



NCERT EXERCISES

13.1. Write IUPAC names of the following compounds and classify them into primary, secondary and tertiary amines.

- (i) $(\text{CH}_3)_2\text{CHNH}_2$
- (ii) $\text{CH}_3(\text{CH}_2)_2\text{NH}_2$
- (iii) $\text{CH}_3\text{NHCH}(\text{CH}_3)_2$
- (iv) $(\text{CH}_3)_3\text{CNH}_2$
- (v) $\text{C}_6\text{H}_5\text{NHCH}_3$
- (vi) $(\text{CH}_3\text{CH}_2)_2\text{NCH}_3$
- (vii) $m\text{-BrC}_6\text{H}_4\text{NH}_2$

Ans:

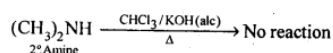
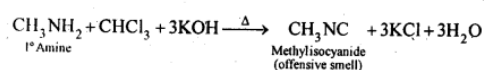
- (i) Propan-2-amine (1°)
- (ii) Propan-1-amine (1°)
- (iii) N-Methylpropan-2-amine (2°)
- (iv) 2-Methylpropan-2-amine (1°)
- (v) N-Methylbenzenamine or N-methylaniline (2°)
- (vi) N-Ethyl-N-methylethanamine (3°)
- (vii) 3-Bromobenzenamine or 3-bromoaniline (1°)

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

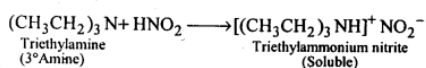
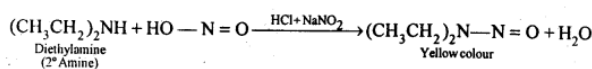
- (i) Methylamine and dimethylamine
- (ii) Secondary and tertiary amines
- (iii) Ethylamine and aniline
- (iv) Aniline and benzylamine
- (v) Aniline and N-Methylaniline.

Ans:

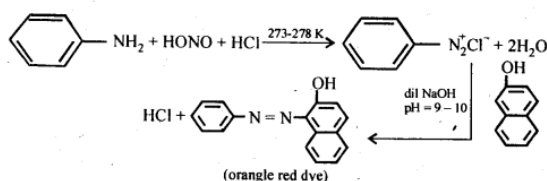
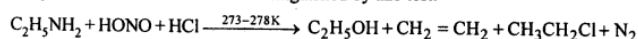
(i) Methylamine and dimethylamine can be distinguished by carbylamine test.



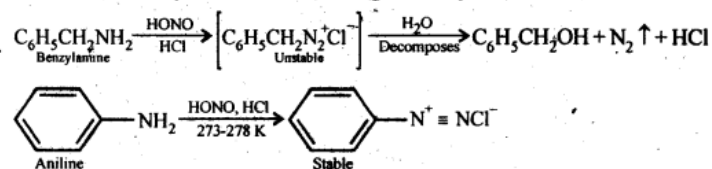
(ii) Secondary and tertiary amine can be distinguished by Liebermann's nitroamine test. Secondary amines give Liebermann nitroamine test while tertiary amines do not.



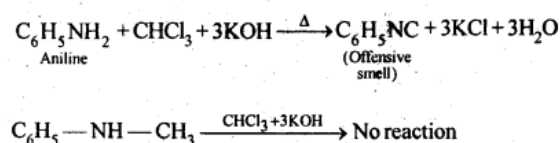
(iii) Ethylamine and aniline can be distinguished by azo test:



(iv) Aniline and benzylamine can be distinguished by nitrous acid test:



(v) Aniline and N-methylaniline can be distinguished by carbylamine test:



13.3. Account for the following

- (i) pK_b of aniline is more than that of methylamine
- (ii) Ethylamine is soluble in water whereas aniline is not.
- (iii) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide.
- (iv) Although amino group is o and p - directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m-nitroaniline.
- (v) Aniline does not undergo Friedel-Crafts reaction.
- (vi) Diazonium salts of aromatic amines are more stable than those of aliphatic amines.
- (vii) Gabriel phthalimide synthesis is preferred for synthesising primary amines.

