Date: 26/10/2021

Q1. How do you convert the following: Ethanenitrile to ethanamine.

Q2. Write the chemcial reaction to illustrate the following: Ammonolysis.

Q3. Why cannot primary aromaic amines be prepared by Gabriel phthalimide sysnthesis?

Q4. State and illustrate the following Gabriel synthesis.

Q5. Write the chemical equation involved in the following reaction: Hofmann bromamide degradation reaction.

Q6. Write the structure for *N*, *N*-ethylmethylamine.

Q7. Give the IUPAC name of $H_2N - CH_2 - CH_2 - CH = CH_2$.

Q8. Write the structure of 2-aminotoluene.

Q9. Write the structure of *N*-methylethanamine.

Q10. Write theIUPAC name of the given compound:

Q11. Arrange the following in increasing order of basic strength: Aniline, *p*-nitroaniline and *p*-toluidine.

Q12. Account for the following: Nitro compounds have higher boiling points than the hydrocarbons having almost the same molecular mass.

Q13. Account for the following: Ethylamine is soluble in water whereas aniline is not.

Q14. Out of CH_3NH_2 and $(CH_3)_3N$, which one has higher boiling point?

Q15. Account for the following: Primary amines ($R - NH_2$) have higher boliling point than tertiary amines (R_2N).

Q16. Arrange the following in the increasing order of their boiling point:

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

Q17. Give reasons for the following: Primary amines have higher boiling point than tertiary amines.

Q18. Write chemical equations for the following conversion: Benzyl chloride to 2-phenylehanamine.

Q19. Arrange the following compounds in increasing order of solubility in water:

$C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_2H_5NH_2$.

Q20. Arrange the following in increasing order of basic strength:

$C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5CH_2NH_2$.

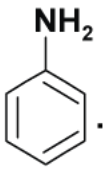
Q21. Arragne the following in increasing order of basic strength:

$C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5N(CH_3)_2$.

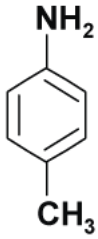
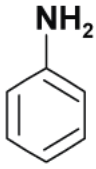
Q22. Arrange the following in increasing order of their basic strength in aqueous solution:

CH_3NH_2, $(CH_3)_3N$, $(CH_3)_2NH$.

Q23. Which of the two is more basic and why?

CH_3NH_2 or  .

Q24. Which of the two is more basic and why?

 and 

Q25. Which of the two is more basic and why?

CH_3NH_2 or NH_3.

Q26. Account for the following: Amines are basic substances while amides are neutral.

Q27. Why do amines act as nucleophiles?

Q28. Assign reason for the following: The pK_b of aniline is higher than that of methylamine.

Q29. Why is an alkylamine more basic than ammonia?

Q30. How will you differentiate between aniline and ethylamine?

Q31. State reasons for the following: pK_b value for aniline is more than that for ethylamine.

Q32. 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.

Q33. Complete the following reaction equation:

$$C_6H_5NH_2 + Br_2(aq) \longrightarrow$$

Q34. Describe the following giving the relevant chemical equation: Carbylamine reaction.

Q35. Arrange the following in the decreasing order of their basic strength in aqueous solution:

CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$ and NH_3.

Q36. Complete the following reactions:

$$C_6H_5N_2^+Cl^- \xrightarrow[(Room Temp.)]{H_2O}$$

Q37. The conversion of primary aromatic amines into diazonium salts is known as _____.

Q38. Complete the following reaction equation:

$$C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow ....$$

Q39. Give a simple chemical test to distinguish between the following pair of compounds:

$(CH_3)_2NH$ and $(CH_3)_3N$

Q40. How will you bring about the folowing conversion: Ethanamine to ethanoic acid.

Q41. How will you convert the following: Aniline into *N*-phenylethanamide. Write the chemical equations involved.

Q42. State and illustrate the following. Coupling reaction.

Q43. How is the following conversion carried out: Aniline to p-hydroxyazobenzene.

Q44. How would you acieve the following conversion: Aniline to benzonitrile. Write the chemical equation with reaction conditions in each case,

Q45. Write a chemical reaction in which the iodide ion replaces the diazonium group in a diazonium salt.

Q46. How will you bring about the following conversion: Aniline to benzonitrile.

Q47. How will you bring about the following conversion: Aniline to chlorobenzene. Write the chemical equation involved.

Q48. How will you bring about the following conversion: Nitrobenzene to phenol.

Q49. Give reasons for the following:

(a) Aniline does not undergo Friedel-Crafts reaction.

(b) $(CH_3)_2NH$ is more basic than $(CH_3)_3N$ in an aqueous solution.

Q50. State reasons for the following:

(a) Ethylamine is soluble in water whereas aniline is not soluble in water.

(b) Primary amines have higher boiling points than tertiary amines.

Q51. How would you achieve the following conversions:

(a) Nitrobenzene to aniline.

(b) An alkyl halide to a quaternary ammonium salt.

Write the chemical equation with reaction conditions in each case.

Q52. How are the following conversions carried out?

(a) CH_3CH_2Cl to $CH_3CH_2CH_2NH_2$. (b) Bebzebe to aniline.

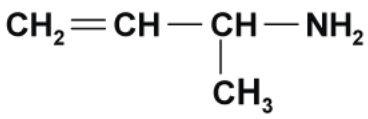
Q53. How will you convert the following:

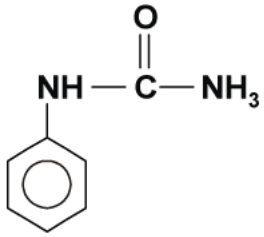
(a) Nitrobenzene into aniline. (b) Ethanoic acid into methanamine.

Q54. Illustrate the following reactins giving a chemical equation in each case:

(a) Gabriel phthalimide synthesis. (b) Hofmann's bromamide reaction.

Q55. Give IUPAC names of the following compounds:

(a) 

(b) 

Q56. (a) Arrange the following compounds in an increasing order of basic strength:

$C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_2H_5)_2NH$ and CH_3NH_2.

(b) Arrange the following compounds in a decreasing order of pK_b values:

$C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$.

Q57. Account for the following:

(a) Aniline does not give Friedel-Crafts reaction.

(b) pK_b of methylamine is less than that of aniline.

Q58. Give the structures of *A*, *B* and *C* in the following reactions:

(a) $C_6H_5NO_2 \xrightarrow{Sn + HCl} A \xrightarrow[273\ K]{NaNO_2 + HCl} B \xrightarrow{H_2O} C$

(b) $CH_3CN \xrightarrow{H_2O/H^+} A \xrightarrow[\Delta]{NH_3} B \xrightarrow{Br_2 + KOH} C$

Q59. Account for the following:

(a) pK_b of aniline is more than that of methylamine.

(b) Aniline does not undergo Friedel-Crafts reaction.

Q60. Write one chemical reaction each to illustrate the following:

(a) Carbylamine reaction. (b) Acetylation reaction.

Q61. How would you account for the following:

(a) Aniline is a weaker base than cyclohexylamine.

(b) Methylamine in aqueous medium gives reddish-brown precipitate with $FeCl_3$.

Q62. Assign reason for the following:

(a) Amines are less acidic than alcohols of comparable molecular masses.

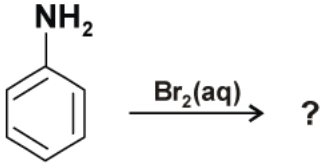
(b) Aliphatic amines are stronger bases than aromatic amines.

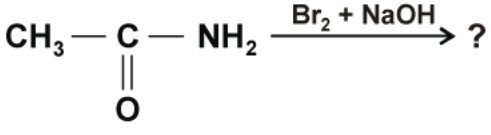
Q63. Give reasons:

(a) Electrophilic substitution in aromatic amines takes place more readily than benzene.

(b) CH_3CONH_2 is weaker base than $CH_3CH_2NH_2$.

Q64. Write the main products of the following reactions:

(a) 

(b) 

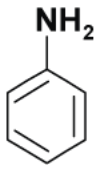
Q65. Give reasons:

(a) Aniline is a weaker base than cyclohexyl amine.

(b) It is difficult to prepare pure amines by ammonolysis of alkyl halides.

