NCERT Solutions for Class-XII Chemistry

CHAPTER -9

NCERT Chemistry Class 12

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

(i) $(CH_3)_2$ $CHNH_2$ (ii) $CH_3(CH_2)_2NH_2$

(iii) $CH_3NHCH(CH_3)_2$ (iv) $(CH_3)_3CNH_2$

(v) $C_6H_5NHCH_3$ (vi) $(CH_3CH_2)_2NCH_3$

(vii) m-$BrC_6H_4NH_2$

1. (i) 1-Methylethanamine (1° amine)

(ii) Propan-1-amine (1° amine)

(iii) N-Methyl-2-methylethanamine (2° amine)

(iv) 2-Methylpropan-2-amine (1° amine)

(v) N-Methylbenzamine or N-methylaniline (2° amine)

(vi) N-Ethyl-N-methylethanamine (3° amine)

(vii) 3-Bromobenzenamine or 3-bromoaniline (1° amine)

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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.

2. (i) Methylamine and dimethylamine:

Carbylamine test.

Methylamine, on heating with alc. KOH solution and chloroform form foul-smelling methyl isocyanide. This test is not given by dimethylamine.

(ii) Secondary and tertiary amines:

Secondary amines give Libermann nitrosoamine test.

On heating with nitrous acid (prepared in situ), they give yellow coloured oily N-nitrosoamine.

Tertiary amines do not give such test.

(iii) Ethylamine and aniline:

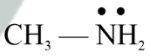
Azo dye test.

Aniline on diazotization (ice cold nitrous acid solution) followed by coupling with 2-naphthol (in alkaline solution) forms brilliant orange or red dye. Ethylamine will not form dye. It will give brisk effervescence (due to liberation of nitrogen gas) but solution remains clear.

(iv) Aniline and benzylamine:
Azo dye test.
Aniline on diazotization (ice cold nitrous acid solution) followed by coupling with 2-naphthol (in alkaline solution) forms brilliant orange or red dye. Benzylamine will not give such test.
(v) Aniline and N-methylaniline:
Carbylamine test.
Aniline, on heating with alc. KOH solution and chloroform form foul-smelling methyl isocyanide. This test is not given by N-methyl aniline.

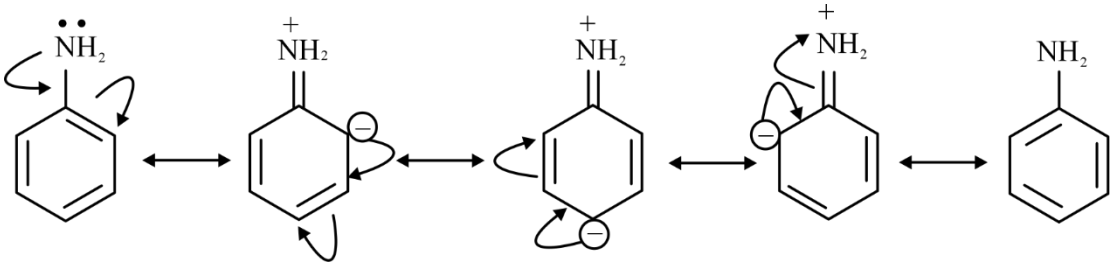
3. Account for the following:
(i) pK_b of aniline is more than that of methylamine.
(ii) Ethylamine is soluble in water whereas aniline is not.
(iii) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide.
(iv) Although amino group is o, p- directing in aromatic electrophilic 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 synthesizing primary amines.

3. (i) pK_b of aniline is more than that of methylamine:



Aniline Methylamine

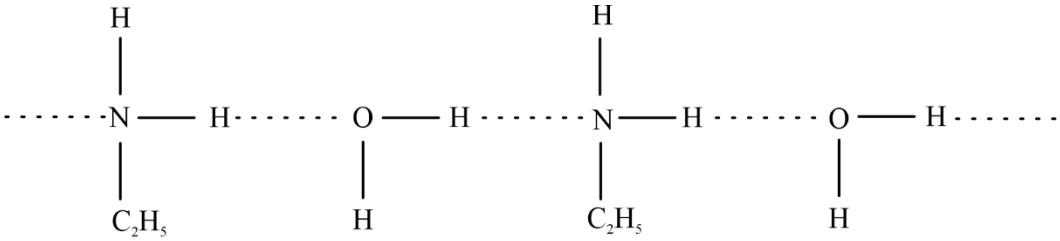
Aniline undergoes resonance and as a result, the electrons on the N-atom are delocalized over the benzene ring. Therefore, the electrons on the N-atom are less available to donate.



On the other hand, in case of methylamine (due to the +I effect of methyl group), the electron density on the N-atom is increased. As a result, aniline is less basis than methylamine. Thus, pK_b of aniline is more than that of methylamine.

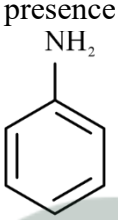
(ii) Ethylamine is soluble in water whereas aniline is not:

Ethylamine when added to water forms intermolecular H-bonds with water. Hence, it is soluble in water.



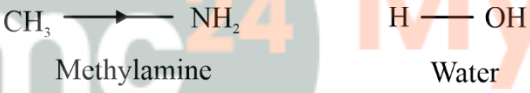
Ethylamine

But aniline does not undergo H-bonding with water to a very large extent due to the presence of a large hydrophobic $-C_6H_5$ group. Hence, aniline is insoluble in water.



Aniline

(iii) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide:



Methylamine Water

Due to the +I effect of $-CH_3$ group, methylamine is more basic than water. Therefore, in water methylamine produces OH^- ions by accepting H^+ ions from water.

$$CH_3-NH_2+H-OH\longrightarrow CH_3-\overset{+}{N}H_3+OH^-$$

Ferric chloride ($FeCl_2$) dissociates in water to form Fe^{2+} and Cl^- ions.

$$FeCl_3\longrightarrow Fe^{3+}+3Cl^-$$

Then, OH^- ion reacts with Fe^{3+} ion to form a precipitate of hydrated ferric oxide.

$$2Fe^{3+}+6OH^-\longrightarrow \underset{\text{Hydrated ferric oxide}}{Fe_2O_3\cdot 3H_2O}$$

(iv) Although amino group is o, p– directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m nitroaniline:

Nitration is carried out in an acidic medium. In an acidic medium, aniline is protonated to give anilinium ion (which is meta-directing).

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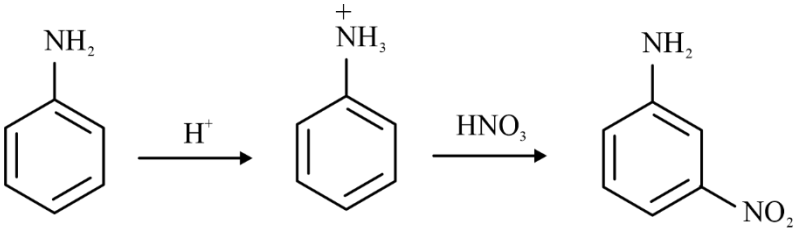
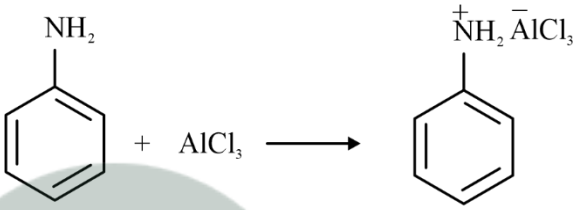


Aniline Anilinium ion m-Nitroaliline (47%)

For this reason, aniline on nitration gives a substantial amount of m-nitroaniline.

(v) Aniline does not undergo Friedel-Crafts reaction:

A Friedel-Crafts reaction is carried out in the presence of $AlCl_3$. But $AlCl_3$ is acidic in nature, while aniline is a strong base. Thus, aniline reacts with $AlCl_3$ to from a salt (as shown in the following equation).

