

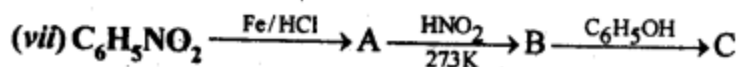
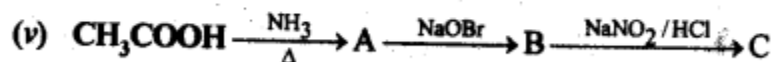
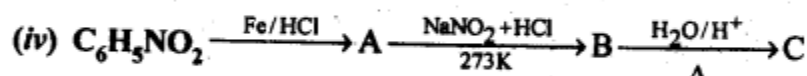
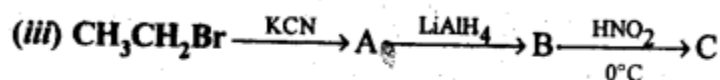
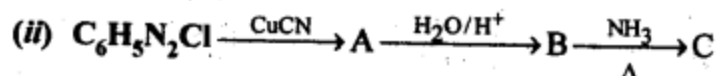
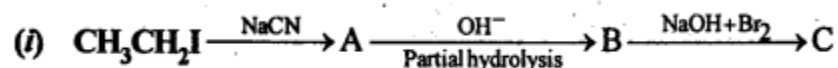
CHAPTER 9

AMINES

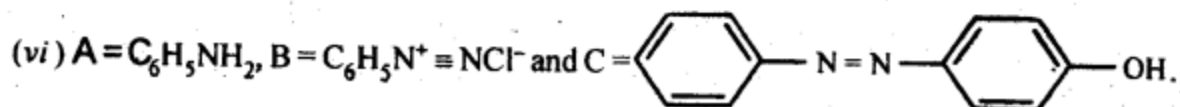
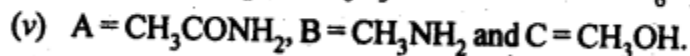
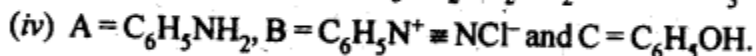
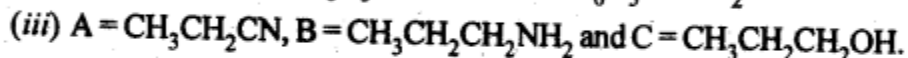
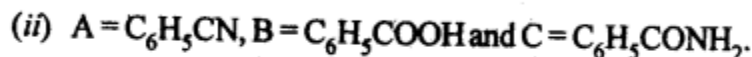
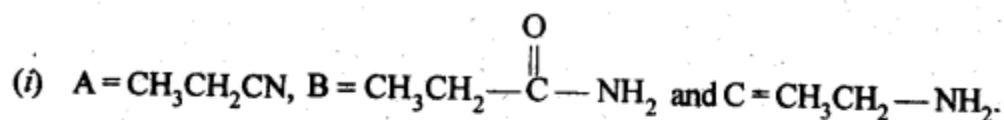
QUESTION AND ANSWERS

5MARKS

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

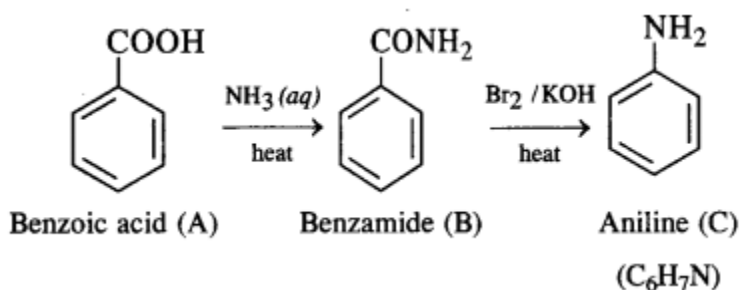


Ans:

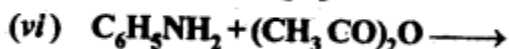
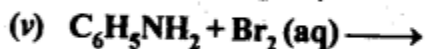
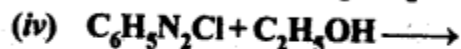
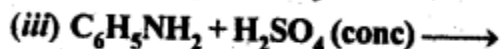
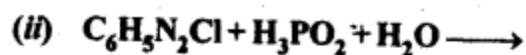


Ans:

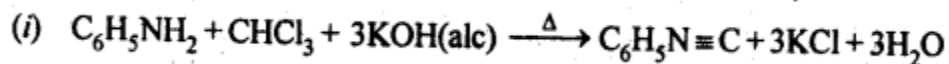
It is benzoic acid. The reactions involved are given as follows:

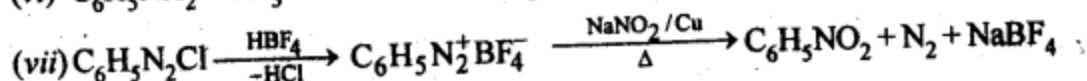
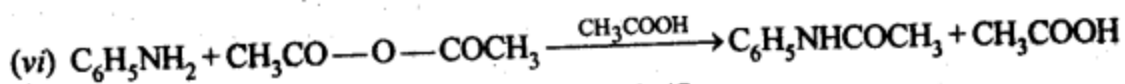
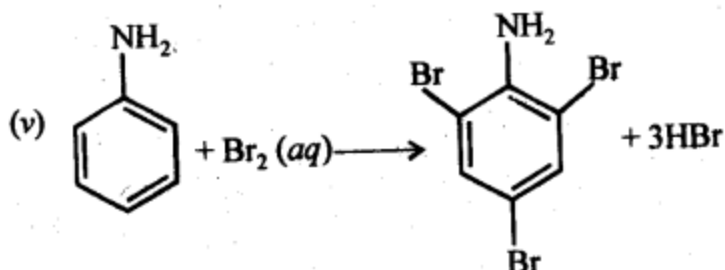
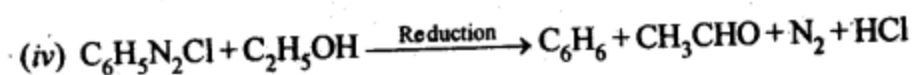
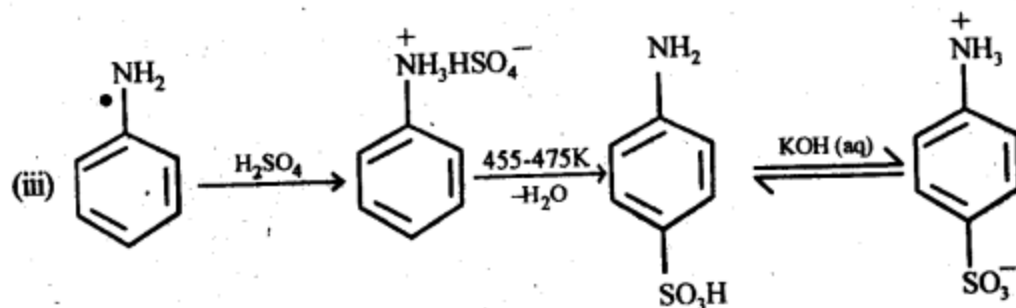
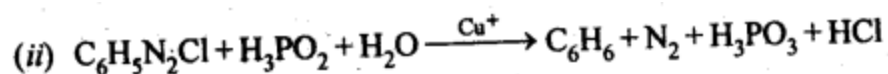