Q66. Complete the following reactions:

(a) $CH_3CH_2NH_2 + CHCl_3 + \text{alc. KOH} \longrightarrow$

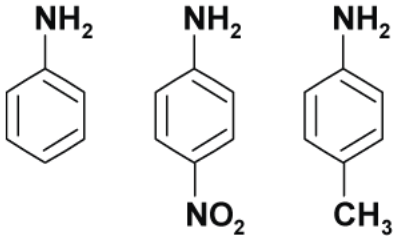
(b)  $+ HCl(aq) \longrightarrow$

Q67. Illustrate the following reactions giving suitable example in each case:

(a) Ammonolysis. (b) Acetylation of amines.

Q68. Arrange the following in increasing order of their basic strength:

(a) $C_6H_5 — NH_2$, $C_6H_5 — CH_2 — NH_2$, $C_6H_5 — NH — CH_3$

(b) 

Q69. Give the chemical tests to distinguish between the following pairs of compounds:

(a) Methylamine and dimethylamine. (b) Aniline and *N*-methylaniline.

Q70. Give the chemical tests to distinguish between the following pairs of compounds:

(a) Ethylamine and aniline. (b) Aniline and benzylamin.

Q71. Give the chemical tests to distinguish between the following pairs of compounds:

(a) Aniline and ethylamine. (b) Ethylamine and dimethylamine.

Q72. How do you convert the following:

(a) $C_6H_5CONH_2$ to $C_6H_5NH_2$. (b) Aniline to phenol.

Q73. Account for the following:

(a) Aniline does not undergo Friedel-Crafts reaction.

(b) Aliphatic amines are stronger bases than aromatic amines.

Q74. Give one chemical test each to distinguish between the following pairs of compounds:

(a) Ethylamine and aniline. (b) Aniline and *N*-methylaniline.

Q75. Write the chemical equations for the following conversions:

(a) Nitrobenzene to benzoic acid. (b) Aniline to benzyl alcoho.

Q76. Illustrate the following with an an example of reaction in each case"

(a) Sandmeyer's reaction. (b) Coupling reaction.

Q77. Describe a chemical test each to distinguish between the following:

(a) Ethylamine and aniline. (b) Methylamine and dimethylamine.

Q78. Write the structure of *A*, *B* and *C* in the following:

(a) $C_6H_5-CONH_2 \xrightarrow{Br_2/aq.\ KOH} A \xrightarrow[0.5°C]{NaNO_2 + HCl} B \xrightarrow{KI} C$

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

Q79. Write the structures of *A*, *B* and *C* in the following reactions:

(a) $C_6H_5NO_2 \xrightarrow{Sn/HCl} A \xrightarrow[273\ K]{NaNO_2 + HCl} B \xrightarrow[\Delta]{H_2O} C$

(b) $CH_3Cl \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[273\ K]{HNO_2} C$

Q80. Write the chemical equations involved when aniline is treated with the following reagents:

(a) Br_2 water (b) $CHCl_3$ + KOH (c) HCl

Q81. Write the structures of main products when anilie reacts with the following reagents:

(a) Br_2 water (b) HCl (c) $(CH_3CO)_2O$/pyridine

Q82. Give the structures of products *A*, *B* and *C* in the following reactions:

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

(b) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{NaOH + Br_2} B \xrightarrow{CHCl_3 + Alc.\ NaOH} C$

Q83. Give the structures of *A*, *B* and *C* in the following reactions:

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

(b) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{Br_2 + KOH} B \xrightarrow{CHCl_3 + NaOH} C$

Q84. 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*.

Q85. (a) $C_6H_5N_2^+Cl^- \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow[\Delta]{NH_3} C$

(b) $C_6H_5NO_2 \xrightarrow{Sn + HCl} A \xrightarrow[273\ K]{NaNO_2 + HCl} B \xrightarrow{H_2O/H^+} C$

Q86. Account for the following observations:

(a) pK_b for aniline is more than that for methylamine.

(b) Methylamine solution in water reacts with ferric chloride solution to give a percipitate of ferric hydroxide.

(c) Aniline does not undergo Friedel-Crafts reaction.

Q87. (a) Write the structures of main products when benzenediazonium chloride ($C_6H_5N_2^+Cl^-$) reacts with the following reagents:

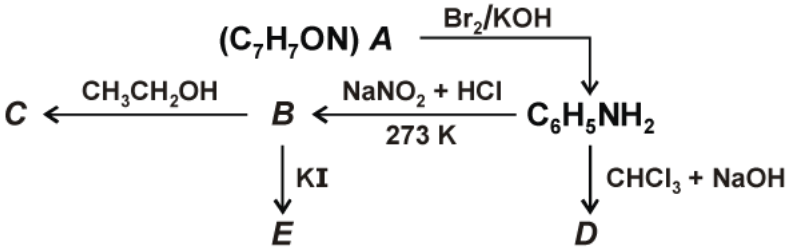
(i) HBF_4/Δ (ii) Cu/HBr

(b) Write the structures of *A*, *B* and *C* in the following reactions:

(i) $C_6H_5NO_2 \xrightarrow{Sn/HCl} A \xrightarrow[273\ K]{NaNO_2 + HCl} B \xrightarrow[\Delta]{H_2O} C$

(ii) $CH_3Cl \xrightarrow{KCN} A \xrightarrow[273\ K]{LiAlH_4} B \xrightarrow[273\ K]{HNO_2} C$

Q88. An aromiatic compound 'A' of molecular formula C_7H_7ON undergoes a series of reactions as shown below. Write the structures of *A*, *B*, *C*, *D* and *E* in the following reactions:



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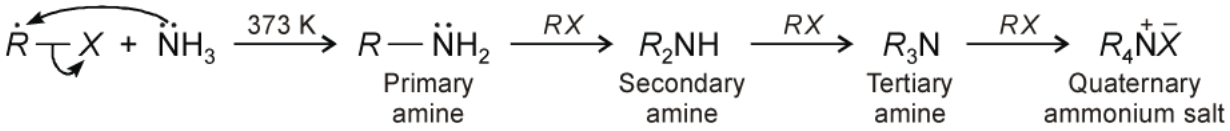
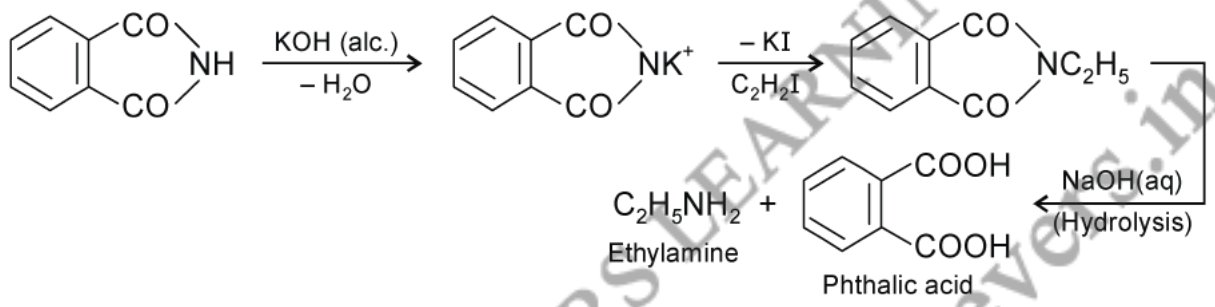
S1. $CH_3CN + 4[H] \xrightarrow{Na + C_2H_5OH} CH_3CH_2NH_2$
Ethanenitrile — Ethanamine

S2. Alkyl halides when treated with ethanolic solution of ammonia give a mixture of primary, secondary tertiary amines and quaternary ammonium salt.



S3. Aromatic amines cannot be prepared by Gabriel phthalimide synthesis becase aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

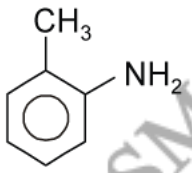
S4. **Gabriel phthalimide synthesis:** In this reaction phthalimide is converted into its potassium salt by treating it with alcoholic potassium hydroxide. Then potassium phthalimide is heated with an alkyl halide to yield an *N*-alkylpthalimide which is hydrolysed to phthalic acid and primary amine by alkaline hydrolysis.



S5. $R-CONH_2 + Br_2 + 4NaOH \longrightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$
Acid amide — 1° amine

S6. $CH_3N(H)C_2H_5$ (*N*, *N*-ethylmethylamine).