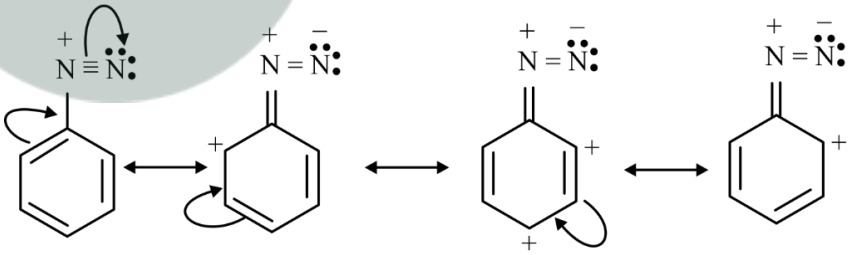


Aniline Salt

Due to the positive charge on the N-atom, electrophilic substitution in the benzene ring is deactivated. Hence, aniline does not undergo the Friedel-Crafts reaction.

(vi) Diazonium salts of aromatic amines are more stable than those of aliphatic amines:

The diazonium ion undergoes resonance as shown below:



This resonance accounts for the stability of the diazonium ion. Hence, diazonium salts of aromatic amines are more stable than those of aliphatic amines.

(vii) Gabriel phthalimide synthesis is preferred for synthesizing primary amines:

Gabriel phthalimide synthesis results in the formation of 1° amine only. 2° or 3° amines are not formed in this synthesis. Thus, a pure 1° amine can be obtained. Therefore, Gabriel phthalimide synthesis is preferred for synthesizing primary amines.

4. Arrange the following:

(i) In decreasing order of the pK_b values:

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

(ii) In increasing order of basis strength:

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

(b) $C_6H_5NH_2$, $C_6H_5NH_3$, $C_6H_5CH_2NH_2$.

(iii) In decreasing order of basis strength:

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

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

$C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_2N$ and NH_3

(v) In increasing order of boiling point:

C_2H_5OH, $(CH_3)_2NH$, $C_2H_5NH_2$

4. The correct answer is

(i) $C_2H_5NH_2 > C_6H_5NHCH_3 > C_6H_5NH_2 > (C_2H_5)_2NH$

(ii) (a) p-nitroaniline < aniline < p-toluidine

(b) $C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$

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

(iv) $(C_2H_5)N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$

(v) $(CH_3)_2NH < C_2H_5NH_2 < C_2H_5OH$

5. How will you convert:

(i) Ethanoic acid into methenamine

(ii) Hexanenitrile into 1-aminopentane

(iii) Methanol to ethanoic acid

(iv) Ethanamine into methanamine

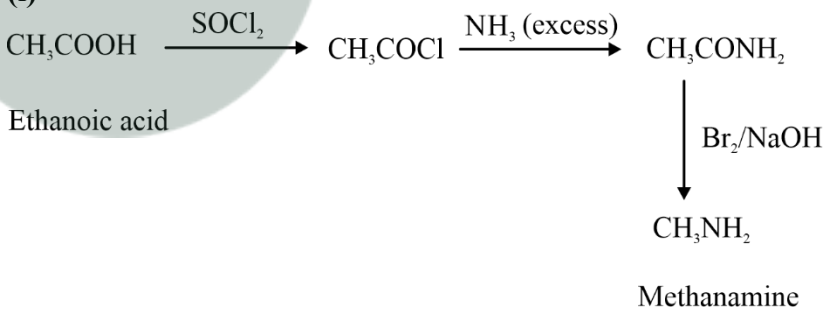
(v) Ethanoic acid into propanoic acid

(vi) Methanamine into ethanamine

(vii) Nitromethane into dimethylamine

(viii) Propanoic acid into ethanoic acid

5. **(i)**



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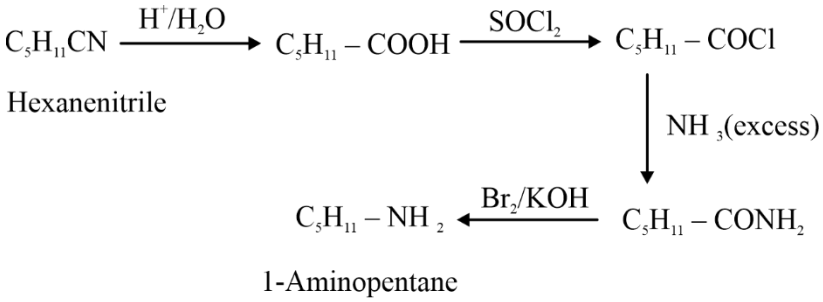

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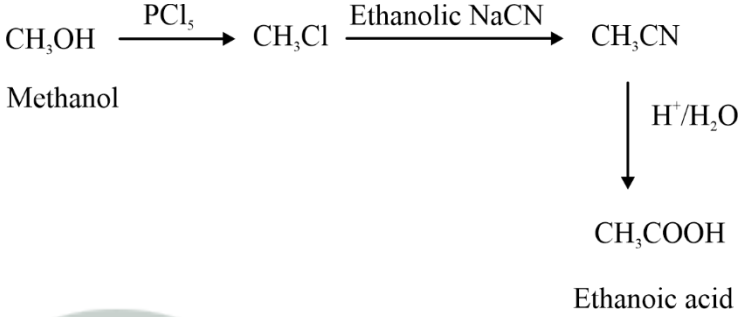

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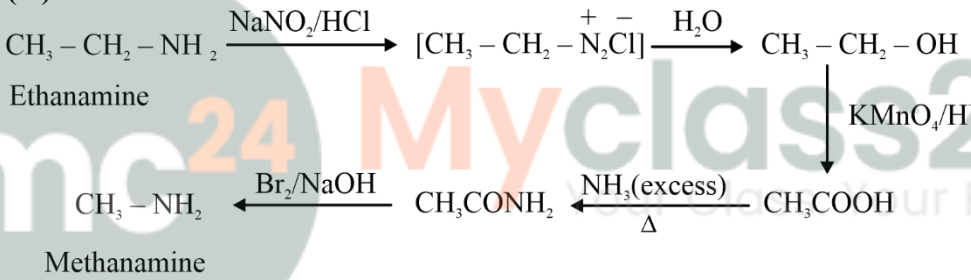

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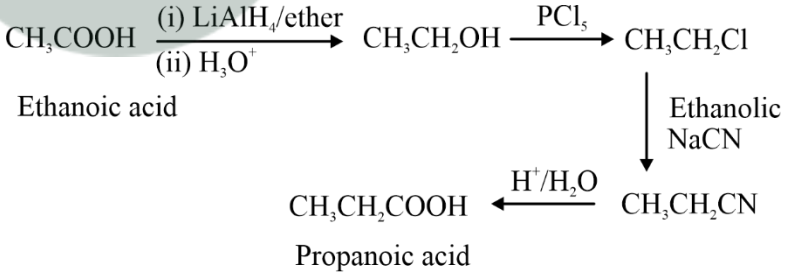

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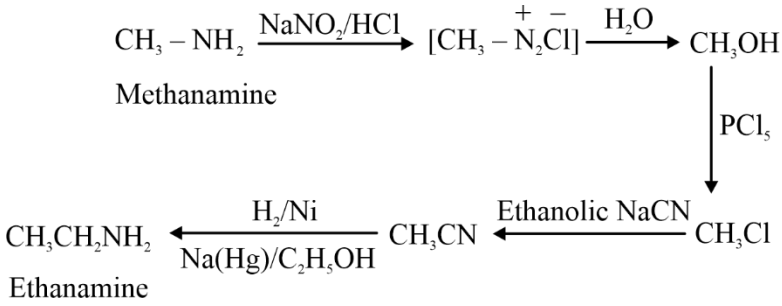

