

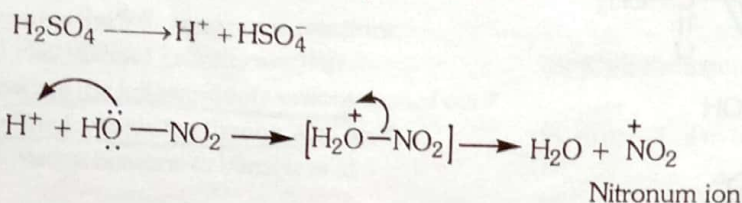
ORGANIC COMPOUNDS CONTAINING NITROGEN

SOLVED SUBJECTIVE EXERCISE

Very Short Answer Type Questions (1 mark)

1. During nitration of benzene with a mixture of concentrated nitric acid and concentrated sulphuric acid, nitric acid acts as a base. Explain.

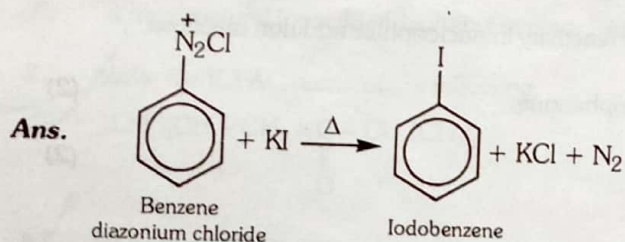
Ans. Both HNO_3 and H_2SO_4 are strong acids but H_2SO_4 is a stronger acid than HNO_3 . Therefore, during nitration, H_2SO_4 acts as an acid releasing a proton. HNO_3 , on the other hand, accepts this proton and thus acts as a base. The protonated nitric acid then loses a proton to form nitronium ion which then brings about the nitration.



2. Why does acetylation of $-\text{NH}_2$ group of aniline reduce its activating effect?

Ans. Due to electron-withdrawing effect of the acetyl group, the lone pair of electrons on N-atom is attracted by the $\text{C}=\text{O}$ group. As a result, lone pair of electrons on N-atom is not exclusively available for donation to the benzene ring and hence activating effect of the NH_2 group is reduced.

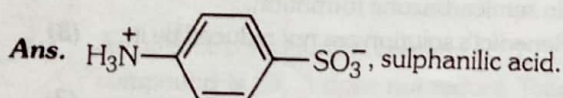
3. Write a chemical reaction in which the iodide ion replaces the diazonium group in a diazonium salt.



4. Why is an alkylamine more basic than ammonia?

Ans. Alkyl amine is more basic than ammonia because the +I effect or electron donating nature of alkyl group increases electron density on 'N' atom in alkyl amine.

5. Give an example of a zwitter ion.



6. How is the basic strength of aromatic amines affected by the presence of electron releasing group on the benzene ring?

Ans. An electron releasing group increases the electron density on the N-atom. As a result, its tendency to donate an electron pair to a proton increases and hence the basicity of the amine increases.

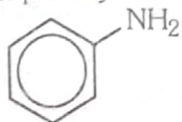
7. Aniline gets coloured on standing in air for a long time. Why?

Ans. Due to strong electron-donating effect (+R-effect) of NH_2 group, the electron density on the benzene ring increases. As a result, aniline is easily oxidised on standing in air for a long time to form coloured products.

8. Give a chemical test to distinguish between aniline and N-methyl aniline.

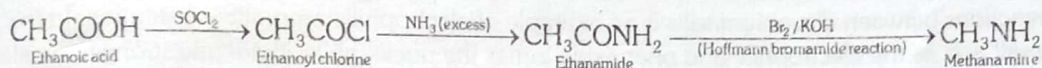
Ans. On adding CHCl_3 and KOH , aniline gives offensive smelling isocyanide, whereas N-methyl aniline does not react.

9. Write structures and IUPAC names of : the amine produced by the Hoffmann's degradation of benzamide.
Ans. Benzamide is an aromatic amide containing seven carbon atoms. Hence, the amine formed from benzamide is aromatic primary amine containing six carbon atoms.