(i) $\text{C}_6\text{H}_5\text{NH}_2 + \text{CHCl}_3 + \text{alc. KOH}$



Ans:



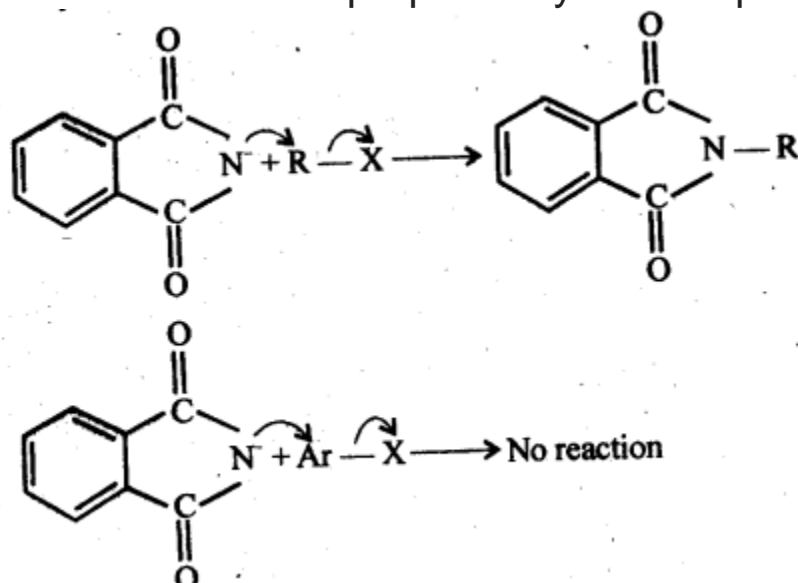


4. Why cannot aromatic primary amines be prepared by Gabriel phthalimide synthesis?

Ans: The success of Gabriel phthalimide reaction depends upon the nucleophilic attack by the phthalimide anion on the organic halogen compound.

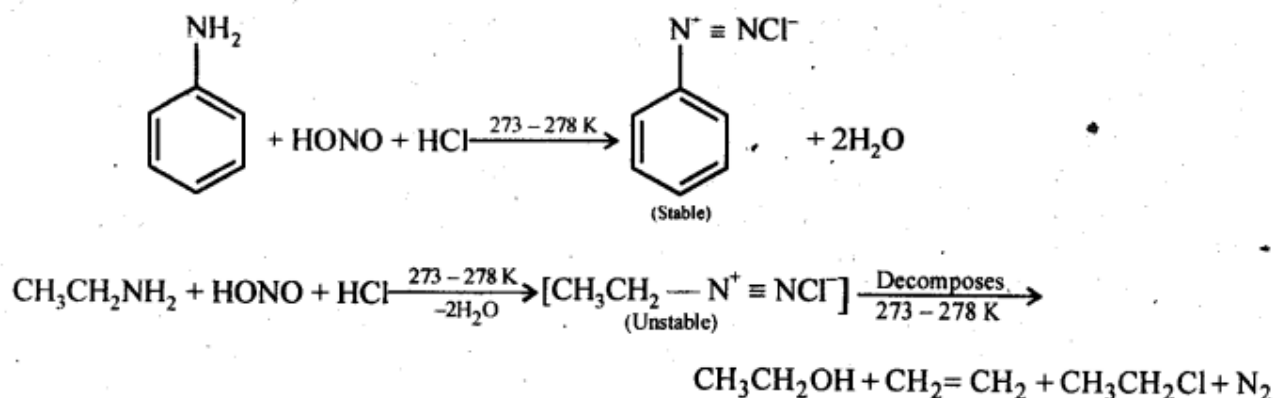
Since aryl halides do not undergo nucleophilic substitution reactions easily, therefore, arylamines, i.e., aromatic, primary

amines cannot be prepared by Gabriel phthalimide reaction.



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

Ans: Both aromatic and aliphatic primary amines react with HNO_2 at 273-278 K to form aromatic and aliphatic diazonium salts respectively. But aliphatic diazonium salts are unstable even at this low temperature and thus decompose readily to form a mixture of compounds. Aromatic and aliphatic primary amines react with HNO_2 as follows



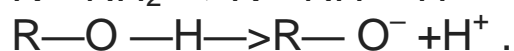
6. Give plausible explanation for each of the following:

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

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

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

Ans: (i) Loss of proton from an amine gives an amide ion while loss of a proton from alcohol give an alkoxide ion.



Since O is more electronegative than N, so it will attract positive species more strongly in comparison to N. Thus, RO^- is more stable than RNH^- . Thus, alcohols are more acidic than amines. Conversely, amines are less acidic than alcohols.

(ii) Due to the presence of two H-atoms on N-atom of primary amines, they undergo extensive intermolecular H-bonding while tertiary amines due to the absence of H-atom on the N-atom do not undergo H-bonding. As a result, primary amines have higher boiling points than tertiary amines of comparable molecular mass.

(iii) Aromatic amines are far less basic than ammonia and aliphatic amines because of following reasons:

(a) Due to resonance in aniline and other aromatic amines, the lone pair of electrons on the nitrogen atom gets delocalised over the benzene ring and thus it is less easily available for protonation. Therefore, aromatic amines are weaker bases than ammonia and aliphatic amines.

(b) Aromatic amines are more stable than corresponding protonated ion; Hence, they have very less tendency to combine with a proton to form corresponding protonated ion, and thus they are less basic.

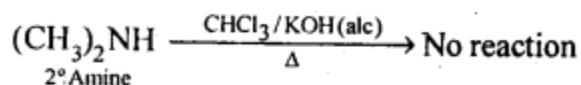
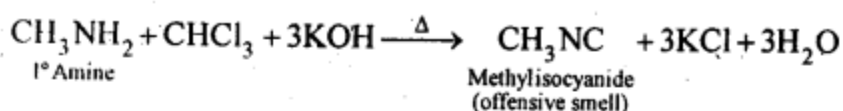
7MARKS

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

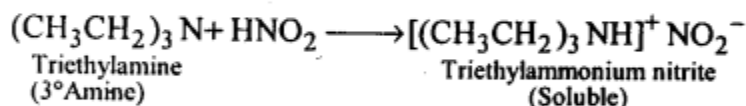
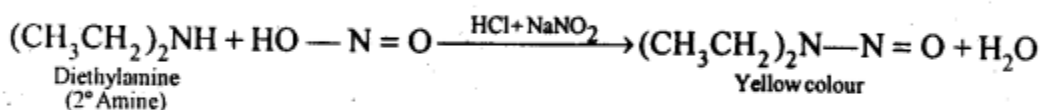
- (i) Methylamine and dimethylamine
- (ii) Secondary and tertiary amines
- (iii) Ethylamine and aniline
- (iv) Aniline and benzylamine
- (v) Aniline and N-Methylaniline.