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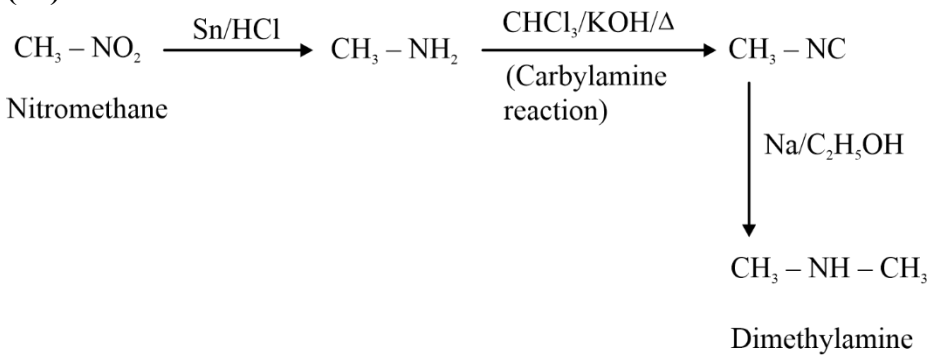
(vii)



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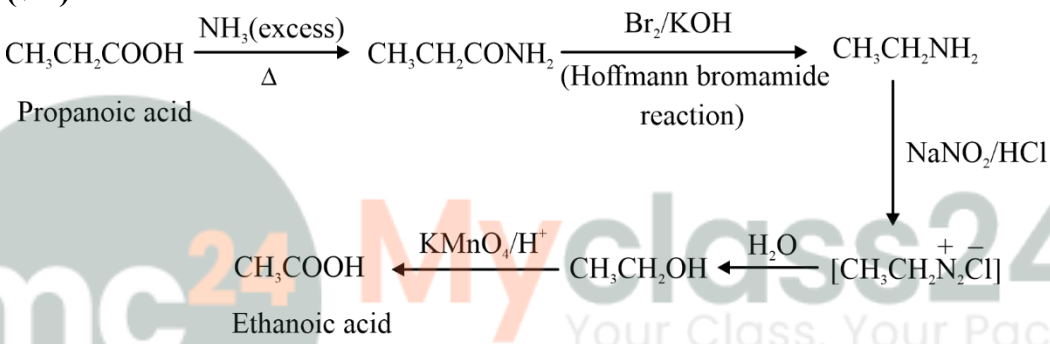

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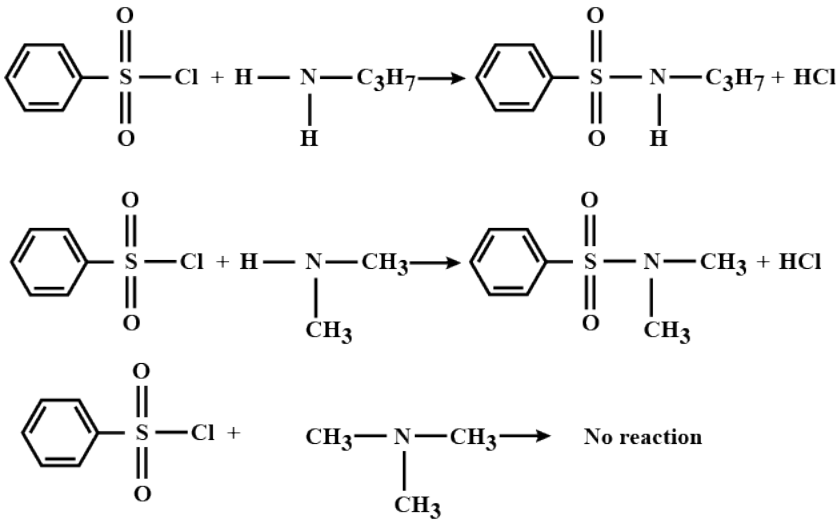
6. Describe a method for the identification of primary, secondary and tertiary amines. Also write chemical equations of the reactions involved.

6. Hinsberg's test is used for the identification of primary, secondary, and tertiary amines.
Hinsberg's reagent is benzenesulphonyl chloride ($C_6H_5SO_2Cl$).
It reacts differently with primary, secondary, and tertiary amines.
(i) Hinsberg's reagent reacts with primary amines to form N− alkylbenzenesulphonyl amide which is acidic in nature and soluble in alkali.
Note: N− alkylbenzenesulphonyl amide contains a strong electron-withdrawing sulphonyl group. Due to this, the H− atom attached to nitrogen can be removed easily. Hence, it is acidic.
(ii) Hinsberg's reagent reacts with secondary amines to form a sulphonamide which is insoluble in alkali.
Note: As there is no hydrogen atom attached to the N atom in the sulphonamide, it is not acidic and insoluble in alkali.
(iii) Hinsberg's reagent does not react with tertiary amines.



7. 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.

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7. (i) Carbylamine reaction

Carbylamine reaction is used as a test for the identification of primary amines. When aliphatic and aromatic primary amines are heated with chloroform and ethanolic potassium hydroxide, carbylamines (or isocyanides) are formed. These carbylamines have very unpleasant odours. Secondary and tertiary amines do not respond to this test.

$$R-NH_2 + CHCl_3 + 3KOH(alc.) \xrightarrow{\Delta} R-NC + 3KCl + 3H_2O$$

Primary amine — Chloroform — Potassium hydroxide — Carbylamine

For example,

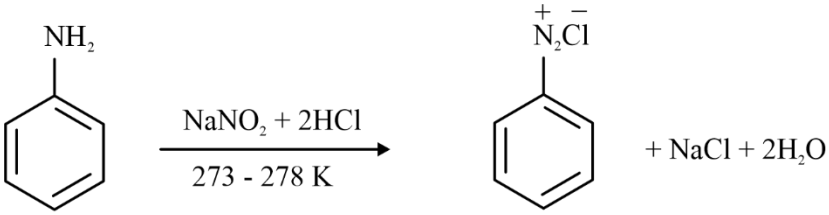
$$CH_3-NH_2 + CHCl_3 + 3KOH(alc.) \xrightarrow{\Delta} CH_3-NC + 3KCl + 3H_2O$$

Methanamine — Methyl carbylamine or methyl isocyanide

(ii) Diazotisation

Aromatic primary amines react with nitrous acid (prepared in situ from $NaNO_2$ and a mineral acid such as HCl) at low temperatures (273-278 K) to form diazonium salts. This conversion of aromatic primary amines into diazonium salts is known as diazotization.

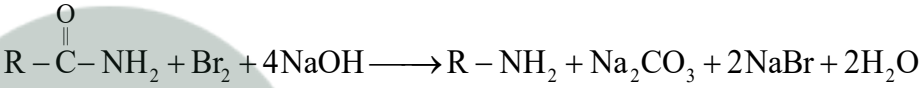
For example, on treatment with $NaNO_2$ and HCl at 273-278 K, aniline produces benzenediazonium chloride, with NaCl and H_2O as by-products.



Aniline — Benzenediazonium chloride

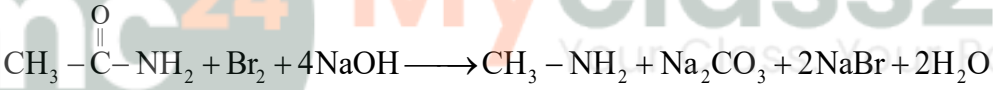
(iii) Hoffmann bromamide reaction

When an amide is treated with bromine in an aqueous or ethanolic solution of sodium hydroxide, a primary amine with one carbon atom less than the original amide is produced. This degradation reaction is known as Hoffmann bromamide reaction. This reaction involves the migration of an alkyl or aryl group from the carbonyl carbon atom of the amide to the nitrogen atom.

