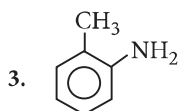


AMINES

Detailed Solutions

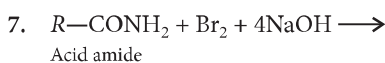
- 2, 4, 6-Tribromoaniline
- CH₃CH₂NHCH₃ (*N*-methylethanamine)



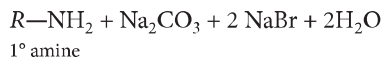
2-Aminotoluene

- But-3-en-1-amine
- CH₃N—C₂H₅ (*N,N*-ethylmethylamine)

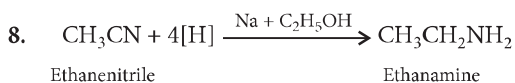
- (a) But-3-en-2-amine
(b) *N*-phenylethanamide



Acid amide



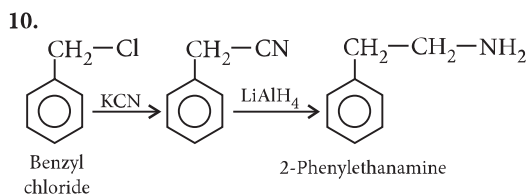
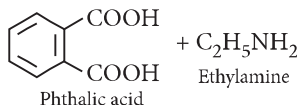
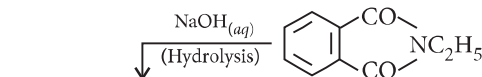
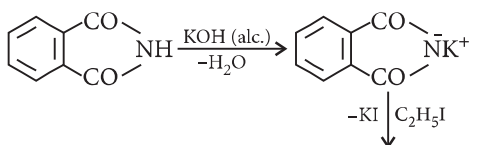
1° amine



Ethanenitrile

Ethanamine

9. 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*-alkylphthalimide which is hydrolysed to phthalic acid and primary amine by alkaline hydrolysis.

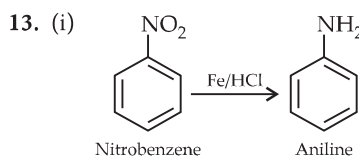
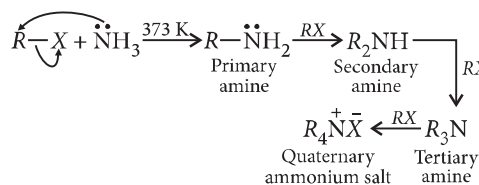


Benzyl chloride

2-Phenylethanamine

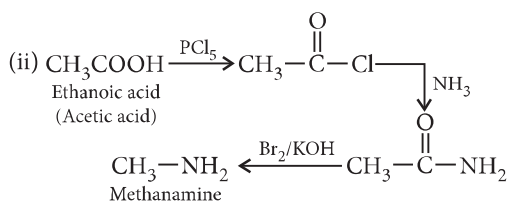
11. Aromatic amines cannot be prepared by Gabriel phthalimide synthesis because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

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

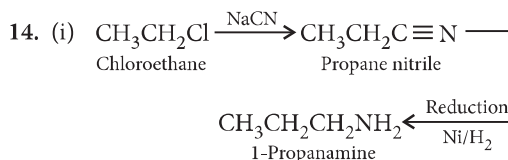


Nitrobenzene

Aniline


 Ethanoic acid
(Acetic acid)

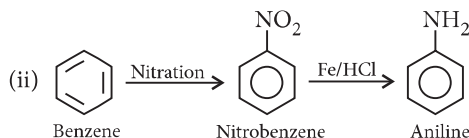
Methanamine



Chloroethane

Propane nitrile

1-Propanamine



Benzene

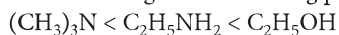
Nitrobenzene

Aniline

- (i) Refer to answer 9.
- (ii) Refer to answer 7.
- (i) Refer to answer 13(i).
- (ii) Refer to answer 12.

17. 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.

18. Increasing order of boiling points :



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.