Ans:

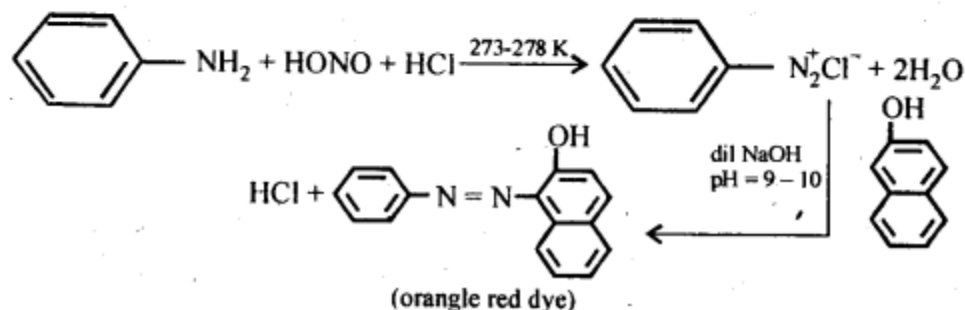
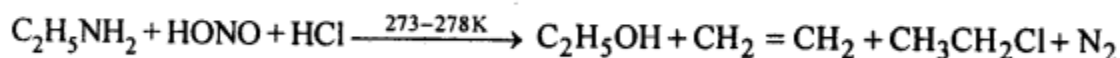
(i) Methylamine and dimethylamine can be distinguished by carbylamine test.



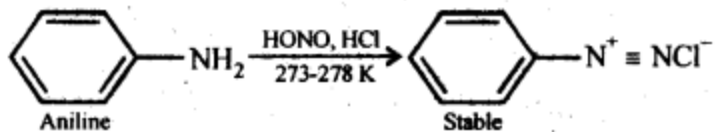
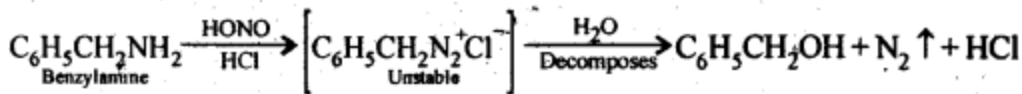
(ii) Secondary and tertiary amine can be distinguished by Liebermann's nitroamine test. Secondary amines give Liebermann nitroamine test while tertiary amines do not.



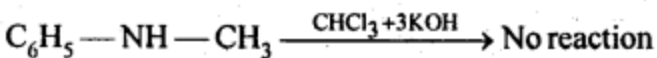
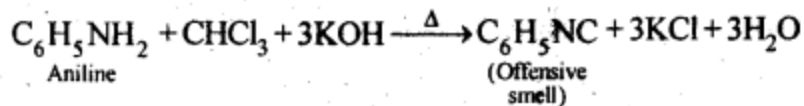
(iii) Ethylamine and aniline can be distinguished by azo test:



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



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



2. 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.

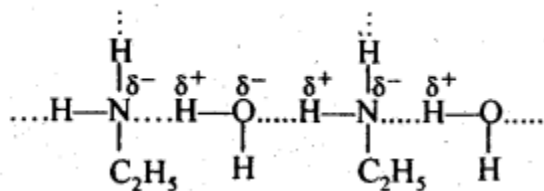
(vii) Gabriel phthalimide synthesis is preferred for synthesising primary amines.

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

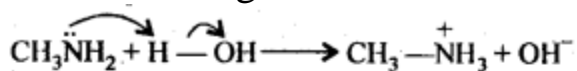
As a result, electron density on the nitrogen atom decreases. Whereas in CH_3NH_2 , +I-effect of $-\text{CH}_3$ group increases the electron density on the N-atom. Therefore, aniline is a weaker base than methylamine and hence its pK_b value is higher than that of methylamine.

(ii) Ethylamine dissolves in water due to intermolecular H-bonding.

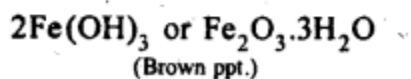
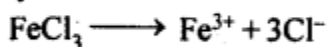
However, in case of aniline, due to the large hydrophobic part, i.e., hydrocarbon part, the extent of H-bonding is very less therefore aniline is insoluble in water.



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

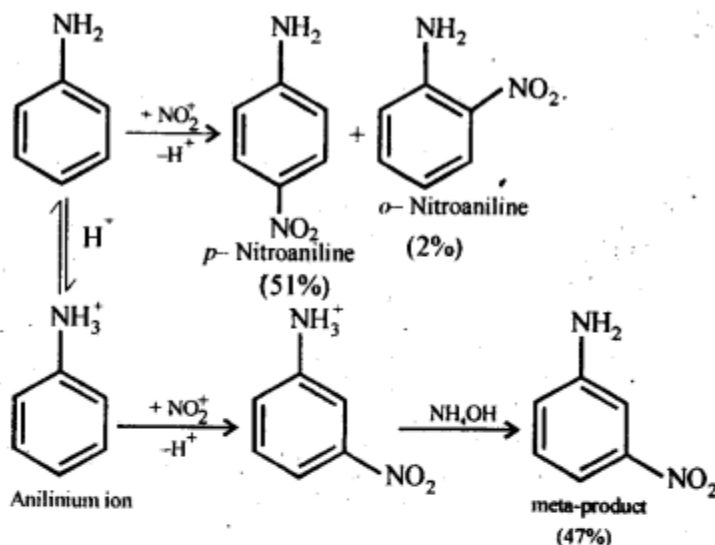


These OH^- ions combine with Fe^{3+} ions present in H_2O to form brown precipitate of hydrated ferric oxide.



(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 consist 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.

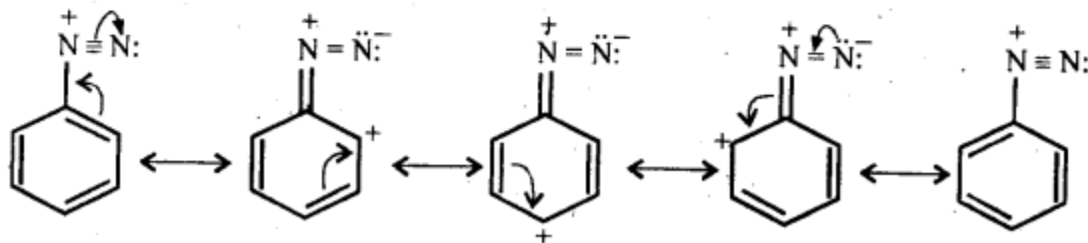


(v). Aniline being a Lewis base reacts with Lewis acid AlCl_3 to form a salt.



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.



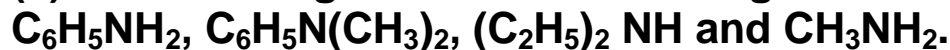
(vii) Gabriel phthalimide reaction gives pure primary amines without any contamination of secondary and tertiary amines. Therefore, it is preferred for synthesising primary amines.