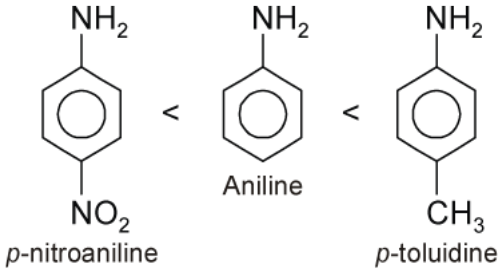
S7. But-3-en-1-amine.

S8.

2-Aminotoluene

S9. $CH_3CH_2NHCH_3$ (*N*-methylethanamine).

S10. 2, 4, 6-Tribromoaniline.

S11. Electron withdrawing group ($-NO_2$) on benzene ring decreases the basicity and electron donating group ($-CH_3$) on benzene ring increases the basicity of compound.



S12. The nitro compounds are highly polar molecules. Due to this polarity they have strong intermolecular dipole-dipole interactions which causes them to have higher boiling points in comparison to the hydrocarbons having almost same molecular mass.

S13. Ethylamine is soluble in water due to formation of intermolecular hydrogen bonds with water molecules. However, in aniline due to large hydrophobic aryl group the extent of hydrogen bonding decreases considerably and hence aniline is insoluble in water.

S14. 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.

S15. 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.

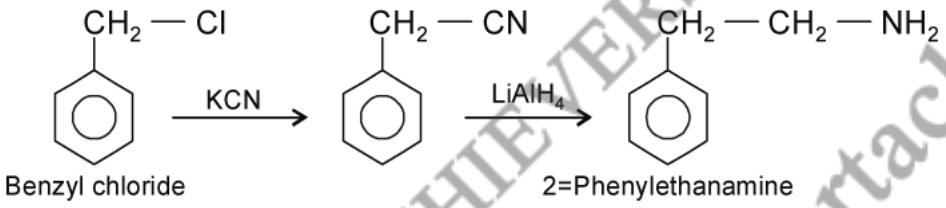
S16. Increasing order of boiling points:

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

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.

S17. 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.

S18.



S19.

$$C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH.$$

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

S20.

$$C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$$

$C_6H_5NH_2$ and $C_6H_5NHCH_3$ are less basic than aliphatic amine $C_6H_5CH_2NH_2$ due to lone pair of nitrogen is in conjugation with benzene ring. But due to + I effect of — CH_3 group in $C_6H_5NHCH_3$, it is more basic than $C_6H_5NH_2$.

S21. Increasing order of basic strength in gaseous state is as follows:

$$C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5N(CH_3)_2$$

As the number of — CH_3 groups (+ I effect) attached to nitrogen increases, its basicity itss basicity will increases.

S22. In case of small alkyl groups like CH_3 the order of basicity is secondary amine > primary amine > tertiary amine due to solvation effect and + I effect of — CH_3 group.

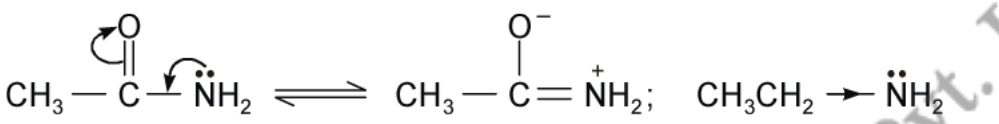
	$(CH_3)_2NH$	>	CH_3NH_2	>	$(CH_3)_3N$
pK_b	3.27		3.38		4.22

S23. CH_3NH_2 is more basic than $C_6H_5NH_2$ because in aniline the lone pair of electrons on nitrogen are involved in resonance.

S24. $CH_3(C_6H_4)NH_2$ is more basic than $C_6H_5NH_2$ due to electron releasing nature of methyl group which pushes electrons towards nitrogen.

S25. Methyl amine is more basic than ammonia because of the presence of electron donating methyl group (+ I effect), which increases the electron density on nitrogen atom.

S26. In CH_3CONH_2, the lone pair of electrons on nitrogen atom is involved in resonance with the carbonyl group. So, the electron pair of nitrogen is not easily available for protonation. Hence, CH_3CONH_2 is a weaker base than $CH_3CH_2NH_2$.

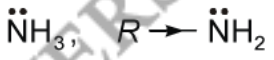


S27. Because the electron pair of nitrogen can coordinate with the electron deficient electrophiles.

S28. In aniline, the lone pair of electrons of N-atom are delocalised over the benzene ring. As a result, electron density on the nitrogen decreases. In contrast, in CH_3 — NH_2, + I effect of — CH_3 group increases the electron density on the N-atom.

Therefore, aniline is a weaker base than methylamie and hence, its pK_b value is higher than that of methylamine.

S29. Electron density of N-atom increases due to the + I effect of the alkyl group. Hence, alkylamines are stronger bases than ammonia.

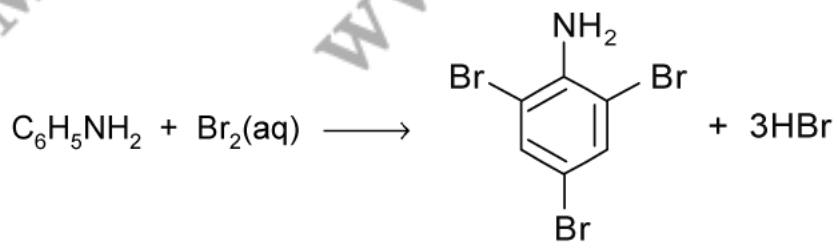


S30. Aniline being an aromatic primary amine on treatment with HNO_2[$NaNO_2$ + HCl (dil.)] at 273 – 278 K followed by treatment with an alkaline solution of β-naphthol gives an orange coloured azo dye. Ethylamine does not give this test.

S31. In aniline, the lone pair of electrons on N-atom is delocalised over benzene ring due to resonance. As a result, electron density on the nitrogen atom decreases. In contrast, in methylamine, + I effect of CH_3 group increases electron density on the nitrogen atom. Therefore, aniline is a weaker base than methylamine hence, its pK_b value is more than that for methylamine.

S32. $(C_6H_5)_2NH < C_6H_5NH_2 < C_6H_5N(CH_3)_2 < CH_3NH_2$

S33.



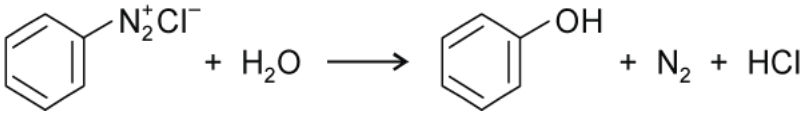
S34. Carbylamine reaction is the reaction in which 1° amines produce a bad smelling compound when treated with chloroform in the presence of alkali.

$$RNH_2 + CHCl_3 + 3KOH \longrightarrow R-N\rightleftarrows C + 3KCl + 3H_2O$$

It is the test for primary amines.

S35. $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

S36.



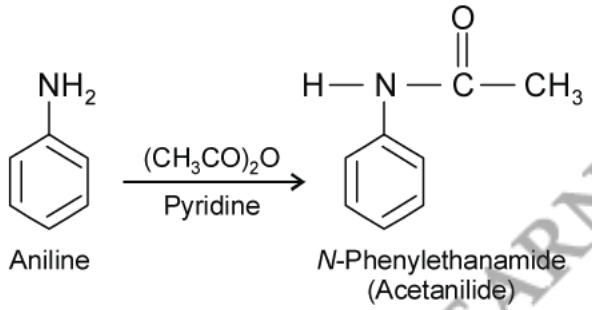
S37. Diazotisation reaction.

S38. $C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow C_6H_6 + N_2 + H_3PO_3 + HCl$

S39. When treated with benzenesulphonyl chloride (Hinsberg's reagent), $(CH_3)_2NH$ forms insoluble *N*, *N*-dialkylbenzene sulphonamide which is insoluble in KOH whereas tertiary amine does not react at all.