19. Refer to answer 17.

20. Refer to answer 17.

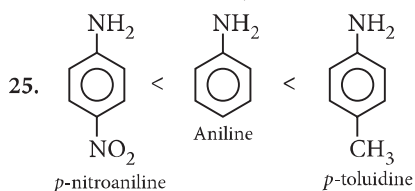
21. Ethylamine is soluble in water due to formation of intermolecular hydrogen bonds with water molecules. However, in aniline due to large hydrophobic aryl group the extent of hydrogen bonding decreases considerably and hence aniline is insoluble in water.

22. 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.

23. (i) Refer to answer 21.

(ii) Refer to answer 17.

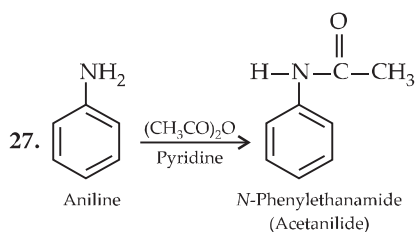
24. When treated with benzenesulphonyl chloride (Hinsberg's reagent), $(CH_3)_2NH$ forms insoluble N,N -dialkylbenzene sulphonamide which is insoluble in KOH whereas tertiary amine does not react at all.



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.



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



$C_6H_5NH_2$ 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 $C_6H_5NH_2$.

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



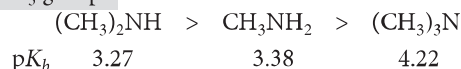
As the number of $-CH_3$ groups ($+I$ effect) attached to nitrogen increases, its basicity will increase.

30. 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.

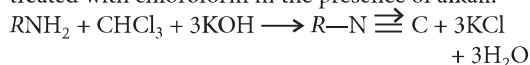
31. $CH_3(C_6H_4)NH_2$ is more basic than $C_6H_5NH_2$ due to electron releasing nature of methyl group which pushes electrons towards nitrogen.

32. 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.

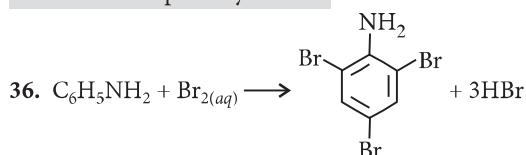
33. In case of small alkyl groups like CH_3 the order of basicity is secondary amine $>$ primary amine $>$ tertiary amine due to solvation effect and $+I$ effect of $-CH_3$ group.

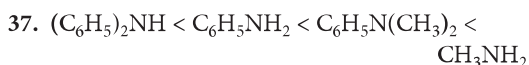


35. Carbylamine reaction is the reaction in which 1° amines produce a bad smelling compound when treated with chloroform in the presence of alkali.



It is the test for primary amines.

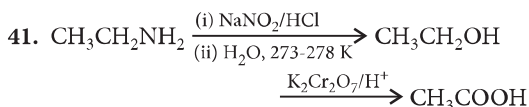
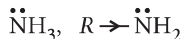




38. In aniline, the lone pair of electrons on N-atom is delocalised over benzene ring due to resonance. As a result, electron density on the nitrogen atom decreases. In contrast, in methylamine, +I-effect of CH_3 group increases electron density on the nitrogen atom. Therefore, aniline is a weaker base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

39. 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.

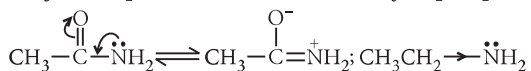
40. Electron density of N-atom increases due to the +I effect of the alkyl group. Hence, alkylamines are stronger bases than ammonia.



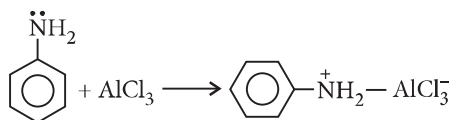
42. In aniline, the lone pair of electrons of N-atom are delocalised over the benzene ring. As a result, electron density on the nitrogen decreases. In contrast, in CH_3-NH_2 , +I effect of $-CH_3$ group increases the electron density on the N-atom. Therefore, aniline is a weaker base than methylamine and hence, its pK_b value is higher than that of methylamine.

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

44. 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 $CH_3CH_2NH_2$.