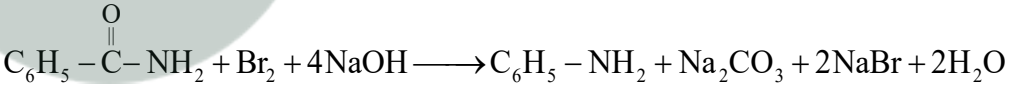


Amide — Primary amine

For example,



Ethanamide — Methanamine



Benzamide — Aniline

(iv) Coupling reaction

The reaction of joining two aromatic rings through the –N=N–bond is known as coupling reaction. Arenediazonium salts such as benzene diazonium salts react with phenol or aromatic amines to form coloured azo compounds.

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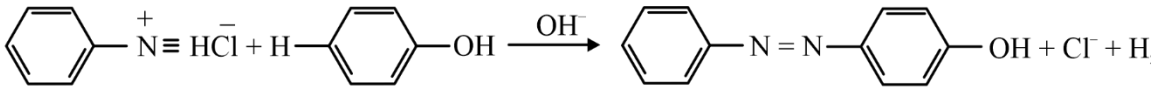
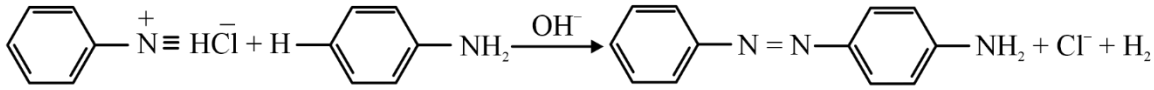


Benzenediazonium chloride | Phenol | p-Hydroxyazobenzene (Orange dye)

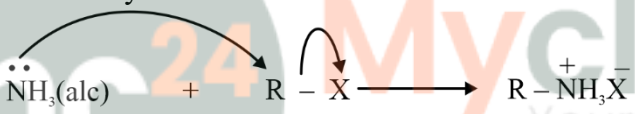


Benzendiazonium chloride | Aniline | p-Aminoazobenzene (yellow dye)

It can be observed that, the para-positions of phenol and aniline are coupled with the diazonium salt. This reaction proceeds through electrophilic substitution.

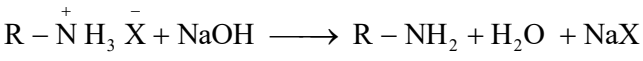
(v) Ammonolysis

When an alkyl or benzyl halide is allowed to react with an ethanolic solution of ammonia, it undergoes nucleophilic substitution reaction in which the halogen atom is replaced by an amino ($-NH_2$) group. This process of cleavage of the carbon-halogen bond is known as ammonolysis.



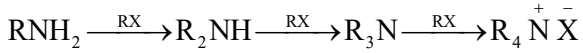
Ammonia (Nucleophile) | Alkyl halide | Substituted ammonium salt

When this substituted ammonium salt is treated with a strong base such as sodium hydroxide, amine is obtained.



Amine

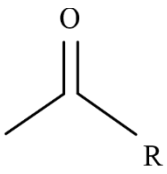
Though primary amine is produced as the major product, this process produces a mixture of primary, secondary and tertiary amines, and also a quaternary ammonium salt as shown.



(1°) (2°) (3°) Quaternary ammonium salt

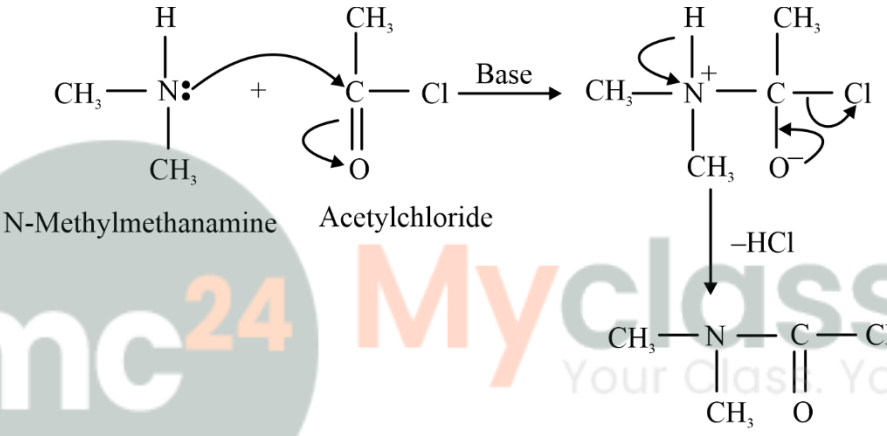
(vi) Acetylation

Acetylation (or ethanoylation) is the process of introducing an acetyl group into a molecule.



Acetyl group

Aliphatic and aromatic primary and secondary amines undergo acetylation reaction by nucleophilic substitution when treated with acid chlorides, anhydrides or esters. This reaction involves the replacement of the hydrogen atom of $-NH_2$ or > NH group by the acetyl group, which in turn leads to the production of amides. To shift the equilibrium to the right hand side, the HCl formed during the reaction is removed as soon as it is formed. This reaction is carried out in the presence of a base (such as pyridine) which is stronger than the amine.



N-Methylmethanamine Acetylchloride N, N-Dimethylethanamide

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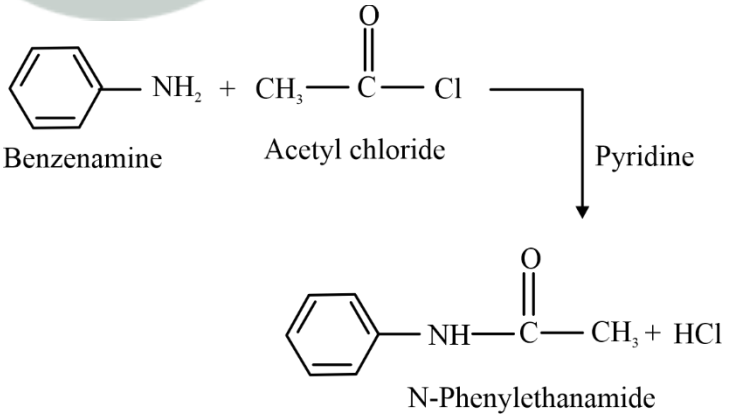
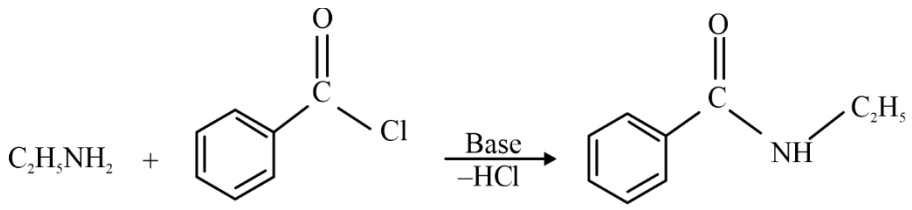