3. 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:

(a) Aniline, p -nitroaniline and p -toluidine

(b) $\text{C}_6\text{H}_5\text{NH}_2, \text{C}_6\text{H}_5\text{NHCH}_3, \text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$

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

$\text{C}_2\text{H}_5\text{NH}_2$, $(\text{C}_2\text{H}_5)_2\text{NH}$, $(\text{C}_2\text{H}_5)_3\text{N}$ and NH_3

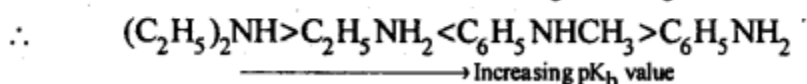
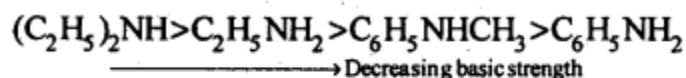
(v) In increasing order of boiling point:

$\text{C}_2\text{H}_5\text{OH}$, $(\text{CH}_3)_2\text{NH}$, $\text{C}_2\text{H}_5\text{NH}_2$

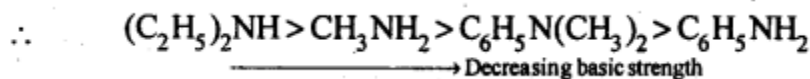
(vi) In increasing order of solubility in water:

$\text{C}_6\text{H}_5\text{NH}_2$, $(\text{C}_2\text{H}_5)_2\text{NH}$, $\text{C}_2\text{H}_5\text{NH}_2$

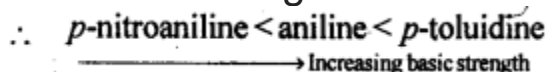
Ans: (i) Due to delocalisation of lone pair of electrons of the N-atom over the benzene ring, $\text{C}_6\text{H}_5\text{NH}_2$ and $\text{C}_6\text{H}_5\text{NHCH}_3$ are far less basic than $\text{C}_2\text{H}_5\text{NH}_2$ and $(\text{C}_2\text{H}_5)_2\text{NH}$. Due to +I-effect of the $-\text{CH}_3$ 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:



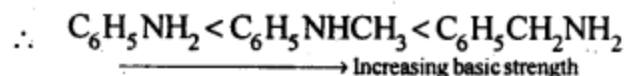
(ii) Among CH_3NH_2 and $(\text{C}_2\text{H}_5)_2\text{NH}$, primarily due to the greater +I-effect of the two $-\text{C}_2\text{H}_5$ groups over one $-\text{CH}_3$ group, $(\text{C}_2\text{H}_5)_2\text{NH}$ is more basic than CH_3NH_2 . In both $\text{C}_6\text{H}_5\text{NH}_2$ and $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$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



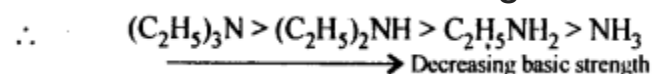
(iii) (a) The presence of electron donating $-\text{CH}_3$ group increases while the presence of electron withdrawing $-\text{NO}_2$ group decreases the basic strength of amines.



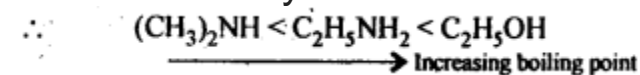
(b) In $\text{C}_6\text{H}_5\text{NH}_2$ and $\text{C}_6\text{H}_5\text{NHCH}_3$, N is directly attached to the benzene ring. As a result, the lone pair of electrons on the N-atom is delocalised over the benzene ring. Therefore, both $\text{C}_6\text{H}_5\text{NH}_2$ and $\text{C}_6\text{H}_5\text{NHCH}_3$ 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.



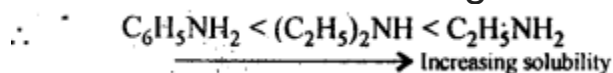
(iv) In gas phase or in non-aqueous solvents such as chlorobenzene etc, the solvation effects i. e., the stabilization of the conjugate acid due to H-bonding are absent. Therefore, basic strength depends only upon the +I-effect of the alkyl groups. The +I-effect increases with increase in number of alkyl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



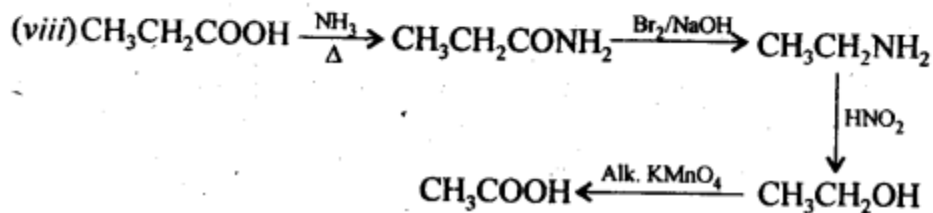
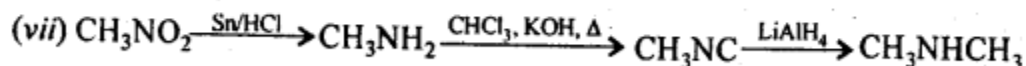
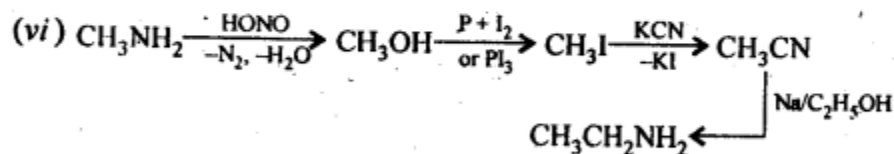
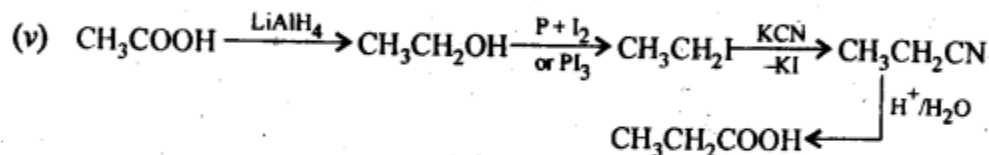
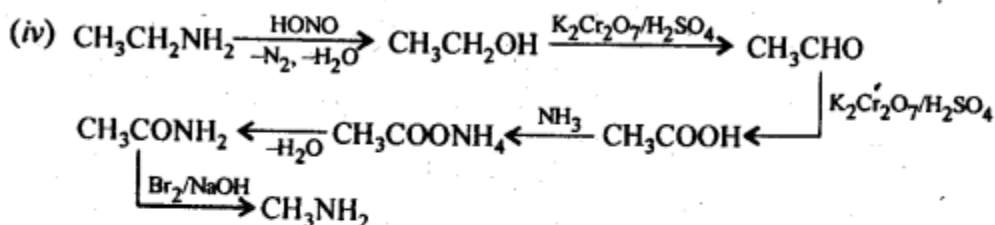
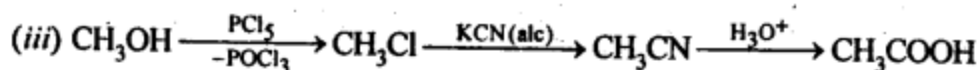
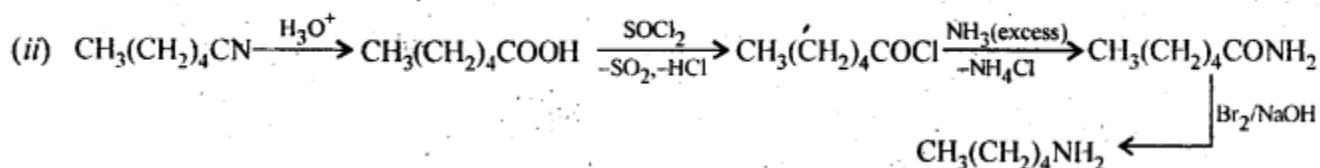
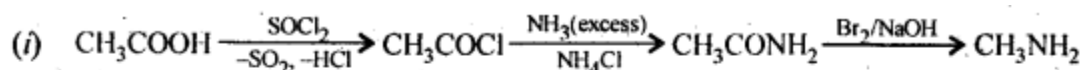
(vi) Solubility decreases with increase in molecular mass of amines due to increase in the size of the hydrophobic hydrocarbon part and with decrease in the number of H-atoms on the N-atom which undergo H-bonding.