Benzenamine

10. How will you convert ethanoic acid to methanamine.
Sol. Ethanoic acid to Methanamine

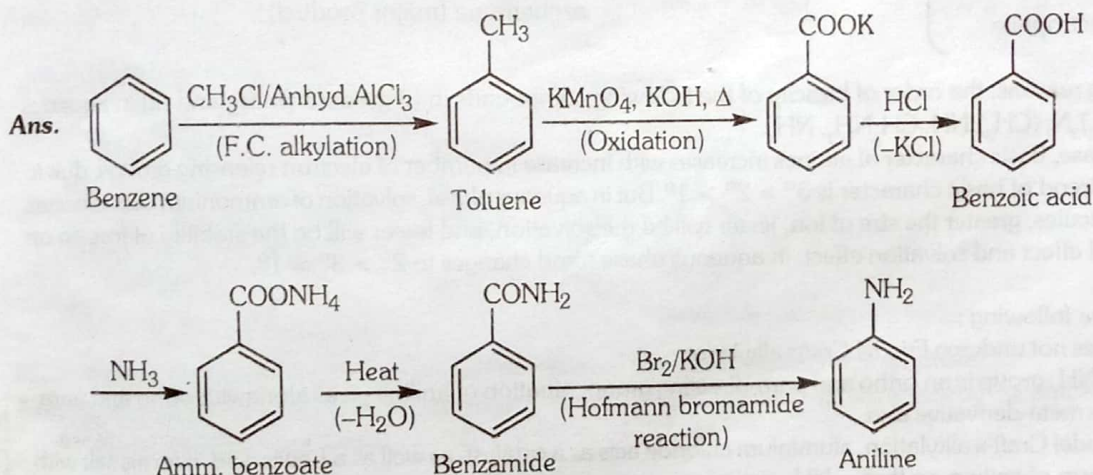


Short Answer Type Questions (2 mark)

11. Why does aniline turn blackish brown in open air.

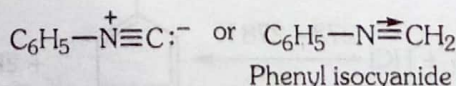
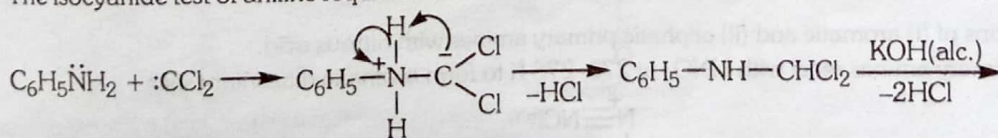
Sol. Due to strong electron-donating effect (+R-effect) or the NH₂ group, the electron density on the benzene ring increases. As a result, aniline is easily oxidised on standing in air for a long time to form coloured blackish brown products.

12. Convert benzene to aniline using the following reagents in correct order :
 Alkaline KMnO₄ followed by HCl; NH₃, heat; Br₂/KOH; CH₃Cl/anhyd. AlCl₃.

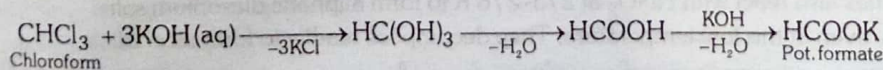


13. Why ethanoic KOH and not aqueous KOH is used in the isocyanide test of aniline?

Ans. The isocyanide test of aniline requires the intermediate formation of dichlorocarbene (: CCl₂).

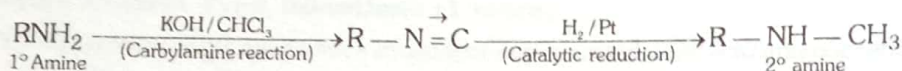


To generate : CCl₂ from CHCl₃, a strong base like alc. KOH is needed. With aq. KOH only hydrolysis of CHCl₃ to HCOOK will occur.



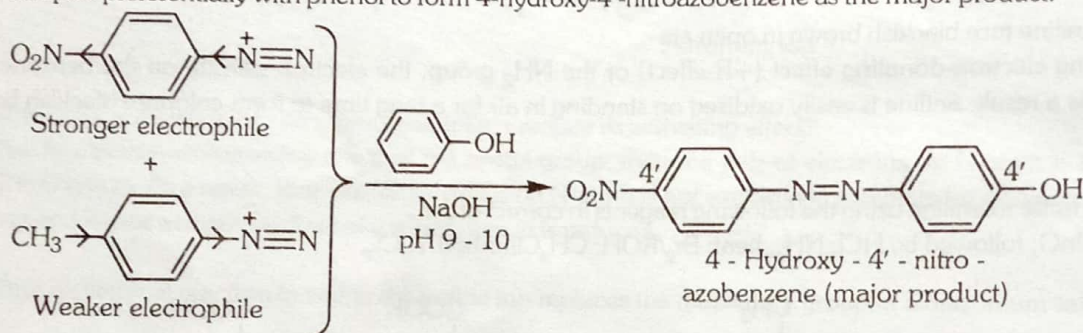
14. A primary amine, RNH_2 can be reacted with $\text{CH}_3\text{-X}$ to get secondary amine, R-NHCH_3 but the only disadvantage is that 3° amine and quaternary ammonium salts are also obtained as side products. Can you suggest a method where RNH_2 forms only 2° amine?