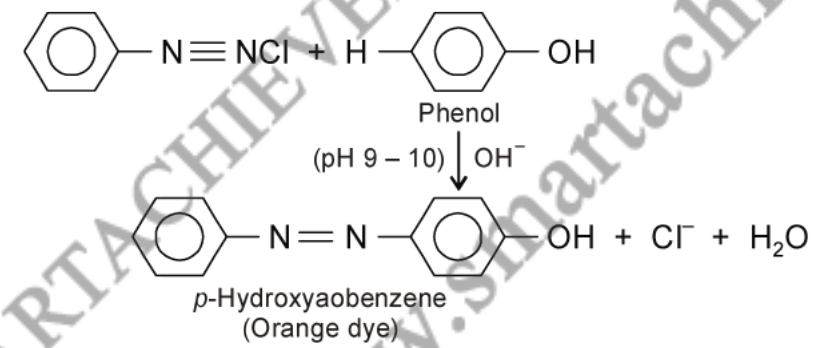
S40. $CH_3CH_2NH_2 \xrightarrow[\text{(ii) } H_2O,\ 273-278\ K]{\text{(i) } NaNO_2/HCl} CH_3CH_2OH \xrightarrow{K_2Cr_2O_7/H^+} CH_3COOH$

S41.

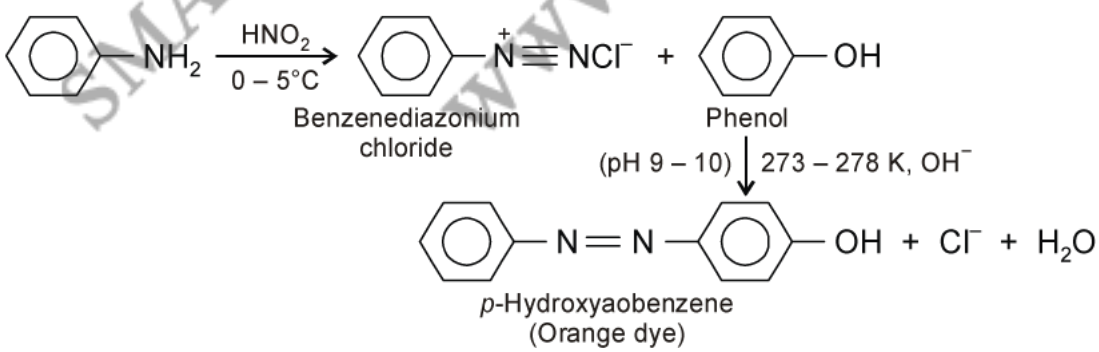


Aniline — *N*-Phenylethanamide (Acetanilide)

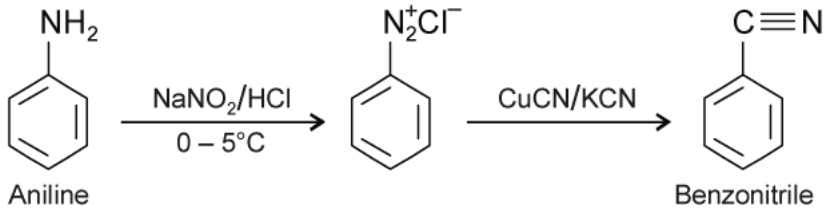
S42. Diazonium salts react with aromatic amines in weakly acidic medium and phenols in weakly alkaline medium to form coloured compounds called azo dyes by coupling at *p*-position of amines or phenols.



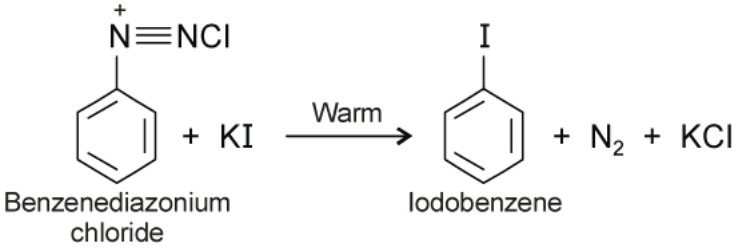
S43.



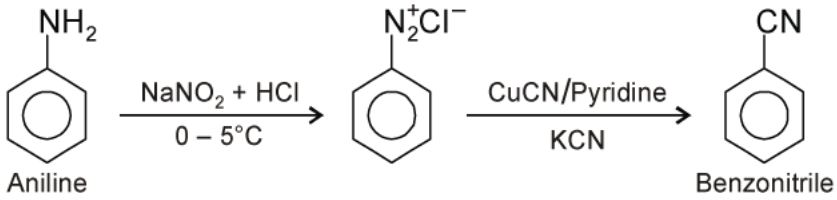
S44.



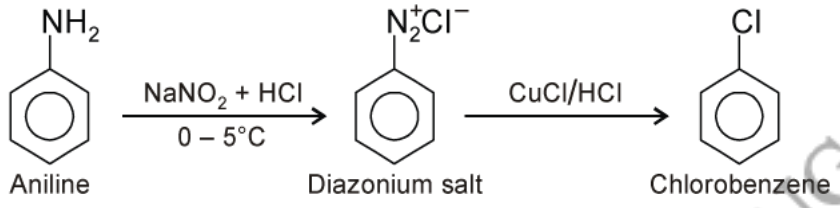
S45.



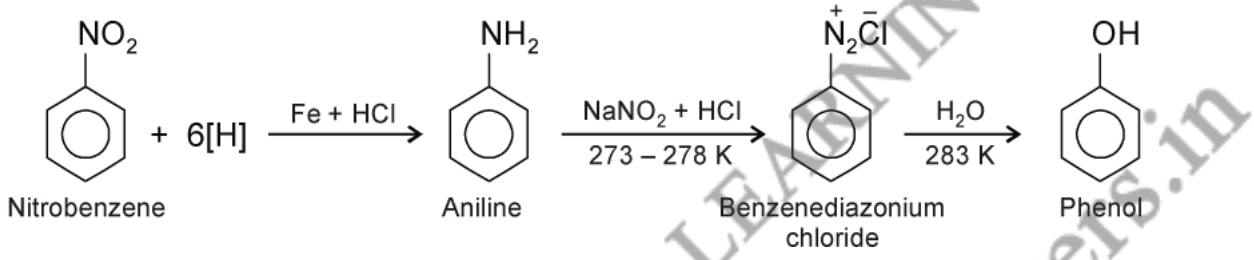
S46.



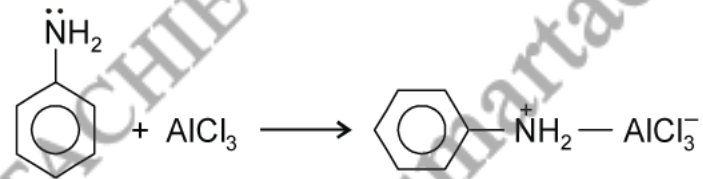
S47.



S48.



S49. (a) 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.

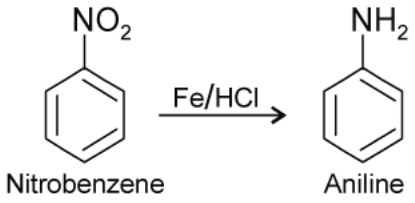


(b) In aquecous solution 2° mine is more basic than 3° amine due to the combination of inductive effect, solvation effect and steric reasons.

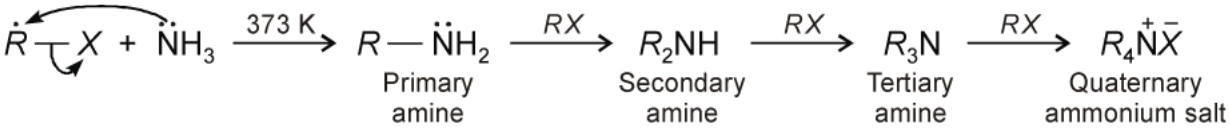
S50. (a) Ethylamine is soluble in water due to formation of intermolecular hydrogen bonds with water molecules. However, in aniline due to large hydrophobic aryl group the extent of hydrogen bonding decreases considerably and hence aniline is insoluble in water.

(b) 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.