4. 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:



5. Describe the method for the identification of primary, secondary and tertiary amines. Also write chemical equations of the reactions involved.

Answer:

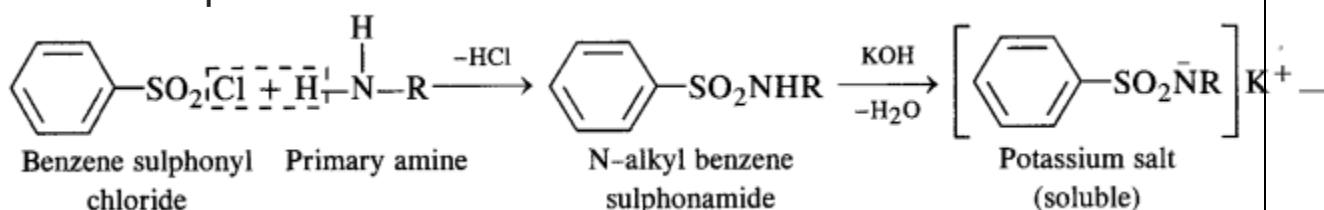
The distinction in the three types of amines can be done by the

following methods :

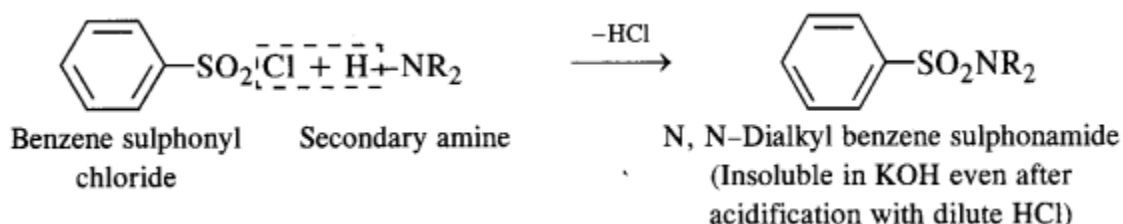
(i) Hinsberg's Test:

This is a very useful test for the distinction of primary, secondary and tertiary amines. An amine is shaken with Hinsberg's reagent (benzene sulphonyl chloride) in the presence of excess of aqueous KOH solution. The reactions taking place are given on the next page.

1. **A primary amine** forms N – alkyl benzene sulphonamide which dissolves in aqueous KOH solution to form potassium salt and upon acidification with dilute HCl regenerates the insoluble sulphonamide.

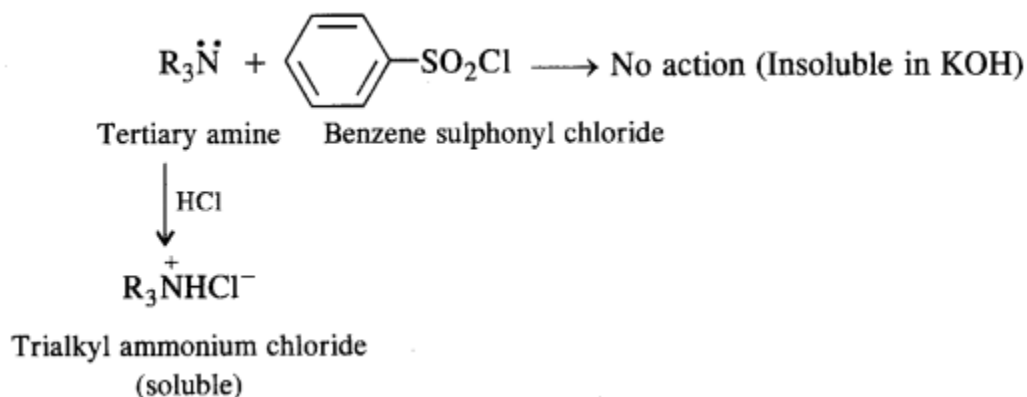


2. **A secondary amine** forms N, N – dialkylbenzene sulphonamide which remains insoluble in aqueous KOH and even after acidification with dilute HCl



3. **A tertiary amine** does not react with benzene sulphonyl chloride and remains insoluble in aqueous KOH. However, on acidification with dilute HCl it gives a clear

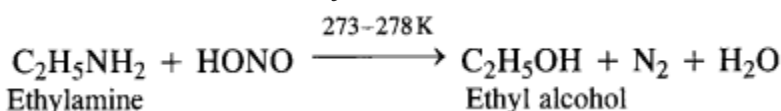
solution due to the formation of the ammonium salt.



(ii) Reaction with nitrous acid:

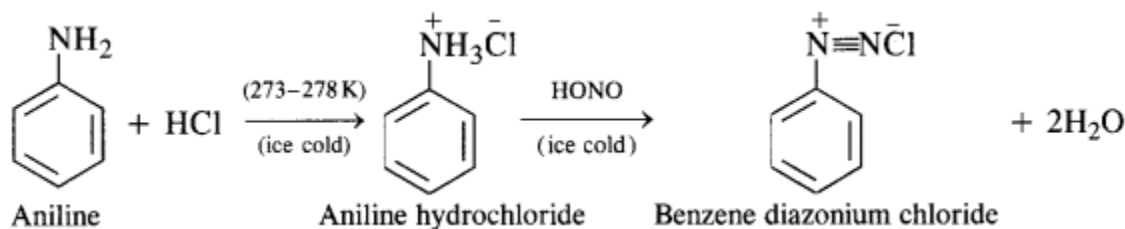
All the three types of amines, aliphatic as well as aromatic, react with nitrous acid under different conditions to form variety of products. Since nitrous acid is highly unstable, it is prepared in situ by the action of dilute hydrochloric acid on sodium nitrite.