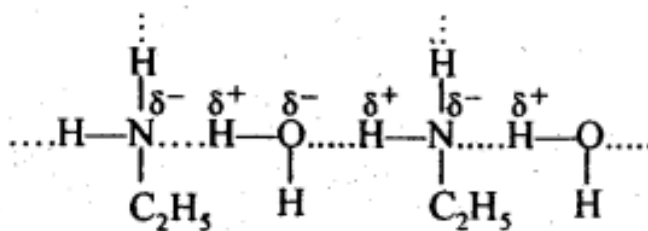
Ans:

(i) In aniline, the lone pair of electrons on the N-atom is delocalised over the benzene ring.

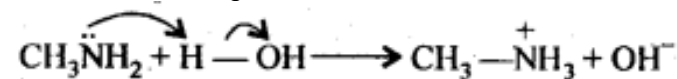
As a result, electron density on the nitrogen atom decreases.

Whereas in CH_3NH_2 , +I-effect of $-\text{CH}_3$ 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.

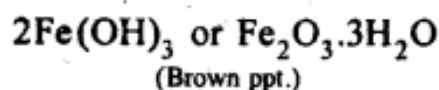
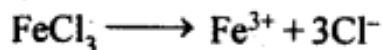
(ii) Ethylamine dissolves in water due to intermolecular H-bonding. However, in case of aniline, due to the large hydrophobic part, i.e., hydrocarbon part, the extent of H-bonding is very less therefore aniline is insoluble in water.



(iii) Methylamine being more basic than water, accepts a proton from water liberating OH^- ions,

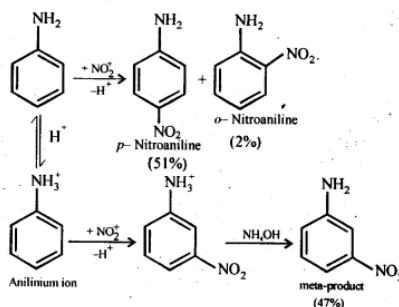


These OH^- ions combine with Fe^{3+} ions present in H_2O to form brown precipitate of hydrated ferric oxide.

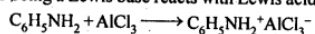


(iv) Nitration is usually carried out with a mixture of cone HNO_3 +

cone H_2SO_4 . In presence of these acids, most of aniline gets protonated to form anilinium ion. Therefore, in presence of acids, the reaction mixture consists of aniline and anilinium ion. Now, $-\text{NH}_2$ group in aniline is activating and o, p-directing while the $-\text{NH}_3^+$ group in anilinium ion is deactivating and m-directing. Nitration of aniline (due to steric hindrance at o-position) mainly gives p-nitroaniline, the nitration of anilinium ion gives m-nitroaniline. In actual practice, approx a 1:1 mixture of p-nitroaniline and m-nitroaniline is obtained. Thus, nitration of aniline gives a substantial amount of m-nitroaniline due to protonation of the amino group.

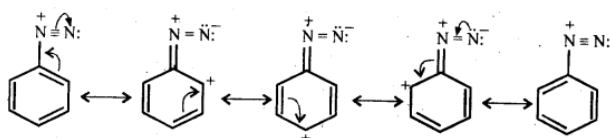


- (v). Aniline being a Lewis base reacts with Lewis acid AlCl_3 to form a salt.



As a result, N of aniline acquires positive charge and hence it acts as a strong deactivating group for electrophilic substitution reactions. Consequently, aniline does not undergo Friedel Crafts reaction.

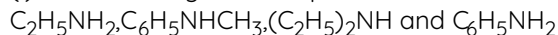
- (vi) The diazonium salts of aromatic amines are more stable than those of aliphatic amines due to dispersal of the positive charge on benzene ring as a result of resonance.



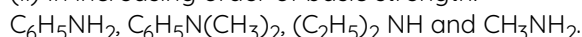
- (vii) Gabriel phthalimide reaction gives pure primary amines without any contamination of secondary and tertiary amines. Therefore, it is preferred for synthesising primary amines.