Benzenamine Acetyl chloride N-Phenylethanamide

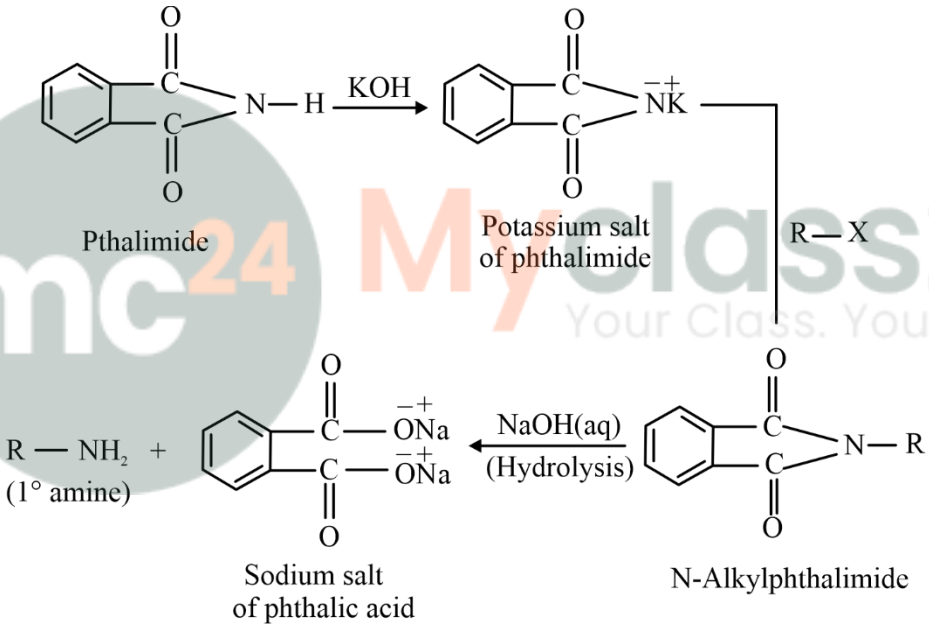
When amines react with benzoyl chloride, the reaction is also known as benzoylation. For example,



Ethanamine Benzoyl chloride N-Ethylebenzamide

(vii) Gabriel phthalimide synthesis

Gabriel phthalimide synthesis is a very useful method for the preparation of aliphatic primary amines. It involves the treatment of phthalimide with ethanolic potassium hydroxide to form potassium salt of phthalimide. This salt is further heated with alkyl halide, followed by alkaline hydrolysis to yield the corresponding primary amine.



Pthalimide

Potassium salt of phthalimide

Sodium salt of phthalic acid

N-Alkylphthalimide

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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

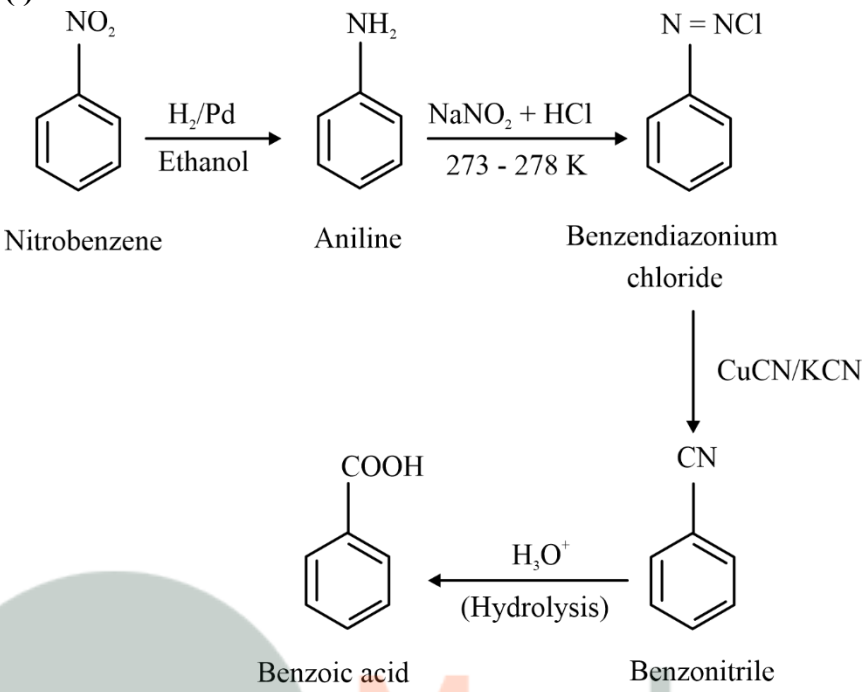
(vi) Chlorobenzene to p-chloroaniline

(vii) Aniline to p-bromoaniline

(viii) Benzamide to toluene.

(ix) Aniline to benzyl alcohol.

8. **(i)**



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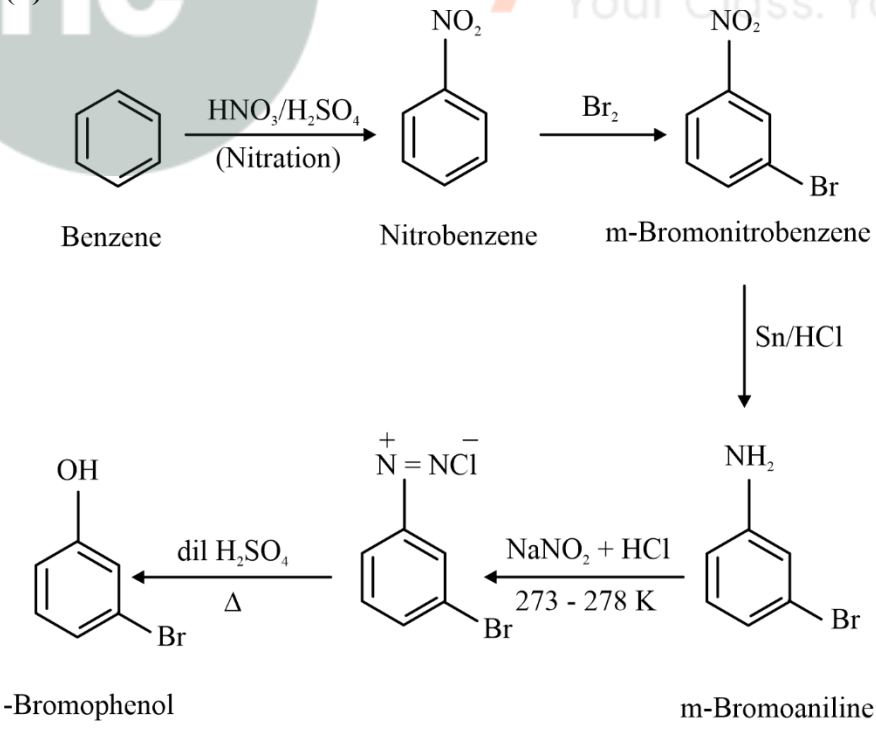
(ii)



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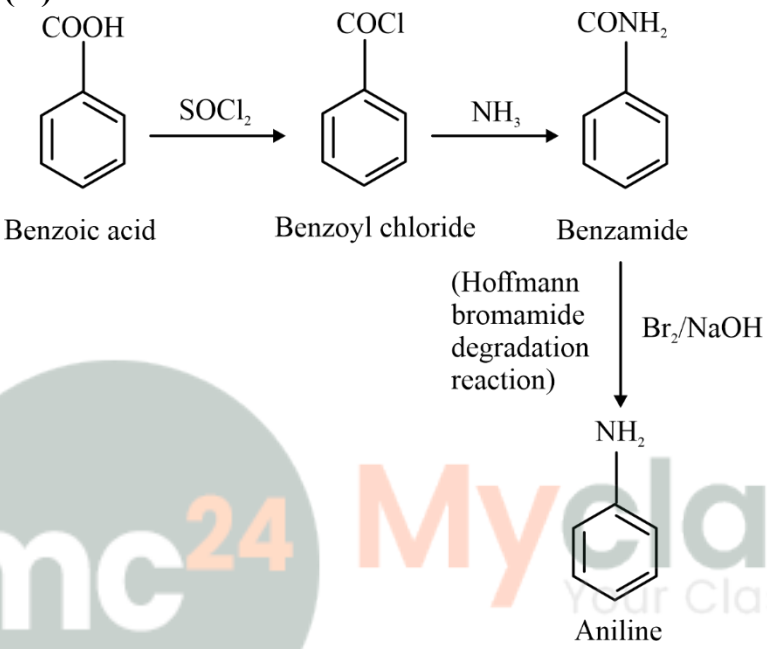