(a) Primary aliphatic amines react with nitrous acid at low temperature (cold conditions) to form primary alcohol and nitrogen gas accompanied by brisk effervescence. Nitrous acid is unstable in nature and is prepared in situ by reacting sodium nitrite with dilute hydrochloric acid. For example,



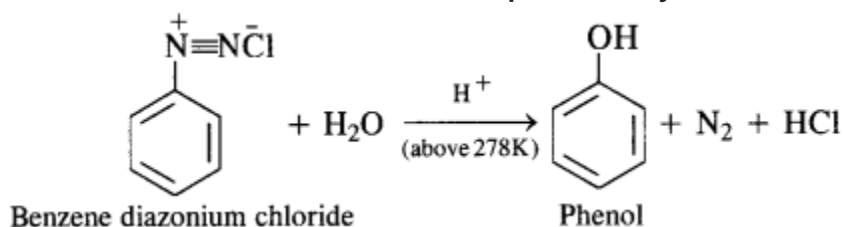
The reaction is used as a test for primary aliphatic amines as no other amine evolves nitrogen with nitrous acid.

(b) Primary aromatic amines such as aniline react with nitrous acid under ice cold conditions (273 – 278 K) to form benzenediazonium salt. The reaction is known as **diazotisation reaction**.

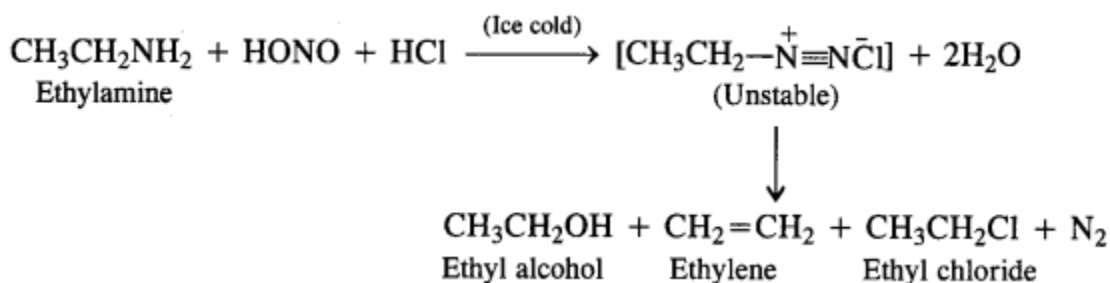


in case, the temperature is allowed to rise above 278 K, benzene

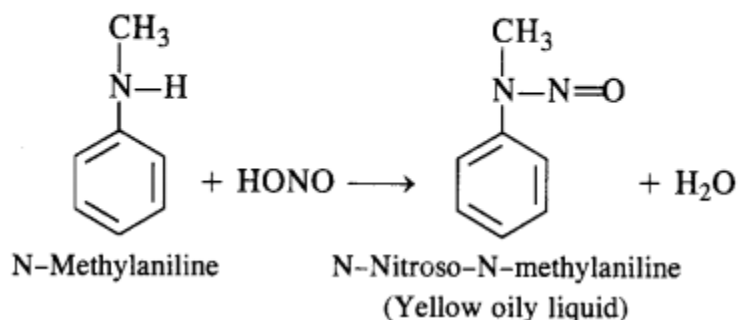
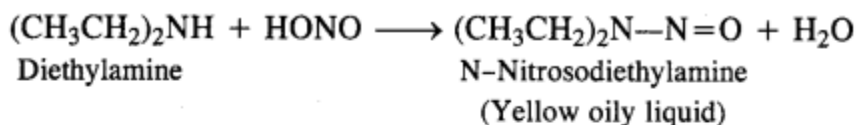
diazonium chloride is decomposed by water to form phenol.



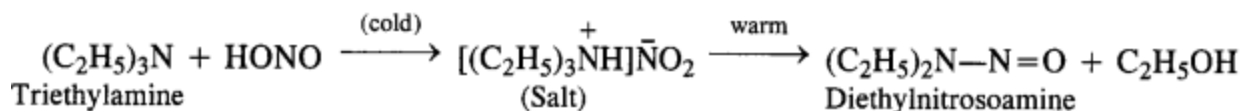
Aliphatic primary amines also react with nitrous acid to form alkyl diazonium salts in a similar manner. But these are quite unstable and decompose to form a mixture of alcohols, alkenes and alkyl halides along with the evolution of N_2 gas.



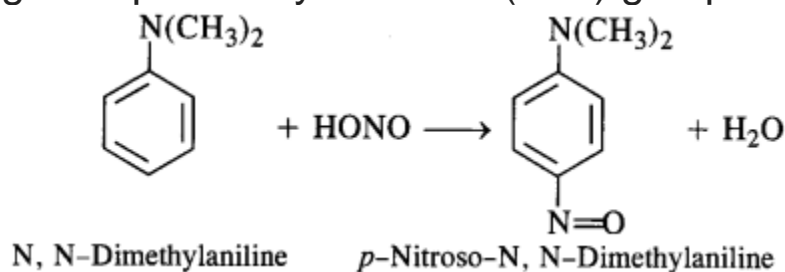
(c) Secondary amines (both aliphatic and aromatic) react with nitrous acid to form nitrosoamines which separate as Yellow oily liquids.



(d) Tertiary aliphatic amines dissolve in a cold solution of nitrous acid to form salts which decompose on warming to give nitrosoamine and alcohol. For example,



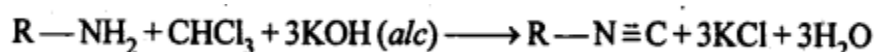
(e) Tertiary aromatic amines react with nitrous acid to give a coloured nitrosoderivative. This reaction is called nitrosation and as a result, a hydrogen atom in the para position gets replaced by a nitroso (-NO) group. For example,



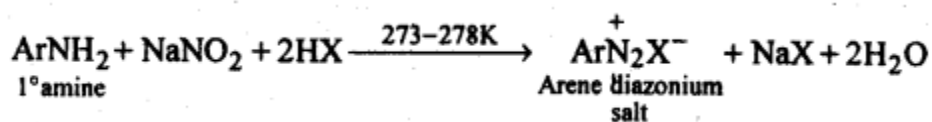
6. Write short notes on the following:

- (i) Carbylamine reaction
- (ii) Diazotisation
- (iii) 'Hofmann's bromamide reaction
- (iv) Coupling reaction
- (v) Ammonolysis
- (vi) Acetylation
- (vii) Gabriel phthalimide synthesis

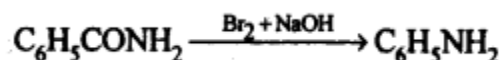
Ans: (i) Carbylamine reaction: Both aliphatic and aromatic primary amines when warmed with chloroform and an alcoholic solution of KOH, produces isocyanides or carbylamines which have very unpleasant odours. This reaction is called carbylamine reaction.



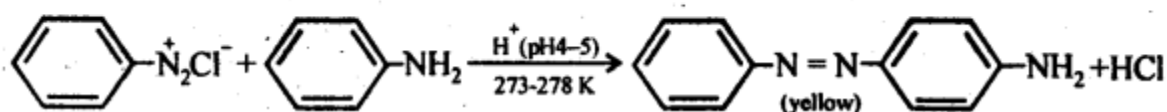
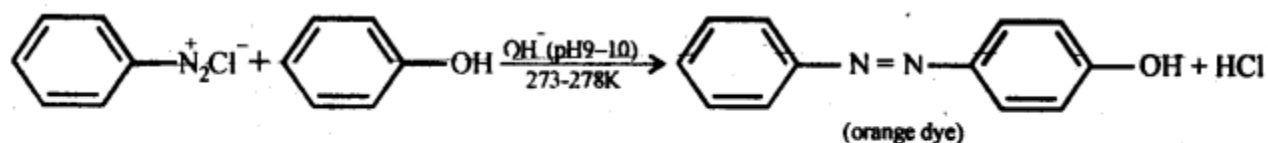
(ii) Diazotisation: The process of conversion of a primary aromatic amino compound into a diazonium salt, is known as diazotisation. This process is carried out by adding an aqueous solution of sodium nitrite to a solution of primary aromatic amine (e.g., aniline) in excess of HCl at a temperature below 5°C.