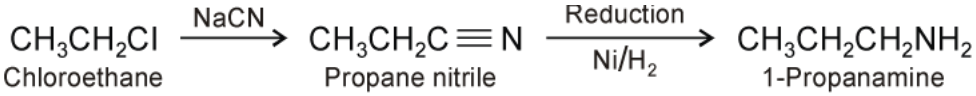
S51. (a)



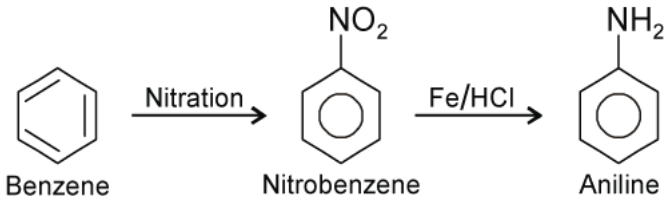
(b)



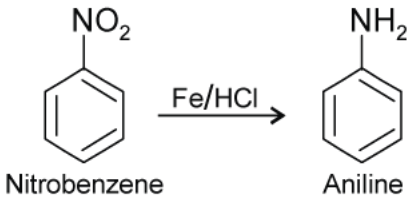
S52. (a)



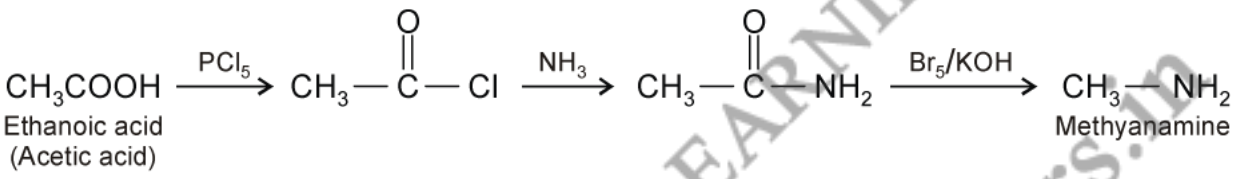
(b)



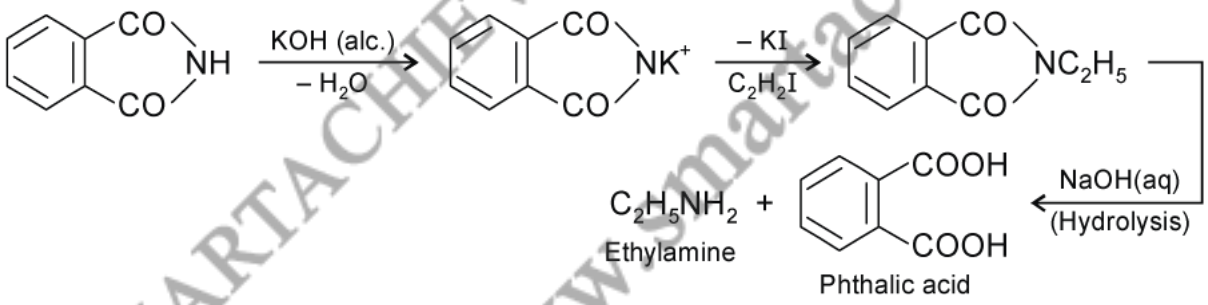
S53. (a)



(b)



S54. (a) **Gabriel phthalimide synthesis:** In this reaction phthalimide is converted into its potassium salt by treating it with alcoholic potassium hydroxide. Then potassium phthalimide is heated with an alkyl halide to yield an *N*-alkylpthalimide which is hydrolysed to phthalic acid and primary amine by alkaline hydrolysis.



(b) $R-CONH_2 + Br_2 + 4NaOH \longrightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$

Acid amide — 1° amine

S55. (a) But-3-en-2-amine. (b) *N*-phenylethanamide.

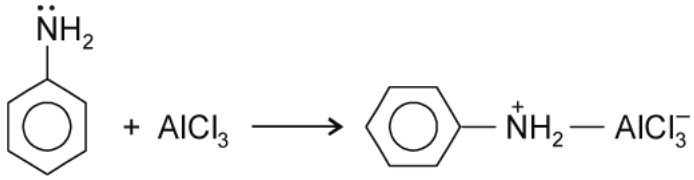
S56. (a) Increasing order of basic strength is

$$C_6H_5NH_2 > C_6H_5N(CH_3)_2 > CH_3NH_2 > (C_2H_5)_2NH$$

(b) Stronger the base lower will be its pK_b value hence, the decreasing order of pK_b values:

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

S57. (a) 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.



(b) In aniline, the lone pair of electrons of N-atom are delocalised over the benzene ring. As a result, electron density on the nitrogen decreases. In contrast, in $CH_3 — NH_2$, $+I$ effect of $— CH_3$ group increases the electron density on the N-atom.

Therefore, aniline is a weaker base than methylamie and hence, its pK_b value is higher than that of methylamine.

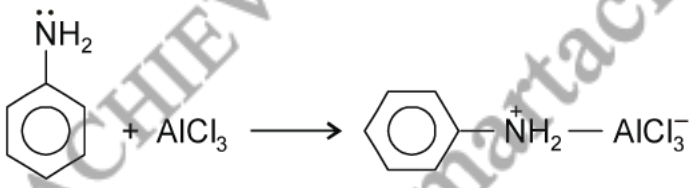
S58. (a) $C_6H_5NO_2 \xrightarrow{Sn + HCl} \underset{A}{C_6H_5NH_2} \xrightarrow[273\ K]{NaNO_2 + HCl} \underset{B}{C_6H_5N_2^+Cl^-} \xrightarrow{H_2O} \underset{C}{C_6H_5OH}$

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

S59. (a) In aniline, the lone pair of electrons of N-atom are delocalised over the benzene ring. As a result, electron density on the nitrogen decreases. In contrast, in $CH_3 — NH_2$, $+I$ effect of $— CH_3$ group increases the electron density on the N-atom.

Therefore, aniline is a weaker base than methylamie and hence, its pK_b value is higher than that of methylamine.

(b) 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.



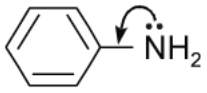
S60. (a) Carbylamine reaction is the reaction in which 1° amines produce a bad smelling compound when treated with chloroform in the presence of alkali.

$$RNH_2 + CHCl_3 + 3KOH \longrightarrow R — N \rightleftarrows C + 3KCl + 3H_2O$$

It is the test for primary amines.

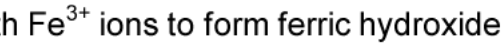
(b) **Acetylation of animes:** The processof introducing an acetyl group $(CH_3 — \overset{\overset{O}{\|}}{C} —)$ into a molecule is called acetylation.

S61. (a) Benzene ring in aromatic amines is highly activated. Due to the displacement of lone pair of nitrogen towards the ring. It results, increase in the electron density on the ring. This facilitates the electrophilic attack on the ring.



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

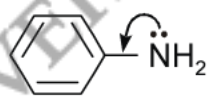
These OH^- ions react with Fe^{3+} ions to form ferric hydroxide.



S62. (a) Loss of proton from amines gives RNH^- ion whereas loss of proton from alcohol forms alkoxide ion. Since, O is more electronegative than N therefore, RO^- can accommodate the negative charge more easily than RN^-H. Further, O — H bond is more polar than N — H bond. Hence, amines are less acidic than alcohols.

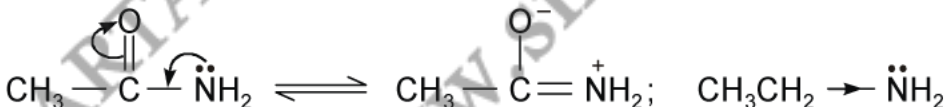
(b) In aromatic amines, the lone pair of electrons present on nitrogen takes part in resonance and hence, not available for donation. However, in aliphatic amines, the lone pair is available for donation. That's why aliphatic amines are more basic than aromatic amines.

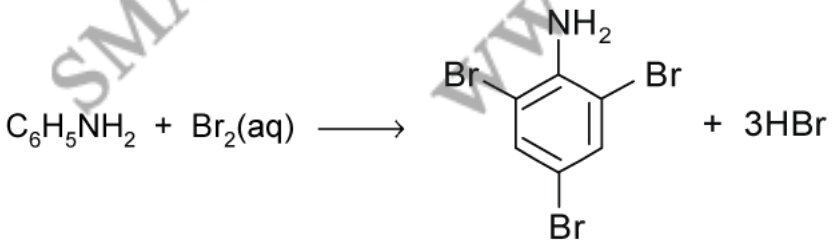
S63. (a) Benzene ring in aromatic amines is highly activated. Due to the displacement of lone pair of nitrogen towards the ring. It results, increase in the electron density on the ring. This facilitates the electrophilic attack on the ring.