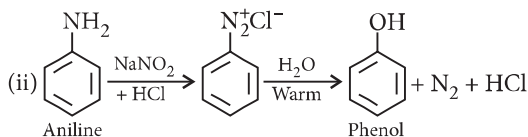
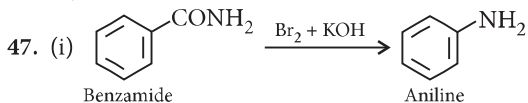
45. (i) In Friedel - Crafts reaction, $AlCl_3$ is added as a catalyst which is a Lewis acid. It forms a salt with aniline due to which the nitrogen of aniline acquires positive charge. This positively charged nitrogen acts as a strong deactivating group, hence aniline does not undergo Friedel - Crafts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



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

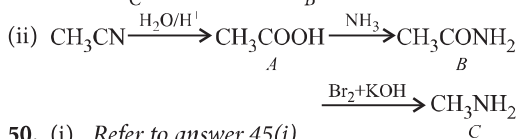
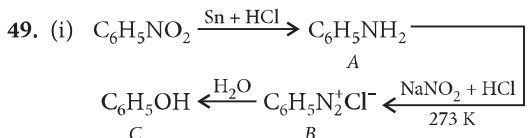
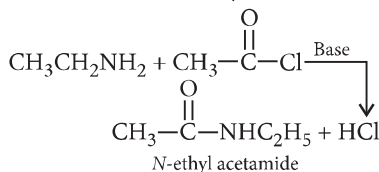
46. (i) Refer to answer 28.

(ii) Refer to answer 25.



48. (i) Refer to answer 12.

(ii) Acetylation of amines : The process of introducing an acetyl group ($CH_3-C(=O)-$) into a molecule is called acetylation.

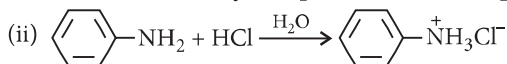
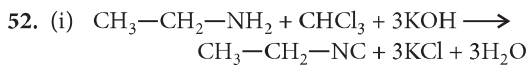
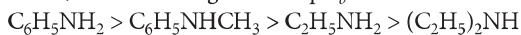


50. (i) Refer to answer 45(i).

(ii) Refer to answer 42.

51. (i) Increasing order of basic strength is $C_6H_5NH_2 < C_6H_5N(CH_3)_2 < CH_3NH_2 < (C_2H_5)_2NH$

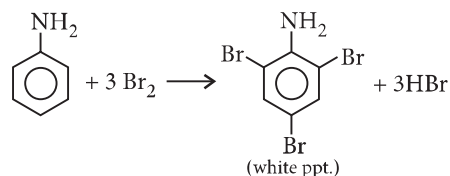
(ii) Stronger the base lower will be its pK_b value hence, the decreasing order of pK_b values :



53. (i) Refer to answer 36.

(ii) $\text{CH}_3\text{—NH}_2$
Methanamine

54. (i) Aniline gives white or brown precipitate with bromine water.

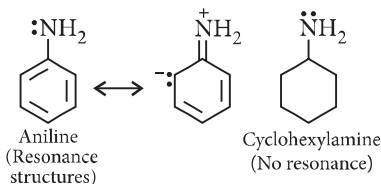


Ethylamine does not react with bromine water.

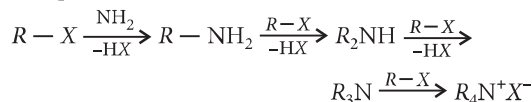
(ii) When heated with an alcoholic solution of KOH and CHCl_3 , ethylamine gives foul smelling ethyl isocyanide. Dimethylamine does not give this test.

55. (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 $\text{—}\ddot{\text{N}}\text{H}_2$ 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.

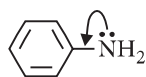


(ii) The ammonolysis of alkyl halides with ammonia is a nucleophilic substitution reaction in which ammonia acts as a nucleophile by donating the electron pair on nitrogen atom to form primary amine as the initial product. Now, the primary amine can act as a nucleophile and combine with alkyl halide (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.



56. (i) Benzene ring in aromatic amines is highly activated. Due to the displacement of lone pair of nitrogen towards the ring. It results, increase in

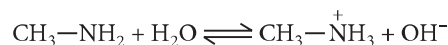
the electron density on the ring. This facilitates the electrophilic attack on the ring.