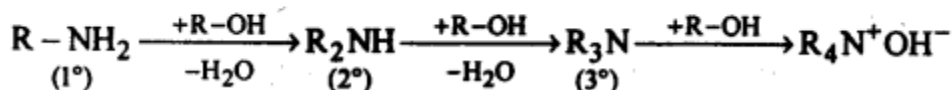
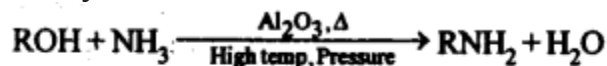
(iii) Hoffmann's bromamide reaction: When an amide is treated with bromine in alkali solution, it is converted to a primary amine that has one carbon atom less than the starting amide. This reaction is known as Hoffmann's bromamide degradation reaction.



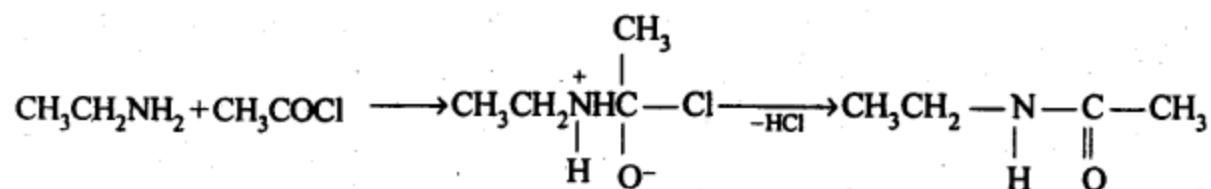
(iv) Coupling reaction: In this reaction, arene diazonium salt reacts with aromatic amino compound (in acidic medium) or a phenol (in alkaline medium) to form brightly coloured azo compounds. The reaction generally takes place at para position to the hydroxy or amino group. If para position is blocked,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



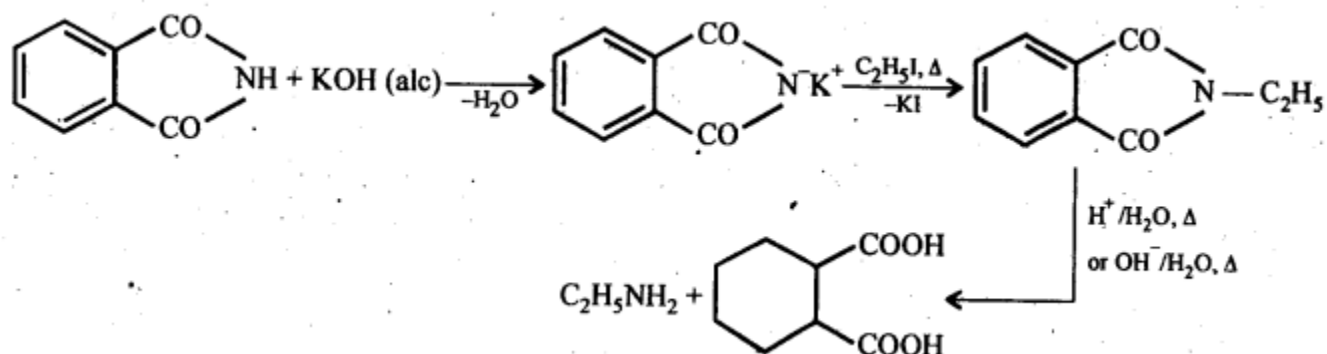
(v) Ammonolysis: It is a process of replacement of either halogen atom in alkyl halides (or aryl halides) or hydroxyl group in alcohols (or phenols) by amino group. The reagent used for ammonolysis is alcoholic ammonia. Generally, a mixture of primary, secondary and tertiary amine is formed.



(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.



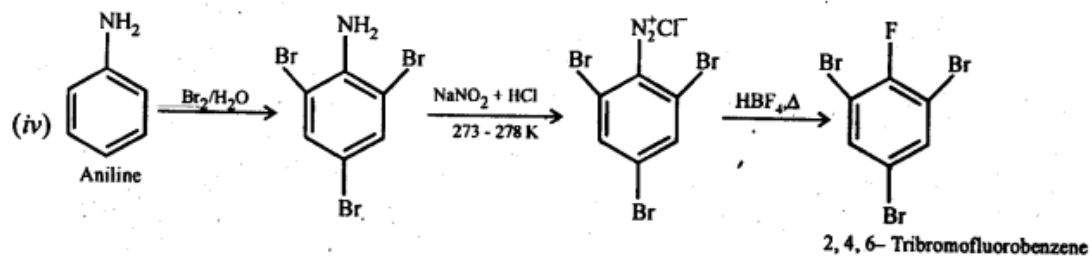
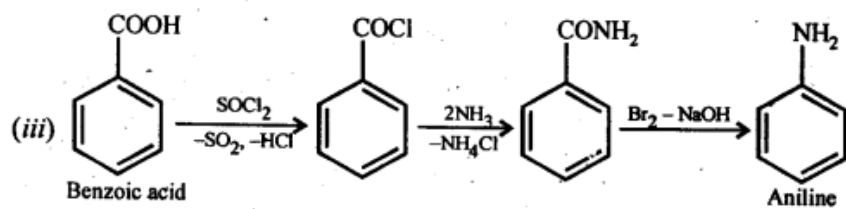
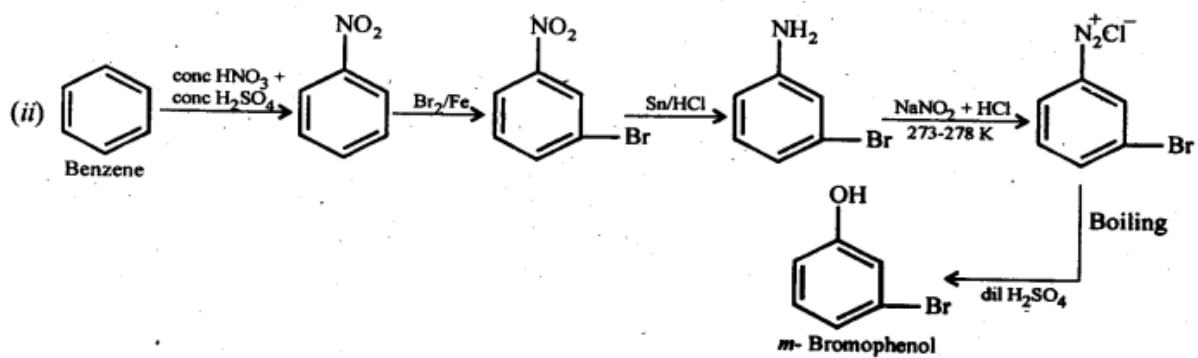
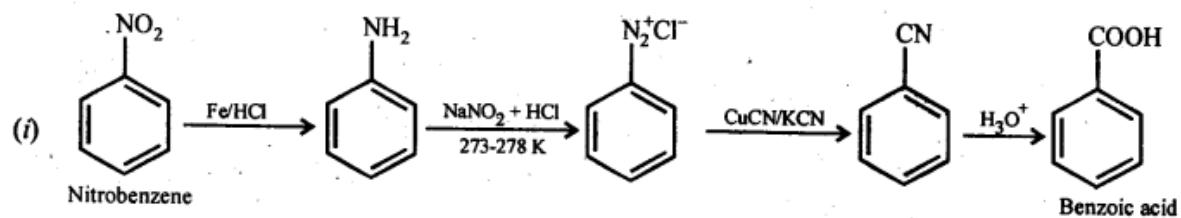
(vii) Gabriel phthalimide synthesis: It is a method of preparation of pure aliphatic and aralkyl primary amines. Phthalimide on treatment with ethanolic KOH gives potassium phthalimide which on heating with a suitable alkyl or aralkyl halides gives N-substituted phthalimides, which on hydrolysis with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

