOH with the compound '*B*' so compound '*B*' can be an amide. It is also indicated because '*B*' is obtained from compound '*A*' by reaction with ammonia following by heating. So compound '*A*' could be an aromatic acid. Formula of compound '*C*' shows that it is aniline, then '*B*' is benzamide and compound '*A*' is benzoic acid. The sequence of reactions can be written as follows :



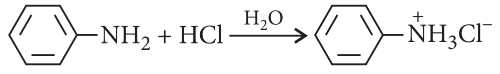
34. Extended π bonding between the amino nitrogen and the ring requires the s bonds on N atom to become coplanar with the ring and its *ortho* bonds.

Presence of bulky substituents in the *ortho* positions (2, 6-positions) sterically hinder the attainment of this geometry (coplanarity) and thus interferes with the base—weakening extended π bonding.

Because of this effect, (called steric inhibition of resonance) 2, 6-dimethyl *N*, *N*-dimethyl aniline is much more basic than 2, 6-dimethyl aniline.



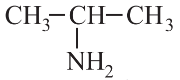
35. (i) After acetylation of aniline, acetanilide is formed in which due to the presence of $-\overset{O}{\overset{\|}{C}}-CH_3$ group having $-I$ effect, electron density on N-atom decreases and hence, activation effect of aniline gets reduced.

(ii) 

(iii) Nitration is carried out with conc. HNO_3 in the presence of conc. H_2SO_4. In the presence of these acids, the $-NH_2$ group of aniline gets protonated and is converted into $-\overset{+}{N}H_3$ group. This positively charged group acts as a strong electron withdrawing and meta-directing group. Hence, the incoming electrophile goes to *m*-position.

36. (a) In all, four structural isomers are possible. These are as follows :

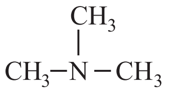
Primary amines : $CH_3CH_2CH_2NH_2$
Propan-1-amine



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

Propan-2-amine

Secondary amines : $CH_3-NH-C_2H_5$
N-Methylethanamine

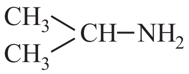
Tertiary amines : 

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

N,*N*-Dimethylmethanamine

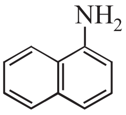
Only primary amines react with HNO_2 to liberate N_2 gas.

(i) $CH_3CH_2CH_2NH_2$
Propan-1-amine

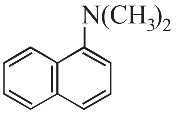
(ii) 

$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH-NH_2$

Propan-2-amine

(b) (i) 

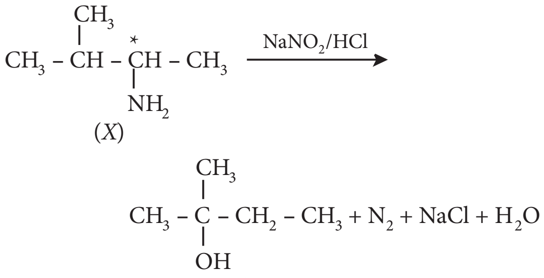
1° Amine

(ii) 

3° Amine

(iii) $(C_2H_5)_2-CHNH_2$
1° Amine

(iv) $(C_2H_5)_2NH$
2° Amine

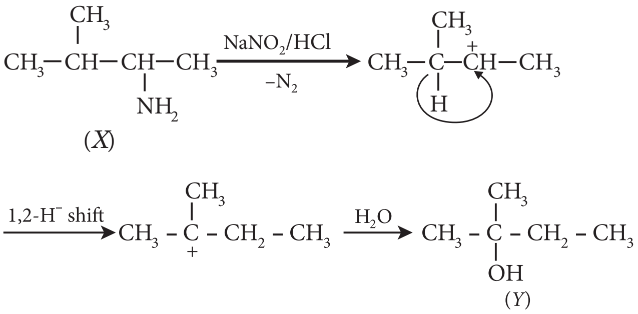
37. (a) 

$$CH_3-\overset{CH_3}{\overset{|}{CH}}-\underset{NH_2}{\underset{|}{\overset{*}{C}H}}-CH_3 \xrightarrow{NaNO_2/HCl}$$

(*X*)

$$CH_3-\overset{CH_3}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-CH_2-CH_3+N_2+NaCl+H_2O$$

Y (rearranged product)