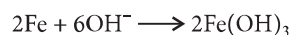
(ii) Refer to answer 44.

57. (i) Refer to answer 55(i).

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

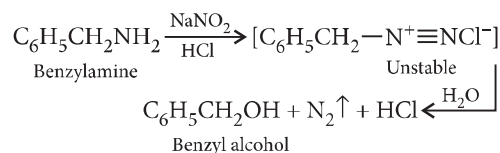


These OH^- ions react with Fe^{3+} ions to form ferric hydroxide.

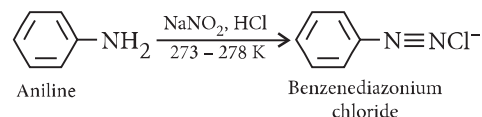


58. (i) Refer to answer 54 (i).

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



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.



59. (i) 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 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.

60. (i) Refer to answer 35.

(ii) Refer to answer 48(ii).

61. (i) Refer to answer 42(ii).

(ii) Refer to answer 45(i).

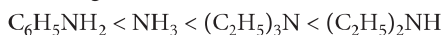
62. (i) Refer to answer 54(i).

(ii) Refer to answer 59(i).

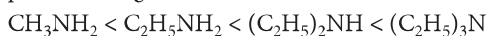
63. (i) Loss of proton from amines gives RNH^- ion whereas loss of proton from alcohol forms alkoxide ion. Since, O is more electronegative than N therefore, RO^- can accommodate the negative charge more easily than RN^-H . Further, O—H bond is more polar than N—H bond. Hence, amines are less acidic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

(ii) 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.

64. (i) The increasing order of basic strength in water of the given amines and ammonia follows the following order :



(ii) The increasing order of basic strength in gas phase of the given amines follows the order :

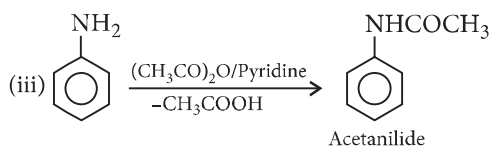
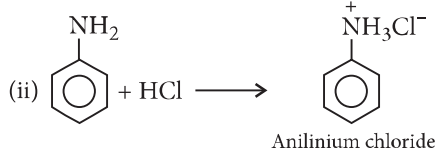
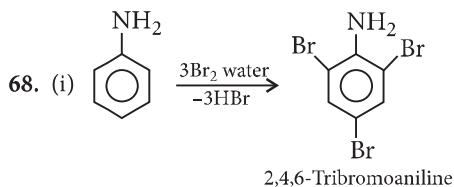
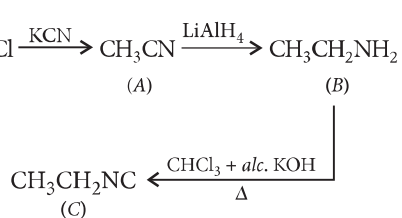
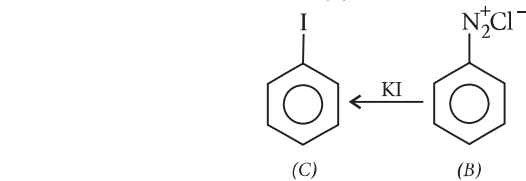
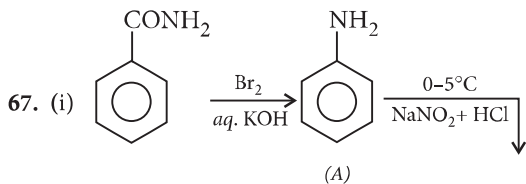


65. (i) Refer to answer 45(i).

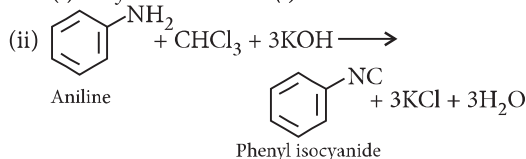
(ii) Refer to answer 63(ii).

66. (i) Refer to answer 54(i).

(ii) Refer to answer 59(ii).