13.4. Arrange the following:

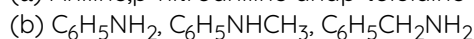
- (i) In decreasing order of pK_b values:



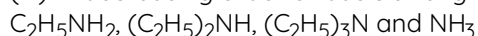
- (ii) In increasing order of basic strength:



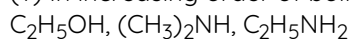
- (iii) In increasing order of basic strength:



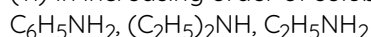
- (iv) In decreasing order of basic strength in gas phase:



- (v) In increasing order of boiling point:

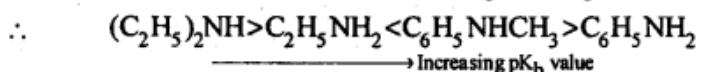
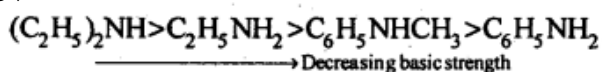


- (vi) In increasing order of solubility in water:



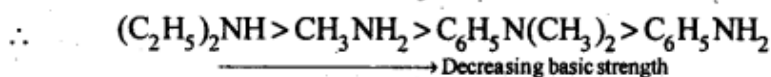
Ans:

(i) Due to delocalisation of lone pair of electrons of the N-atom over the benzene ring, $\text{C}_6\text{H}_5\text{NH}_2$ and $\text{C}_6\text{H}_5\text{NHCH}_3$ are far less basic than $\text{C}_2\text{H}_5\text{NH}_2$ and $(\text{C}_2\text{H}_5)_2\text{NH}$. Due to +I-effect of the $-\text{CH}_3$ group, $\text{C}_6\text{H}_5\text{NHCH}_3$ is little more basic than $\text{C}_6\text{H}_5\text{NH}_2$. Among $\text{C}_2\text{H}_5\text{NH}_2$ and $(\text{C}_2\text{H}_5)_2\text{NH}$, $(\text{C}_2\text{H}_5)_2\text{NH}$ is more basic than $\text{C}_2\text{H}_5\text{NH}_2$ due to greater +I-effect of two $-\text{C}_2\text{H}_5$ groups. Therefore correct order of decreasing pK_b values is:

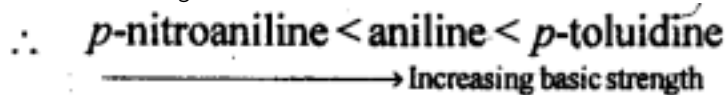


(ii) Among CH_3NH_2 and $(\text{C}_2\text{H}_5)_2\text{NH}$, primarily due to the greater +I-effect of the two $-\text{C}_2\text{H}_5$ groups over one $-\text{CH}_3$ group, $(\text{C}_2\text{H}_5)_2\text{NH}$ is more basic than CH_3NH_2 . In both $\text{C}_6\text{H}_5\text{NH}_2$ and $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$ lone

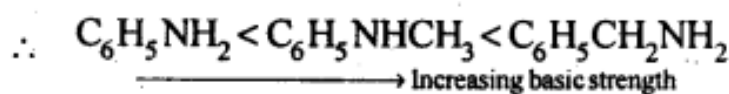
pair of electrons present on N-atom is delocalized over the benzene ring but $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$ is more basic due to +I effect of two- CH_3 groups.



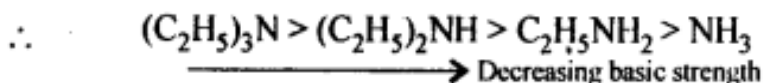
(iii) (a) The presence of electron donating $-\text{CH}_3$ group increases while the presence of electron withdrawing $-\text{NO}_2$ group decreases the basic strength of amines.



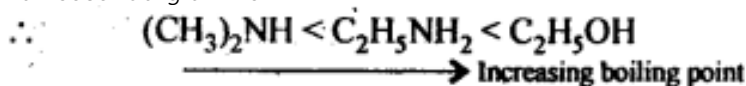
(b) In $\text{C}_6\text{H}_5\text{NH}_2$ and $\text{C}_6\text{H}_5\text{NHCH}_3$, N is directly attached to the benzene ring. As a result, the lone pair of electrons on the N-atom is delocalised over the benzene ring. Therefore, both $\text{C}_6\text{H}_5\text{NH}_2$ and $\text{C}_6\text{H}_5\text{NHCH}_3$ are weaker base in comparison to $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$. Among $\text{C}_6\text{H}_5\text{NH}_2$ and $\text{C}_6\text{H}_5\text{NHCH}_3$, due to +I effect of $-\text{CH}_3$ group $\text{C}_6\text{H}_5\text{NHCH}_3$ is more basic.