(b) In CH_3CONH_2, the lone pair of electrons on nitrogen atom is involved in resonance with the carbonyl group. So, the electron pair of nitrogen is not easily available for protonation. Hence, CH_3CONH_2 is a weaker base than $CH_3CH_2NH_2$.

S64.



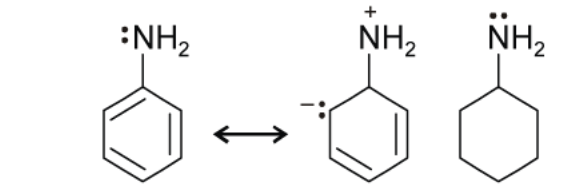
(a) 

(b) $CH_3 — NH_2$

Mathanamine

S65. (a) Aniline is weaker base than cyclohexylamine because of resonance. Due to electromeric effect, the lone pair on nitrogen is attracted by benzene ring.

Hence, donar tendency of $-\ddot{N}H_2$ group decreses. There is no resonance in cyclohezylamine. Electron repelling nature of cyclohexyl group further increases the donor property of NH_2 group. So, cyclohexylamine is a stronger base.

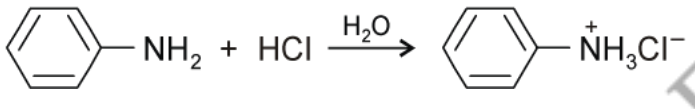


Aniline (Resonance structures) Cylohexylamine (No resonance)

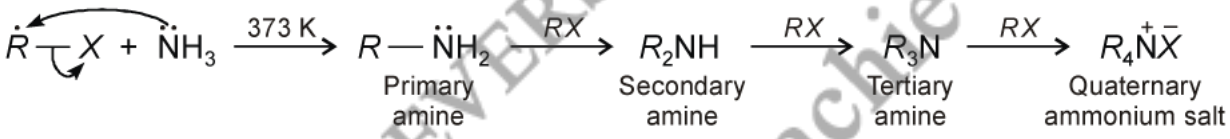
(b) The ammonolysis of alkyl halides with ammonia is a nucleophilic substitution reaction in which ammonia acts as a nucleophile by donating the electron pair on nitrogen atom to form primary amine as the initial product. Now, the primary amine can act as a nucleophile and combine with alkyl halide (if available) to give secondary amine and the reaction continues in the same way to form tertiary amine and finally quaternary ammonium salt. Thus, a mixture of products is formed and it is not possible to separate individual amines from the mixture.

$$R-X \xrightarrow[-HX]{NH_2} R-NH_2 \xrightarrow[-HX]{R-X} R_2NH \xrightarrow[-HX]{R-X} R_3N \xrightarrow[-HX]{R-X} R_4N^+X^-$$

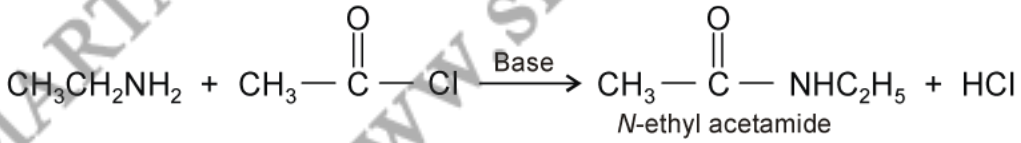
S66. (a) $CH_3-CH_2-NH_2 + CHCl_3 + 3KOH \longrightarrow CH_3-CH_2-NC + 3KCl + 3H_2O$

(b) 

S67. (a) Alkyl halides when treated with ethanolic solution of ammonia give a mixture of primary, secondary tertiary amines and quaternary ammonium salt.



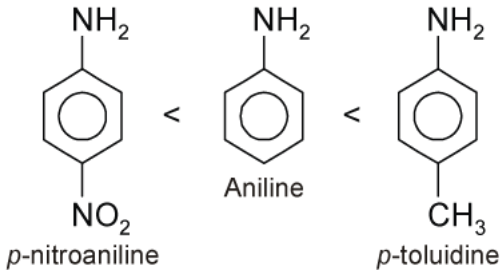
(b) **Acetylation of animes:** The processof introducing an acetyl group ($CH_3-\overset{O}{\overset{\|}{C}}-$) into a molecule is called acetylation.



S68. (a) $C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$

$C_6H_5NH_2$ and $C_6H_5NHCH_3$ are less basic than aliphatic amine $C_6H_5CH_2NH_2$ due to lone pair of nitrogen is in conjugation with benzene ring. But due to + *I* effect of $-CH_3$ group in $C_6H_5NHCH_3$, it is more basic than $C_6H_5NH_2$.

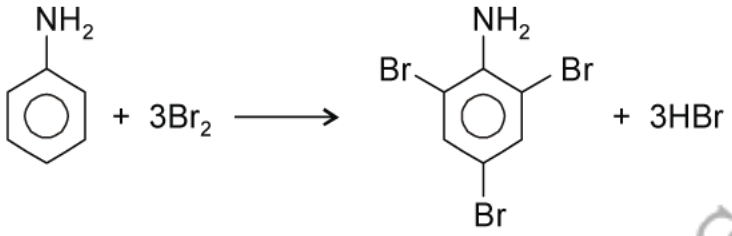
(b) Electron withdrawing group ($-NO_2$) on benzene ring decreases the basicity and electron donating group ($-CH_3$) on benzene ring increases the basicity of compound.



S69. (a) Methyl amine gives carbylamine test, *i.e.*, on treatment with alc. KOH and chloroform, followed by heating it gives offensive odour of methyl isocyanide. Dimethyl amine does not give thai test.

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

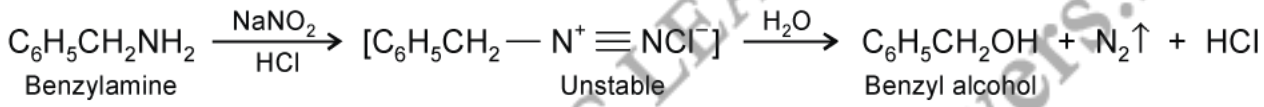
S70. (a) Aniline gives white or brown precipitate with bromine water.



(White ppt.)

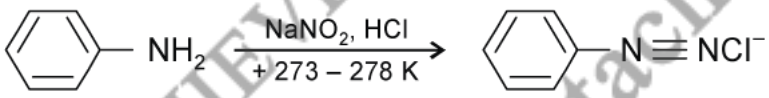
Ethylamine does not react with bromine water.

(b) **Aniline and benzylamin:** Benzylamine reacts with nitrous acid to form a diazonium salt which is unstable at low temperature and decomposes with evolution of N_2 gas.



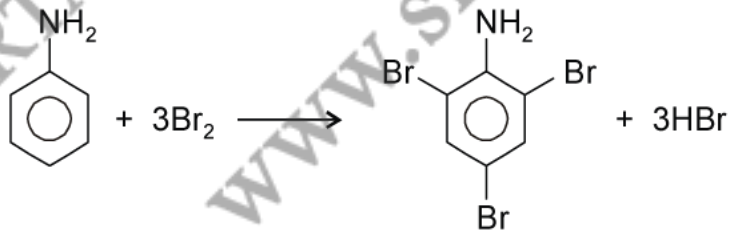
Benzylamine — Unstable — Benzyl alcohol

Aniline reacts with HNO_2 to form benzene diazonium chloride which is stable at 273 – 278 K and hence does not evolve N_2 gas. It forms orange dye with 2-naphthol.



Aniline — Benzenediazonium chloride

S71. (a) Aniline gives white or brown precipitate with bromine water.

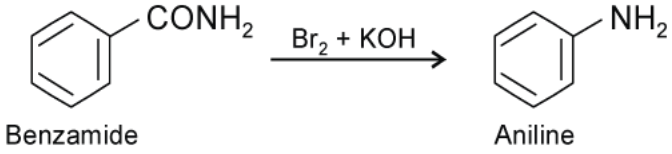


(White ppt.)

Ethylamine does not react with bromine water.