Ans. 1° Amines react with CHCl_3 in presence of alcoholic KOH to form isocyanides which upon catalytic reduction give 2° amines.



15. A solution contains 1 g mol. each of p-toluenediazonium chloride and p-nitrophenyldiazonium chloride. To this 1 g mol. of alkaline solution of phenol is added. Predict the major product. Explain your answer.

Ans. In alkaline medium, phenol forms phenoxide ion which is more electron rich and hence more reactive than phenol. Coupling reactions between diazonium salts is an example of electrophilic aromatic substitution. In this reaction, diazonium salt acts as the electrophile and phenoxide ion as the nucleophile. Evidently stronger the electrophile faster is the reaction. Now due to electronwithdrawing effect of the $-\text{NO}_2$ group, p-nitrophenyldiazonium cation is a stronger electrophile than p-toluenediazonium cation (+I-effect of CH_3 group reduces its electrophilicity) and hence couples preferentially with phenol to form 4-hydroxy-4'-nitroazobenzene as the major product.



16. Predict, giving reasons, the order of basicity of the following compounds in (i) gaseous phase and (ii) in aqueous solutions $(\text{CH}_3)_3\text{N}$, $(\text{CH}_3)_2\text{NH}$, CH_3NH_2 , NH_3 .

Ans. In gaseous phase, basic character of amines increases with increase in number of electron releasing groups, due to + I effect, so trend of basic character is $3^\circ > 2^\circ > 1^\circ$. But in aqueous phase, solvation of ammonium cation occurs by water molecules, greater the size of ion, lesser will be the solvation, and lesser will be the stability of ion, so on combining + I effect and solvation effect, in aqueous phase trend changes to $2^\circ > 3^\circ > 1^\circ$.

17. Account for the following :

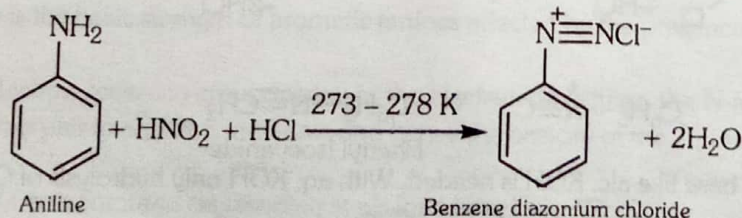
- Aniline does not undergo Friedel Crafts alkylation.
- Although $-\text{NH}_2$ group is an ortho and para-directing group, nitration of aniline gives alongwith ortho and para-derivatives meta-derivative also.

Ans. (a) During Friedel Craft's alkylation, aluminium chloride acts as a catalyst, as well as a Lewis acid, it forms salt with $-\text{NH}_2$ group of aniline, so that $-\text{NH}_2$ group acquires a positive charge, and acts as a deactivating group, so aniline does not undergo FCA.

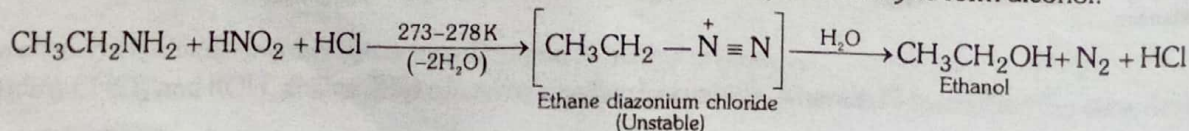
(b) During nitration, in strongly acidic medium aniline is protonated to form anilinium ion, which is a meta directing group, so along with o^- & p^- isomers, meta isomer is also obtained.