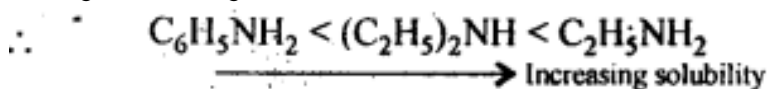
(iv) In gas phase or in non-aqueous solvents such as chlorobenzene etc, the solvation effects i. e., the stabilization of the conjugate acid due to H-bonding are absent. Therefore, basic strength depends only upon the +I-effect of the alkyl groups. The +I-effect increases with increase in number of alkyl groups. Thus correct order of decreasing basic strength in gas phase is,



(v) Since the electronegativity of O is higher than that of N, therefore, alcohols form stronger H-bonds than amines. Also, the extent of H-bonding depends upon the number of H-atoms on the N-atom, thus the extent of H-bonding is greater in primary amine than secondary amine.



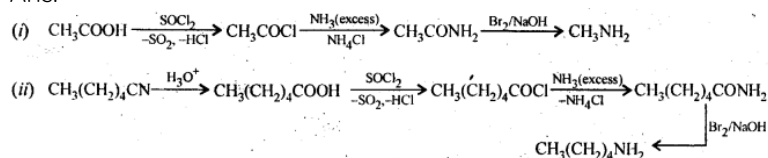
(vi) Solubility decreases with increase in molecular mass of amines due to increase in the size of the hydrophobic hydrocarbon part and with decrease in the number of H-atoms on the N-atom which undergo H-bonding.

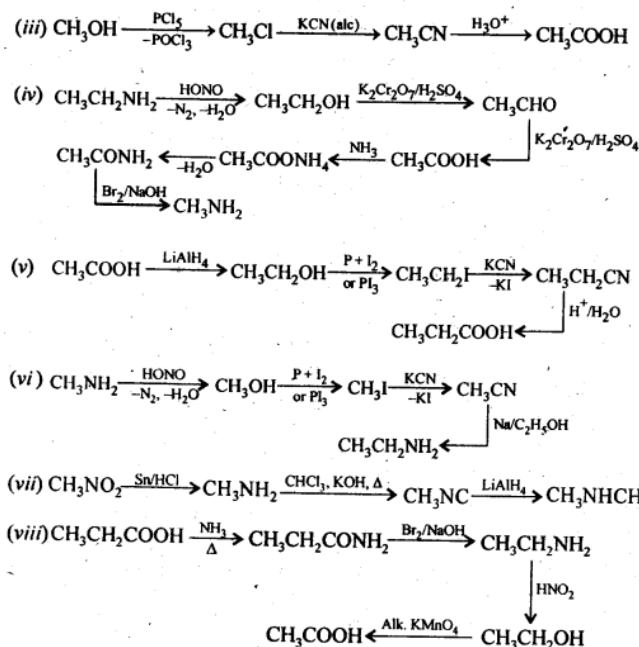


13.5 How will you convert:

- (i) Ethanoic acid into methanamine
- (ii) Hexanenitrile into 1-aminopentane
- (iii) Methanol to ethanoic acid.
- (iv) Ethanamine into methanamine
- (v) Ethanoic acid into propanoic acid
- (vi) Methanamine into ethanamine
- (vii) Nitromethane into dimethylamine
- (viii) Propanoic acid into ethanoic acid?

Ans:

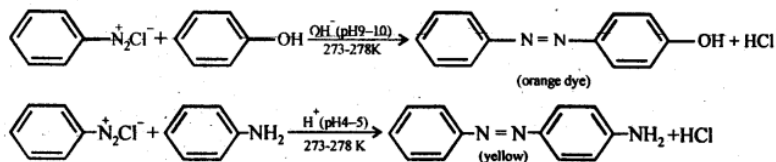




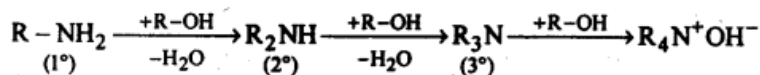
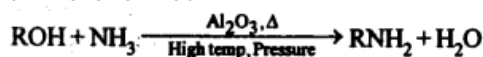
has one carbon atom less than the starting amide. This reaction is known as Hoffmann's bromamide degradation reaction.