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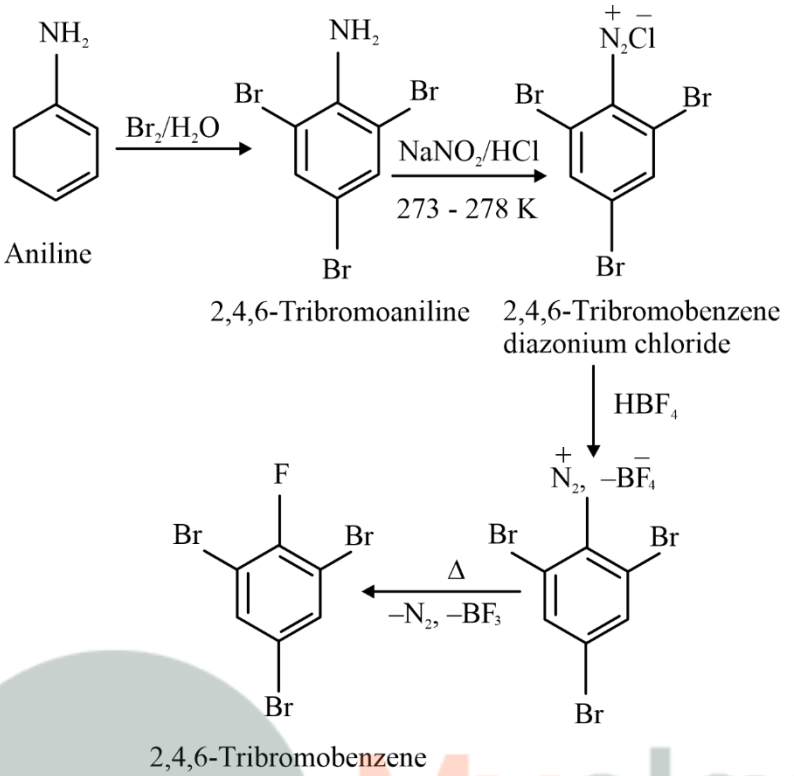
(iv)



Aniline

2,4,6-Tribromoaniline

2,4,6-Tribromobenzene diazonium chloride

2,4,6-Tribromobenzene

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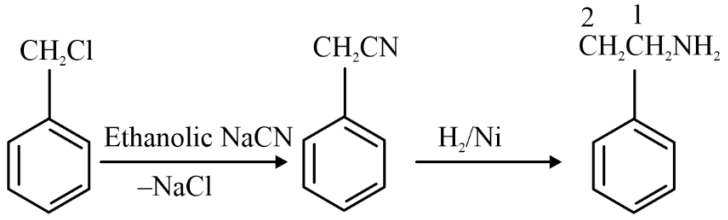
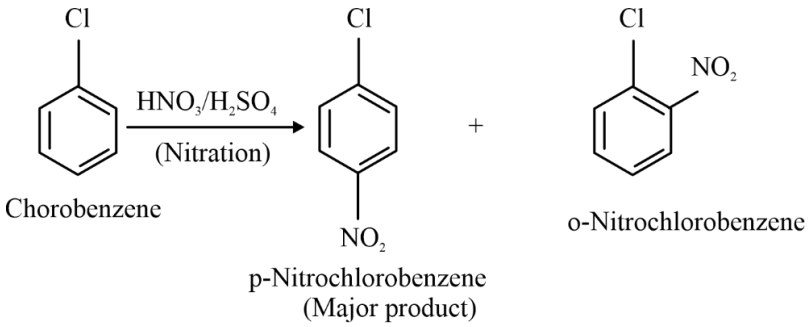
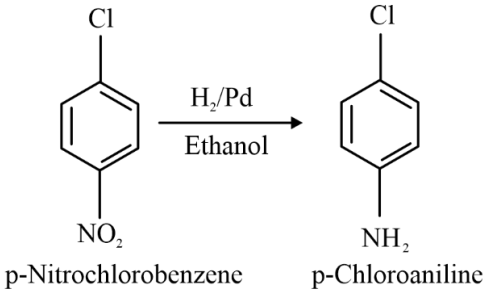
(v)



Benzyl chloride Phenylethanenitrile 2-Phenylethanamine

(vi)





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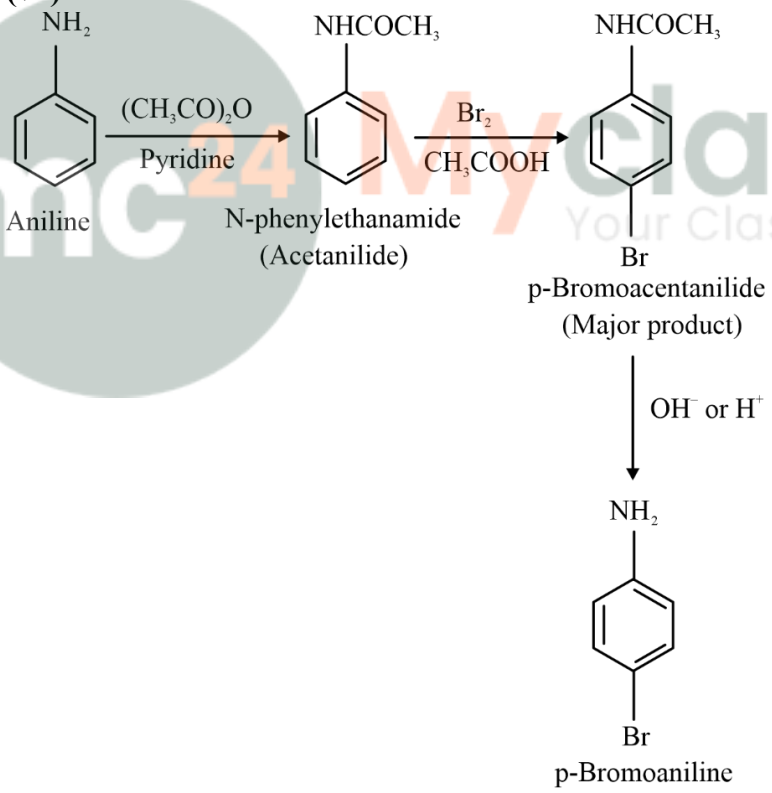

(viii)

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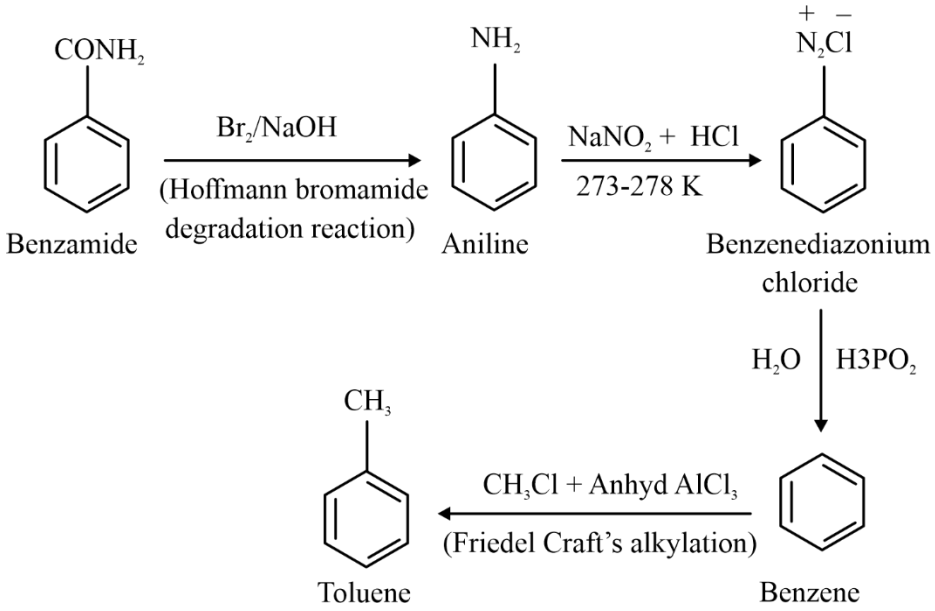