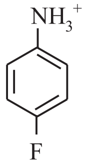


$$CH_3-\overset{CH_3}{\overset{|}{CH}}-\underset{NH_2}{\underset{|}{CH}}-CH_3 \xrightarrow[-N_2]{NaNO_2/HCl} CH_3-\overset{CH_3}{\overset{|}{\underset{H}{\underset{|}{C}}}}-\overset{+}{C}H-CH_3$$

(*X*)

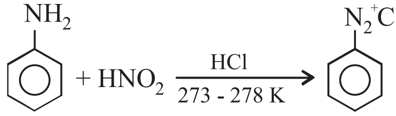
$$\xrightarrow{1,2\text{-}H^-\text{ shift}} CH_3-\overset{CH_3}{\overset{|}{\underset{+}{C}}}-CH_2-CH_3 \xrightarrow{H_2O} CH_3-\overset{CH_3}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-CH_2-CH_3$$

(*Y*)
optically inactive

(b) 

is more acidic due to the strong electron withdrawing power ($-I$ effect) of fluorine.

38. (a) (i) Aromatic primary amines react with nitrous acid to form diazonium salts.

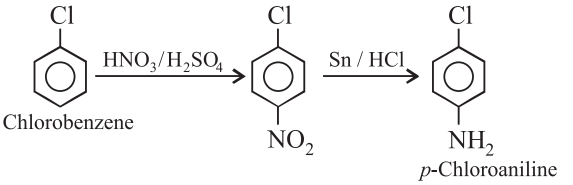


(ii) Aliphatic primary amines also form diazonium salts on reaction with nitrous acid but they are unstable and decompose to give the corresponding alcohols as the major product with the evolution of nitrogen.

$$R-NH_2+HNO_2 \xrightarrow[273-278\text{ K}]{HCl} \left[R-N_2^+Cl^-\right]$$

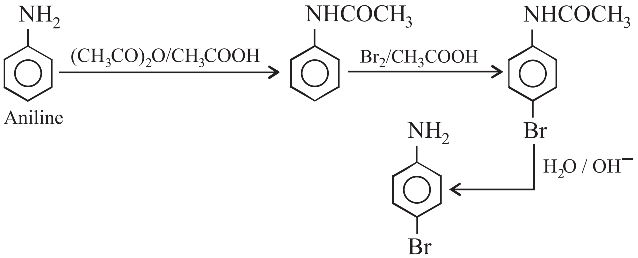
$$\xrightarrow{H_2O} R-OH+N_2+HCl$$

(b) (i)



p-Chloroaniline
(separated from the *ortho* isomer)

(ii)

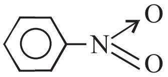


p-Bromoaniline

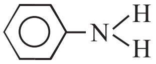
39. Structure of reagents/organic compounds :

A = Benzene 

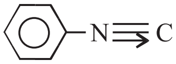
B = Nitrobenzene



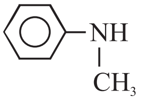
C = Aniline



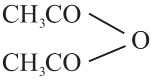
D = Phenyl isocyanide



E = Methyl phenyl amine



F = Acetic anhydride



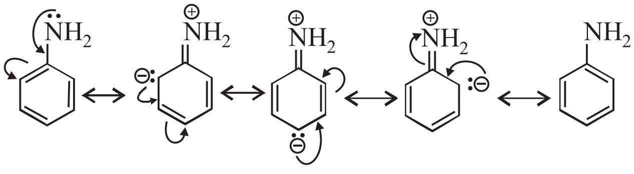
40. (i) In alcohols, the hydrogen atom is attached to more electronegative oxygen atom whereas nitrogen of amines is less electronegative. After the loss of H^+ ion, the negative charge is more easily accommodated on oxygen than in case of nitrogen in amines. Hence, amines have lesser tendency to lose H^+ ions, so they are less acidic than alcohols.

$$R - NH_2 \rightarrow R - NH^- + H^+$$

$$R - O - H \rightarrow R - O^- + H^+$$

(ii) Primary amines ($R - NH_2$) have two hydrogen atoms on nitrogen which can undergo intermolecular hydrogen bonding whereas no such hydrogen bonding is present in tertiary amines (R_3N). So primary amines boil at a higher temperature than tertiary amines.

(iii) In aromatic amines, the lone-pair of electrons on nitrogen atom is involved in resonance with the benzene ring as shown below for aniline.



It shows that this pair of electrons is less available for protonation. In case of aliphatic amines electron releasing alkyl groups increase electron density on nitrogen atom. So, aliphatic amines are stronger bases than aromatic amines.

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