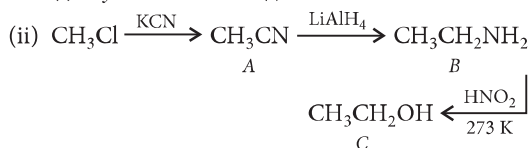


69. (i) Refer to answer 68(i).

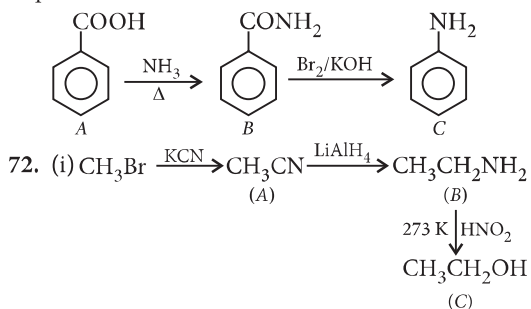


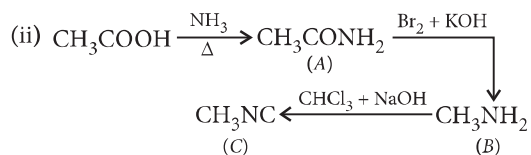
(iii) Refer to answer 68(ii).

70. (i) Refer to answer 49(i).



71. 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. 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 :





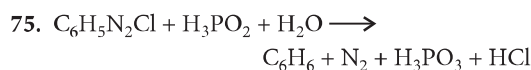
73. (i) A = $\text{CH}_3\text{CH}_2\text{CN}$
 B = $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$
 C = $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$

(ii) Refer to answer 72(ii).

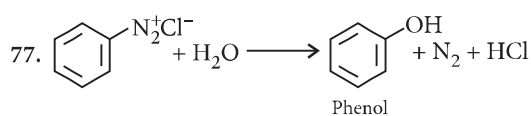
74. (i) Refer to answer 42.

(ii) Refer to answer 57(ii).

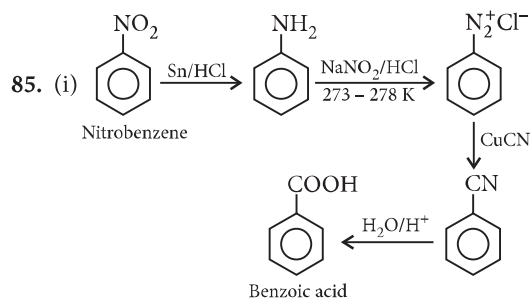
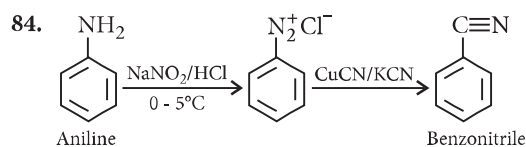
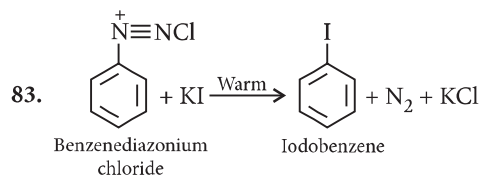
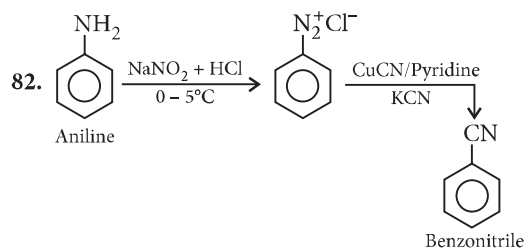
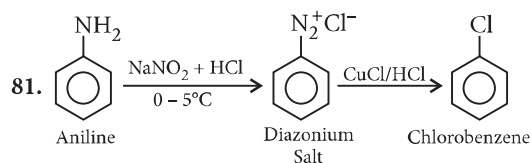
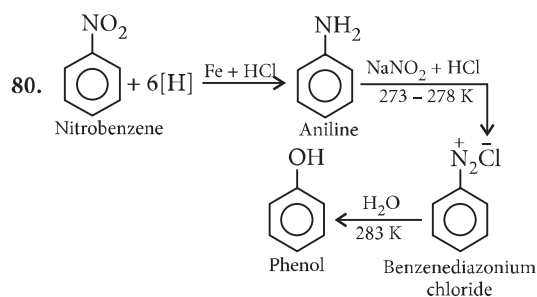
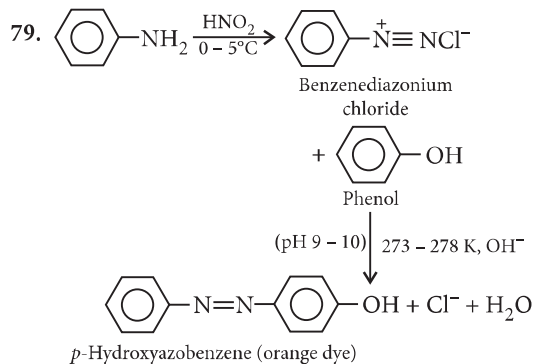
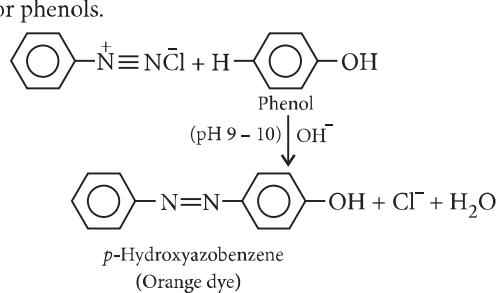
(iii) Refer to answer 45(i).