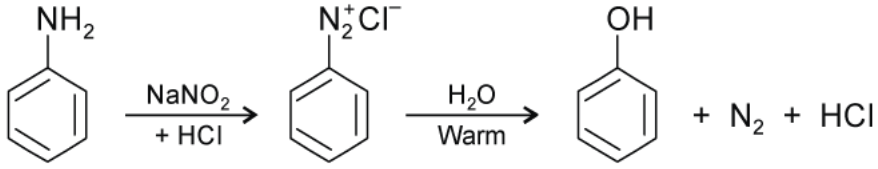
(b) When heated with an alcoholic solution of KOH and $CHCl_3$, ethylamine gives foul smelling ethyl isocyanide. Dimethylamine does not give this test.

S72. (a)



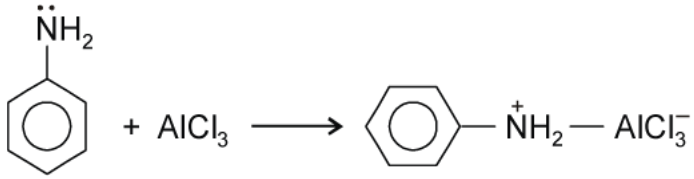
Benzamide Aniline

(b)



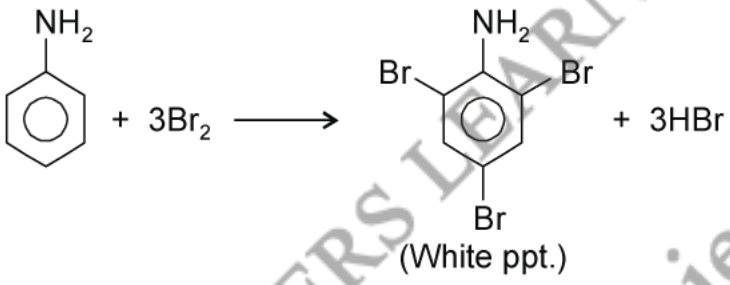
Aniline Phenol

S73. (a) 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.



(b) In aromatic amines, the lone pair of electrons present on nitrogen takes part in resonance and hence, not available for donation. However, in aliphatic amines, the lone pair is available for donation. That's why aliphatic amines are more basic than aromatic amines.

S74. (a) Aniline gives white or brown precipitate with bromine water.

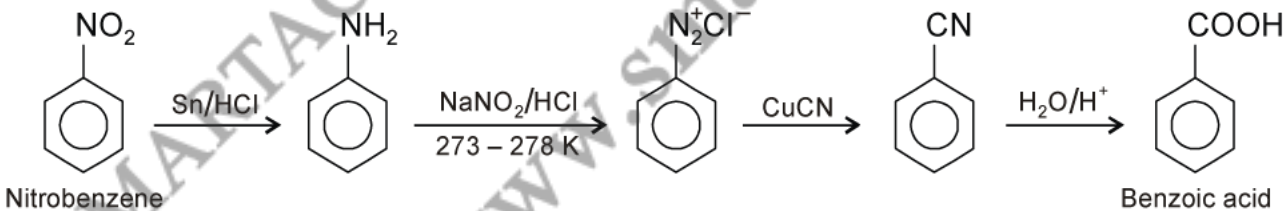


(White ppt.)

Ethylamine does not react with bromine water.

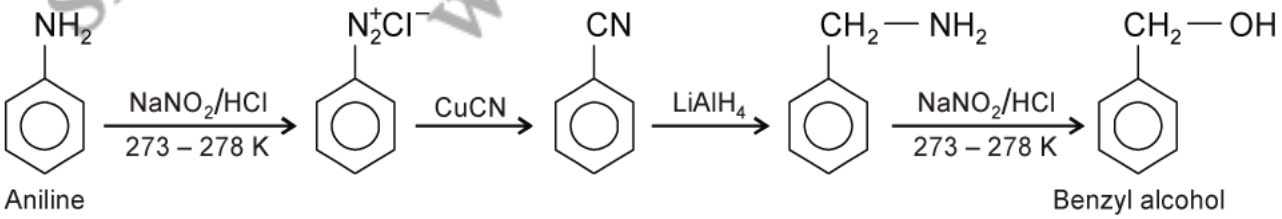
(b) Aniline gives carbylamine test, *i.e.*, on treatment with alc. KOH and chloroform follwed by heating it gives offensive odour of phenylisocyanide but *N*-methylaniline being secondary amine, does not show this test.

S75. (a)



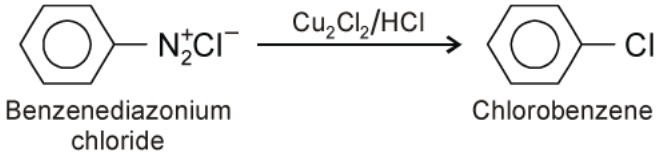
Nitrobenzene Benzoic acid

(b)

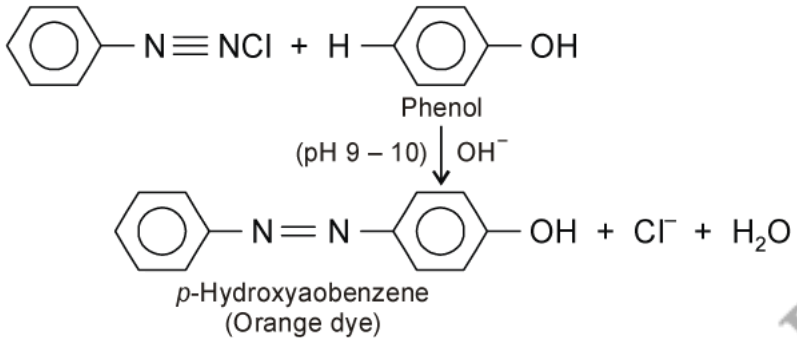


Aniline Benzyl alcohol

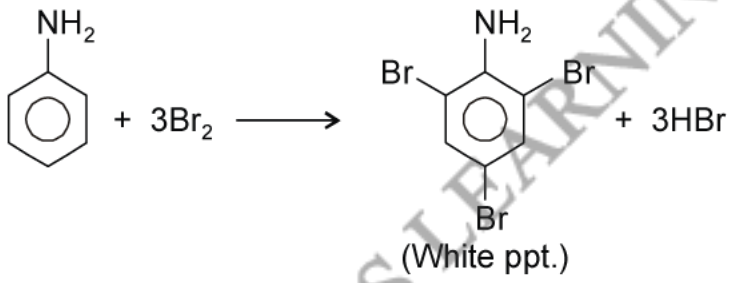
S76. (a) **Sandmeyer reaction:** By this reaction nulceophiles like Cl^-, Br^-, CN^- etc. can easily be introduced in the benzene ring by treating the diazonium salt solution with corresponding halogen acid in the presence of CU(I) ion.



(b) Diazonium salts react with aromatic amines in weakly acidic medium and phenols in weakly alkaline medium to form coloured compounds called azo dyes by coupling at *p*-position of amines or phenols.



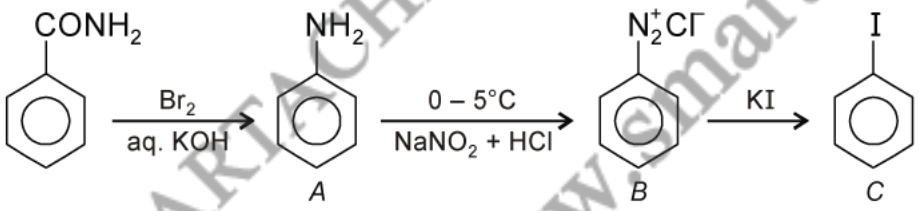
S77. (a) Aniline gives white or brown precipitate with bromine water.



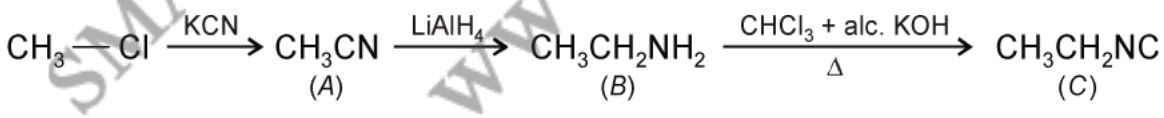
Ethylamine does not react with bromine water.