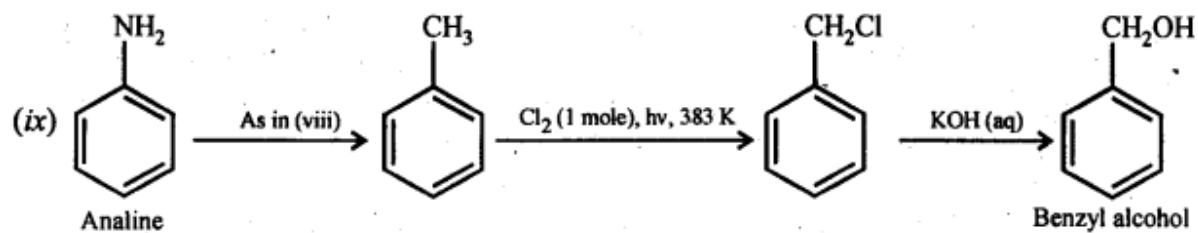
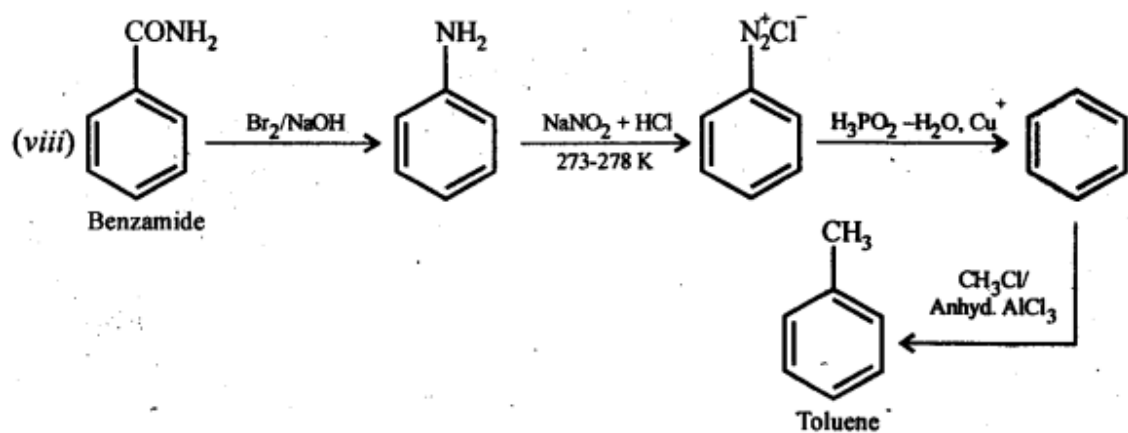
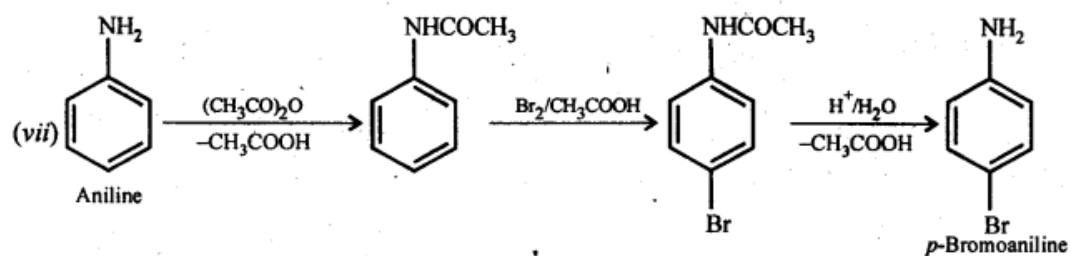
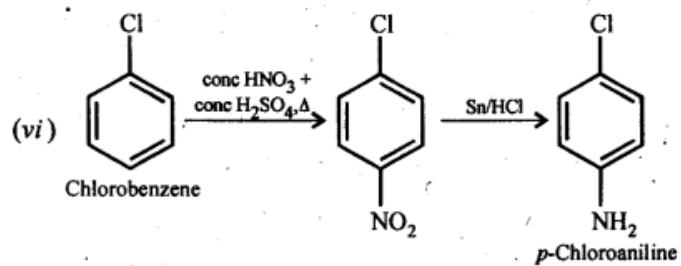
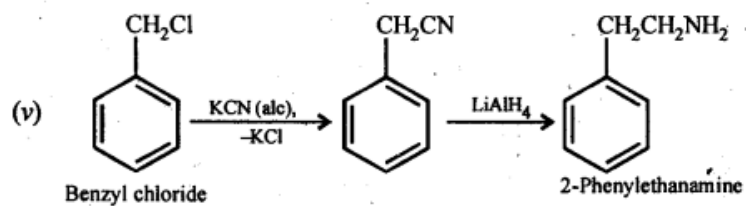


7. Accomplish the following conversions:

- (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:





SUMMARY

1. Amines are the derivatives of ammonia in which one or more hydrogen atoms have been replaced by alkyl groups.

2. Amines are classified as **primary, secondary, or tertiary** according as one, two or three hydrogen atoms in the ammonia molecule have been substituted by alkyl groups.

3. Preparation of amines:

- (i) By reduction of nitro compounds.
- (ii) An alkyl or benzyl halide on reaction with an ethanolic solution of ammonia undergoes nucleophilic substitution reaction in which the halogen atom is replaced by an amino ($-\text{NH}_2$) group.
- (iii) By reduction of nitriles.
- (iv) By reduction of amides.
- (v) By Gabriel phthalimide synthesis: For primary alkyl amines only, not for aromatic amines.
- (vi) By Hoffmann bromide degradation reaction:

4. All the three classes of aliphatic amines (1° , 2° and 3°) form H-bonds with water. As a result, lower aliphatic amines are soluble in water.

5. Some important reactions of amines

- (i) Amines are basic in nature they react with acid to form salt.