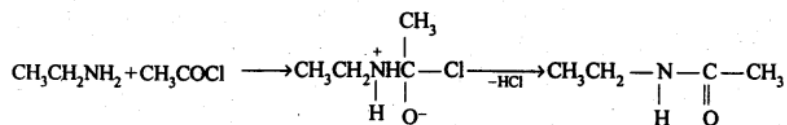
(iv) Coupling reaction: In this reaction, arene diazonium salt reacts with aromatic amino compound (in acidic medium) or a phenol (in alkaline medium) to form brightly coloured azo compounds. The reaction generally takes place at para position to the hydroxy or amino group. If para position is blocked, it occurs at ortho position and if both ortho and para positions are occupied, then no coupling takes place.



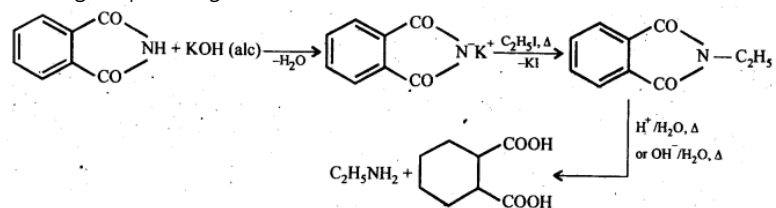
(v) Ammonolysis: It is a process of replacement of either halogen atom in alkyl halides (or aryl halides) or hydroxyl group in alcohols (or phenols) by amino group. The reagent used for ammonolysis is alcoholic ammonia. Generally, a mixture of primary, secondary and tertiary amine is formed.



(vi) Acetylation: The process of introducing an acetyl ($\text{CH}_3\text{CO}-$) group into molecule using acetyl chloride or acetic anhydride is called acetylation.



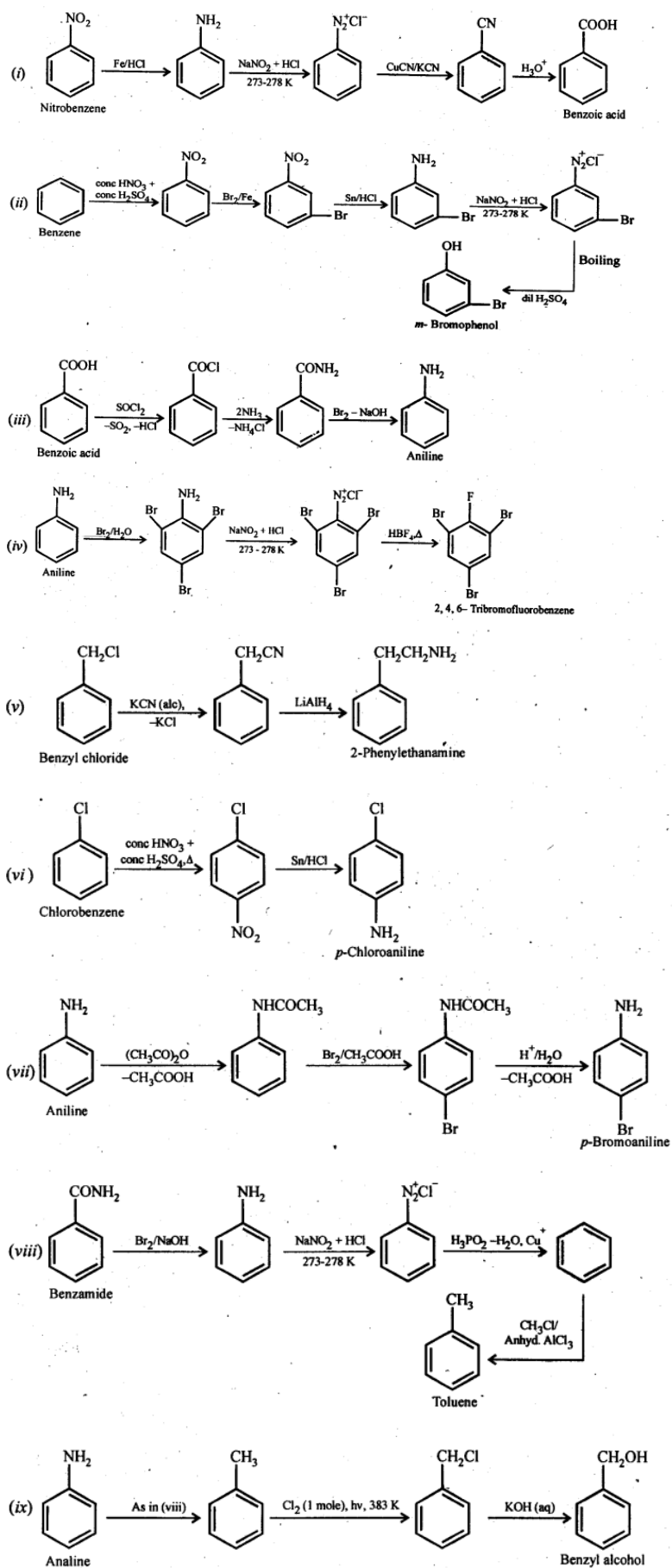
(vii) Gabriel phthalimide synthesis: It is a method of preparation of pure aliphatic and aralkyl primary amines. Phthalimide on treatment with ethanolic KOH gives potassium phthalimide which on heating with a suitable alkyl or aralkyl halides gives N-substituted phthalimides, which on hydrolysis with dil HCl or with alkali give primary amines.