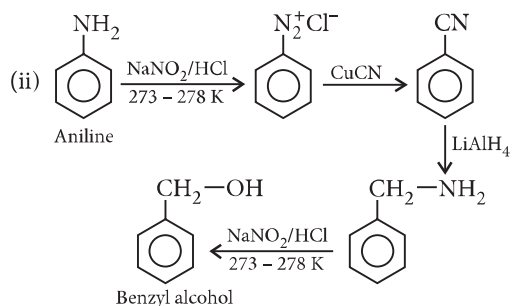


76. Diazotisation reaction.

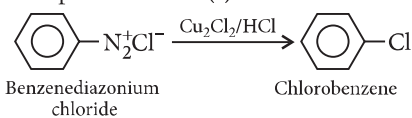


78. Diazonium salts react with aromatic amines in weakly acidic medium and phenols in weakly alkaline medium to form coloured compounds called azo dyes by coupling at *p*-position of amines or phenols.

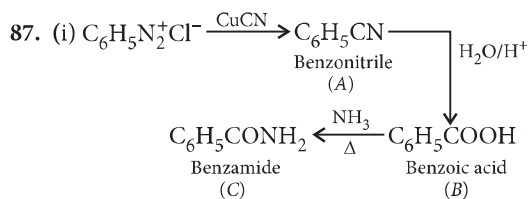




86. (i) Sandmeyer reaction : By this reaction nucleophiles like Cl^- , Br^- , CN^- etc. can easily be introduced in the benzene ring by treating the diazonium salt solution with corresponding halogen acid in the presence of Cu(I) ion.

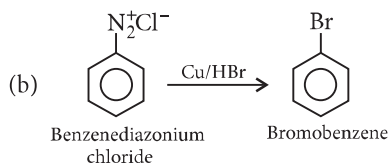
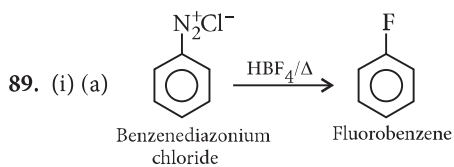
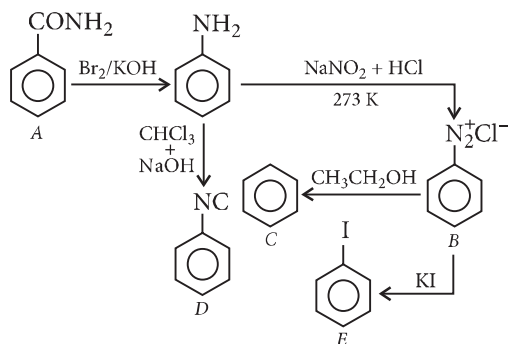


(ii) Refer to answer 78.



(ii) Refer to answer 49(i).

88.



(ii) (a) Refer to answer 49(i).

(b) Refer to answer 70(ii).