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

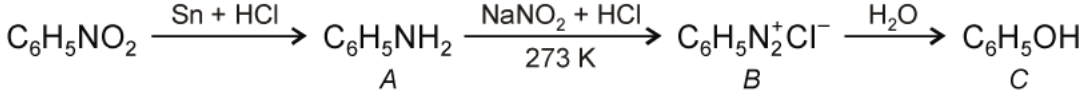
S78. (a)



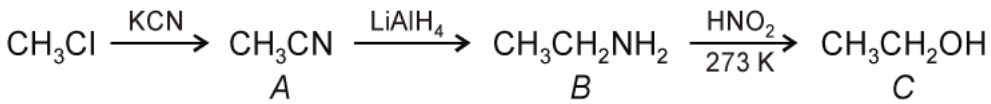
(b)



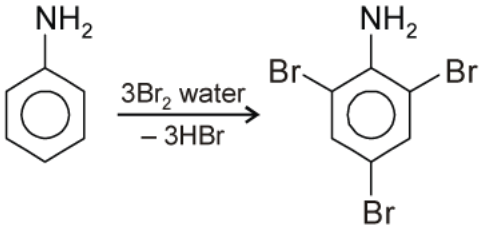
S79. (a)



(b)

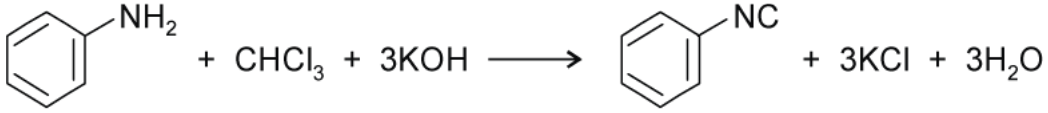


S80. (a)



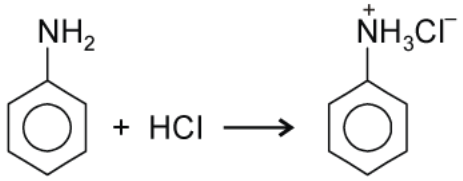
2,4,6-Tribromoaniline

(b)



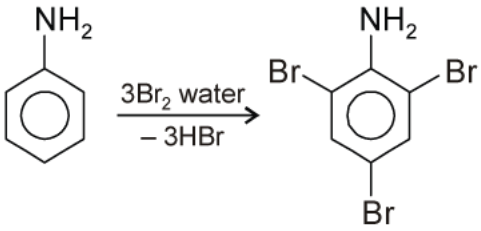
Aniline Phenyl isocyanide

(c)



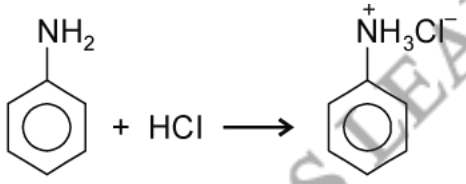
Anilinium chloride

S81. (a)



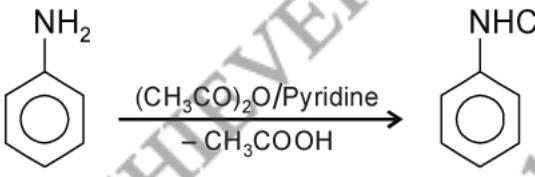
2,4,6-Tribromoaniline

(b)



Anilinium chloride

(c)



Acetanilide

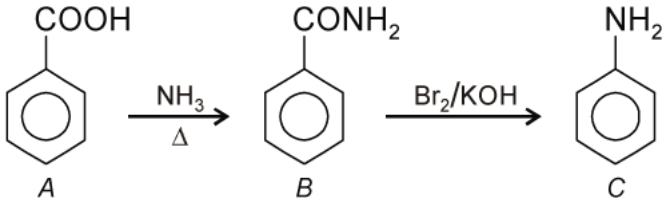
S82. (a) $A = CH_3CH_2CN$; $B = CH_3CH_2CH_2NH_2$; $C = CH_3CH_2CH_2OH$

(b) $CH_3COOH \xrightarrow[\Delta]{NH_3} \underset{(A)}{CH_3CONH_2} \xrightarrow{Br_2 + KOH} \underset{(B)}{CH_3NH_2} \xrightarrow{CHCl_3 + NaOH} \underset{(C)}{CH_3CN}$

S83. (a) $CH_3Br \xrightarrow{KCN} \underset{(A)}{CH_3CN} \xrightarrow{LiAlH_4} \underset{(B)}{CH_3CH_2NH_2} \xrightarrow[273\ K]{HNO_2} \underset{(C)}{CH_3CH_2OH}$

(b) $CH_3COOH \xrightarrow[\Delta]{NH_3} \underset{(A)}{CH_3CONH_2} \xrightarrow{Br_2 + KOH} \underset{(B)}{CH_3NH_2} \xrightarrow{CHCl_3 + NaOH} \underset{(C)}{CH_3CN}$

S84. 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 sompound '*B*' can be an amide. As '*B*' is obtained from compound '*A*' by reaction with ammonia followed by heating so, compound '*A*' could be an aromatic acid. Formula of compound 'C' shows it to be aniline, then '*B*' is benzamide and compound '*A*' is benzoic acid. The sequence of reactions can be written as follows:



S85. (a) $C_6H_5N_2^+Cl^- \xrightarrow{CuCN} \underset{\text{Benzonitrile}}{\underset{A}{C_6H_5CN}} \xrightarrow{H_2O/H^+} \underset{\text{Benzoic acid}}{\underset{B}{C_6H_5COOH}} \xrightarrow[\Delta]{NH_3} \underset{\text{Benzamid}}{\underset{C}{C_6H_5CONH_2}}$

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

S86. (a) In aniline, the lone pair of electrons of N-atom are delocalised over the benzene ring. As a result, electron density on the nitrogen decreases. In contrast, in $CH_3 — NH_2$, $+I$ effect of $— CH_3$ group increases the electron density on the N-atom.

Therefore, aniline is a weaker base than methylamie and hence, its pK_b value is higher than that of methylamine.

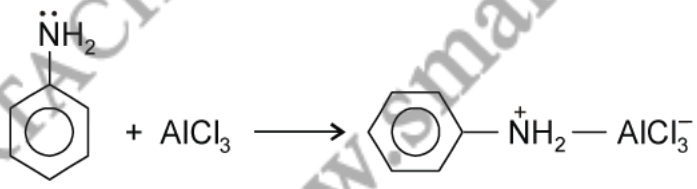
(b) Methylamine forms hydroxide ions when dissolved in water due to the following acid-base equilibrium.

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

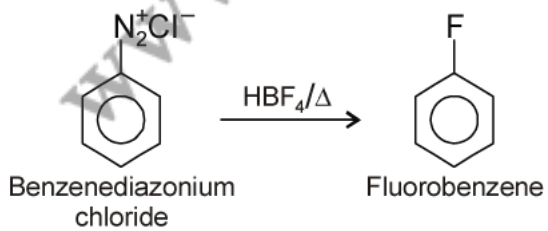
These OH^- ions react with Fe^{3+} ions to form ferric hydroxide.

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

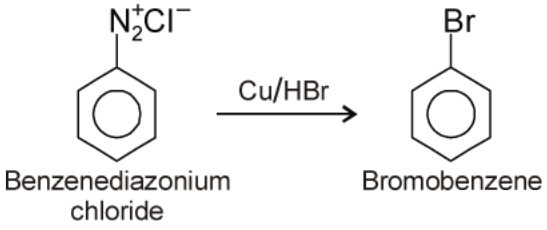
(c) In Friedel-Crafts reaction, $AlCl_3$ is added as a catalyst which is a Lewis acid. It forms a salt with aniline due to which the nitrogen of aniline acquires positive charge. This positively charged nitrogen acts as a strong deactivating group, hence aniline does not undergo Friedel-Crafts reaction.



S87. (a) (i)



(ii)



(b) (i) $C_6H_5NO_2 \xrightarrow{Sn + HCl} C_6H_5NH_2 \xrightarrow[273\ K]{NaNO_2 + HCl} C_6H_5N_2^+Cl^- \xrightarrow{H_2O} C_6H_5OH$

A *B* *C*

(ii) $CH_3Cl \xrightarrow{KCN} CH_3CN \xrightarrow{LiAlH_4} CH_3CH_2NH_2 \xrightarrow[273\ K]{HNO_2} CH_3CH_2OH$

A *B* *C*

S88.