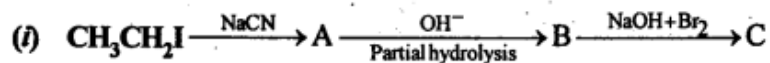
13.8. Accomplish the following conversions:

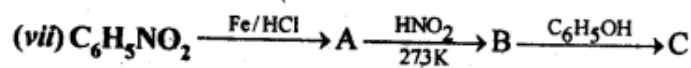
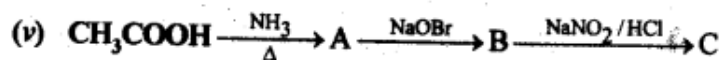
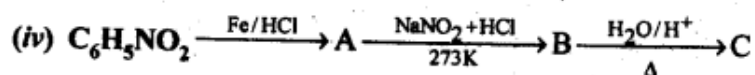
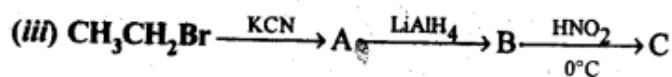
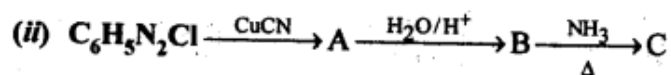
- (i) Nitrobenzene to benzoic acid
- (ii) Benzene to m-bromophenol
- (iii) Benzoic acid to aniline
- (iv) Aniline to 2,4,6-tribromofluorobenzene
- (v) Benzyl chloride to 2-phenylethanamine
- (vi) Chlorobenzene to p-Chloroaniline
- (vii) Aniline to p-bromoaniline
- (viii) Benzamide to toluene
- (ix) Aniline to benzyl alcohol.

Ans:

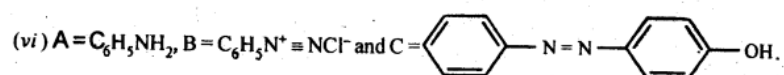
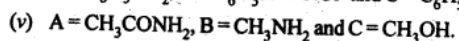
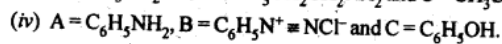
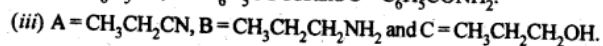
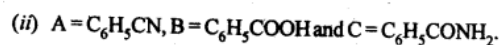
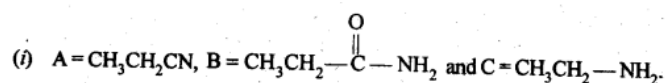


13.9. Give the structures of A,B and C in the following reaction:





Ans:



***** END *****