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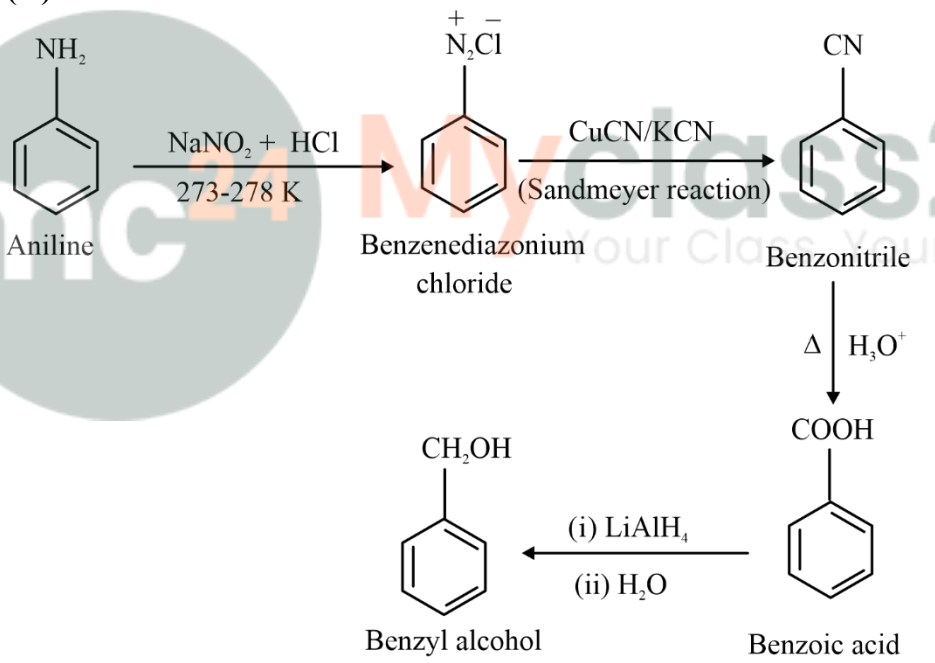

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9. Give the structures of A, B and C in the following reactions:

(i) $CH_3CH_2I \xrightarrow{NaCN} A \xrightarrow[\text{Partial hydrolysis}]{OH^-} B \xrightarrow{NaOH+Br_2} C$

(ii) $C_6H_5N_2Cl \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow[\Delta]{NH_3} C$

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

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

(v) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{NaOBr} B \xrightarrow{NaNO_2/HCl} C$

(vi) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273K]{HNO_2} B \xrightarrow{C_6H_5OH} C$

9. (i)

$CH_3CH_2I \xrightarrow{NaCN}$ CH_3CH_2CN Propanenitrile (A) $\xrightarrow[\text{Partial hydrolysis}]{OH^-}$ $CH_3-\overset{O}{\overset{\|}{C}}-CN$ Ethanamide (B) $\xrightarrow{NaOH + Br_2}$ CH_3-NH_2 Methanamine (C)

(ii)

$C_6H_5N_2Cl \xrightarrow{CuCN}$ C_6H_5CN Cyanobenzene (A) $\xrightarrow{H_2O/H^+}$ C_6H_5COOH Benzoic acid (B) $\xrightarrow{\Delta\ NH_3}$ $C_6H_5CONH_2$ Benzamide (C)

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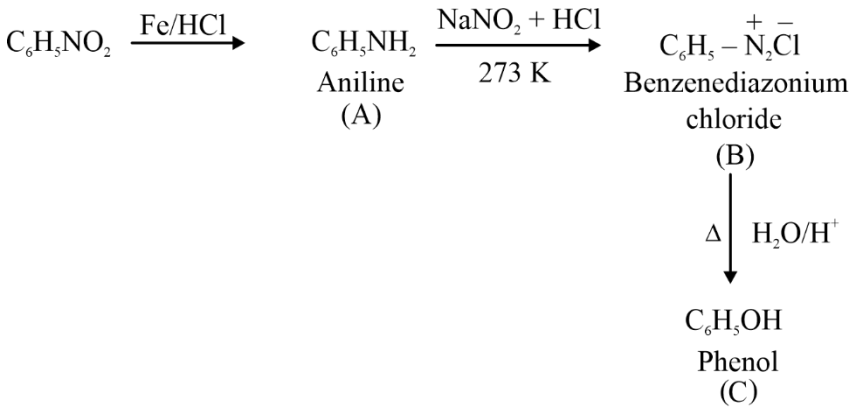
(iii)

$CH_3CH_2Br \xrightarrow{KCN}$ CH_3CH_2CN Cyanoethane (A) $\xrightarrow{LiAlH_4}$ $CH_3CH_2CH_2NH_2$ Propan - 1 - amine (B) $\xrightarrow{0°C\ HNO_2}$ $CH_3CH_2CH_2OH$ Propan - 1- ol (C)

(iv)



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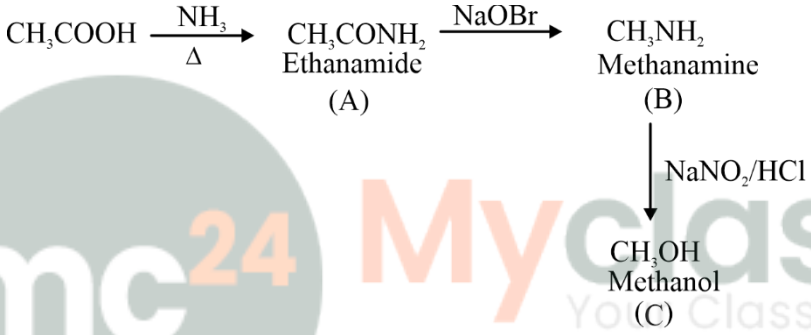

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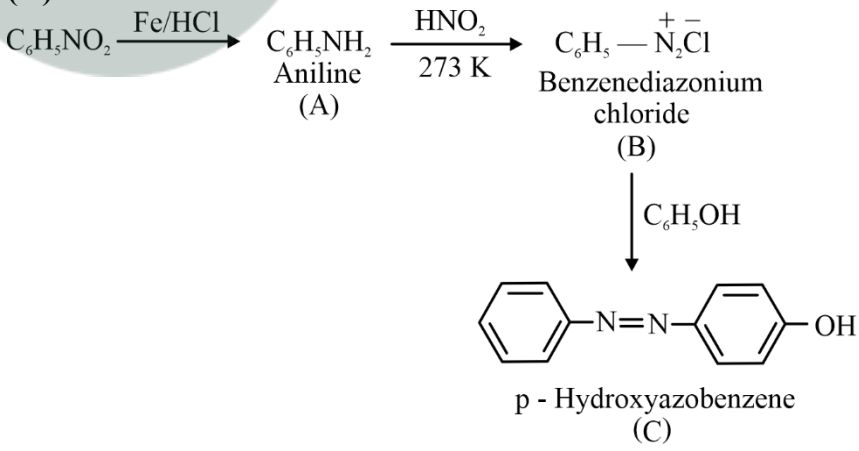
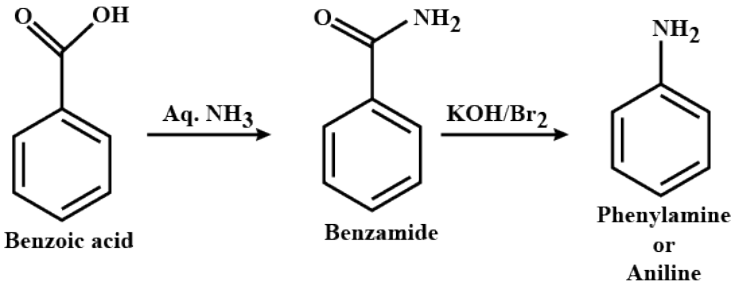


10. An aromatic compound 'A' on treatment with aqueous ammonia and heating forms compound 'B' which on heating with Br_2 and KOH forms a compound 'C' of molecular formula C_6H_7N. Write the structures and IUPAC names of compounds A, B and C.

10. The aromatic compound A is benzoic acid C_6H_5COOH.

On treatment with aqueous ammonia and heating forms compound B, which is benzamide $C_6H_5CONH_2$. Benzamide on heating with bromine and KOH forms a compound C of molecular formula C_6H_7N, which is aniline $C_6H_5NH_2$. The reaction is called Hoffmann bromamide degradation.



11. Complete the following reactions:

(i) $C_6H_5NH_2 + CHCl_3 + \text{alc. KOH} \rightarrow$

(ii) $C_6H_5NH_2 + H_2SO_4 \text{ (conc.)} \rightarrow$

(iii) $C_6H_5NH_2 + H_2SO_4 \text{ (conc.)} \rightarrow$

(iv) $C_6H_5N_2Cl + C_2H_5OH \rightarrow$

(v) $C_6H_5NH_2 + Br_2 \text{ (aq)} \rightarrow$

(vi) $C_6H_5NH_2 + (CH_3CO_2)O \rightarrow$

(vii) $C_6H_5N_2Cl \xrightarrow[(ii)\,NaNO_2/Cu.\Delta]{(i)\,HBF_4}$

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11. (i)

$$C_6H_5NH_2 + CHCl_3 + 3\text{alc. KOH} \xrightarrow[\text{reaction}]{\text{Carbylamine}} 3H_2O + 3KCl + C_6H_5 - NC$$

Aniline — Phenyl isocyanide

(ii)

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

Benzenediazonium chloride — Benzene

(iii)

$$C_6H_5NH_2 + \text{conc. } H_2SO_4 \longrightarrow C_6H_5\overset{+}{N}H_3\overset{-}{HSO_4}$$

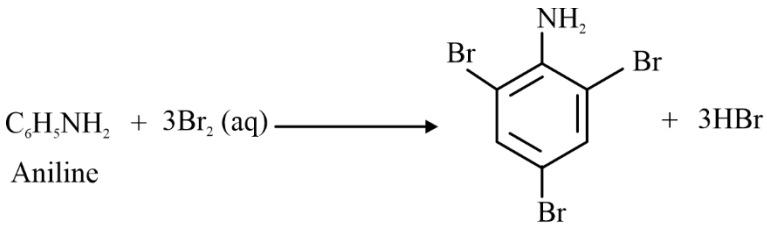
Aniline — Anilinium hydrogen sulphate

(iv)

$$C_6H_5N_2Cl + C_2H_5OH \longrightarrow C_6H_6 + CH_3CHO + N_2 + HCl$$

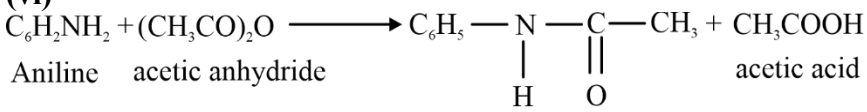
Benzenediazonium chloride — Ethanol — Benzene — Ethanol

(v)



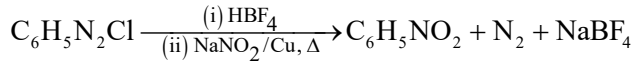
2,4,6 - Tribromoaniline

(vi)



N-Phenylethanamide

(vii)



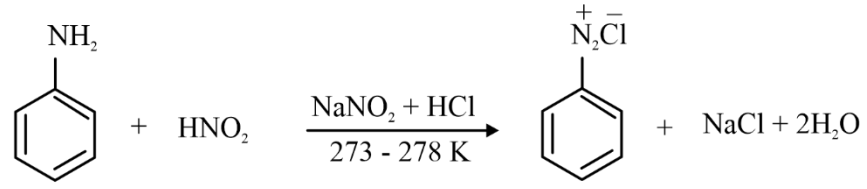
Benzenediazonium chloride — Nitrobenzene

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

12. During Gabriel phthalimide synthesis, the reaction between phthalimide and ethanolic potassium hydroxide gives potassium salt of phthalimide.
The salt on heating with alkyl halide followed by alkaline hydrolysis gives corresponding primary amine.
Aromatic primary amines cannot be prepared by Gabriel phthalimide synthesis as aryl halides do not undergo nucleophilic substitution with the salt formed by phthalimide.

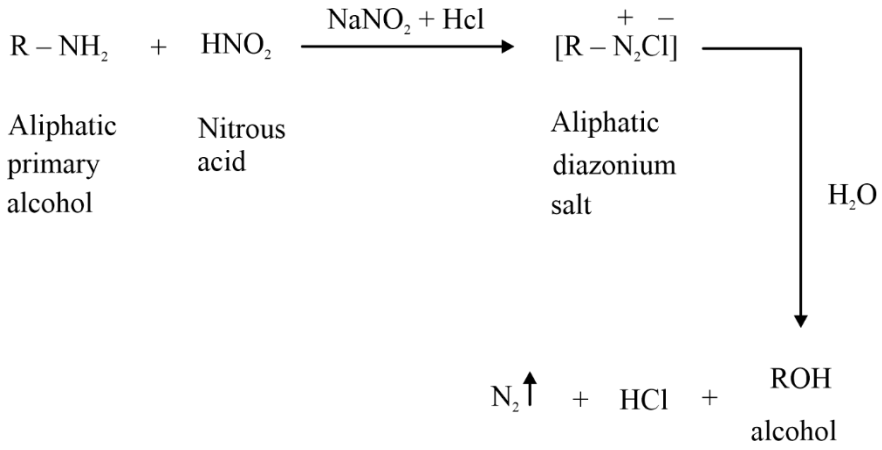
13. Write the reactions of (i) aromatic and (ii) aliphatic primary amines with nitrous acid.

13. (i) Aromatic amines react with nitrous acid (prepared in situ from $NaNO_2$ and a mineral acid such as HCl) at 273 – 278 K to form stable aromatic diazonium salts i.e., NaCl and H_2O.



Aniline — Nitrous acid — Benzendiazonium chloride

(ii) Aliphatic primary amines react with nitrous acid (prepared in situ from $NaNO_2$ and a mineral acid such as HCl) to form unstable aliphatic diazonium salts, which further produce alcohol and HCl with the evolution of N_2 gas.



14. 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?

14. (i) Amines lose a proton to form amide ion. Alcohols lose a proton to form alkoxide ion.
$RNH_2 \rightarrow RNH^- + H^+$
$R - OH \rightarrow R - O^- + H^+$
O is more electronegative than N, the negative charge is more easily accomodated in RO^- than in $R{-}NH^-$. Hence, amines are less acidic than alcohols of comparable molecular masses.
(ii) In primary amines, N atoms have two H atoms which results in extensive intermolecular H bonding. In tertiary amines, N atoms do not have H atoms and hydrogen bonding is not possible.
Hence, primary amines have higher boiling point than tertiary amines.
(iii) Aliphatic amines stronger bases than aromatic amines due to following reasons:
(a) Aromatic amines have resonance due to which lone pair of electrons on N atom is delocalized over benzene ring and is less available for protonation.
(b) The stability of aryl amine ions is lower than the stability of alkyl amines. Protonation of aromatic amines is not favoured.

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