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

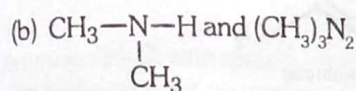
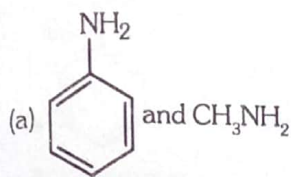
Ans. (i) Aromatic primary amines react with HNO_2 at 273-278 K to form aromatic diazonium salts.



(ii) Aliphatic primary amines also react with HNO_2 at 273-278 K to form aliphatic diazonium salts. But they are not stable even at this low temperature. They decompose readily to form alcohol.

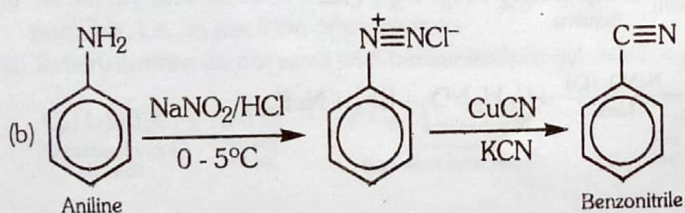
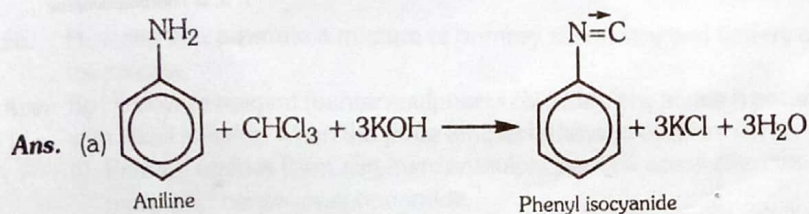


19. How will you distinguish between :



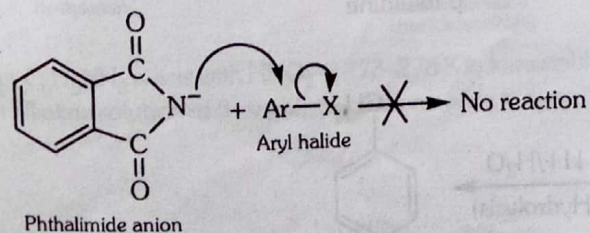
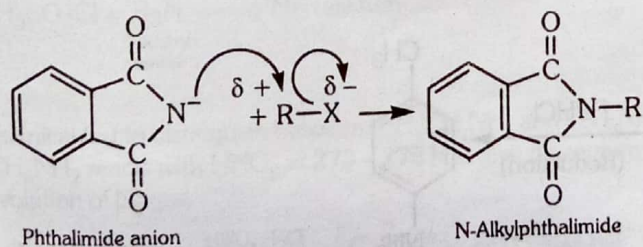
- Ans.** (a) By reacting with NaNO_2 and HCl or HNO_2 at temperature $0-5^\circ\text{C}$.
 Aniline will form diazonium salt.
 CH_3NH_2 will form methanol and bubbles of N_2 gas will come out of the solution.
- (b) By using Hinsberg's reagent, $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$.
 $(\text{CH}_3)_3\text{N}$ will not react.
 $(\text{CH}_3)_2\text{NH}$ will form a product insoluble in alkali.

20. Convert : (a) Aniline to phenyl isocyanide (b) Aniline to Benzonitrile.



21. Why aromatic primary amines cannot 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.

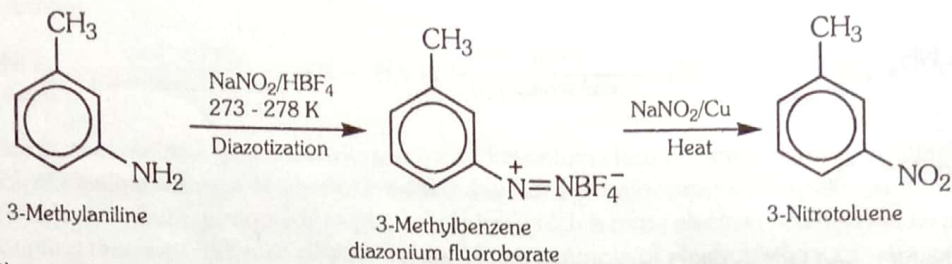


As aryl halides do not undergo nucleophilic substitution reactions easily, aromatic primary amines cannot be prepared by Gabriel phthalimide reaction.

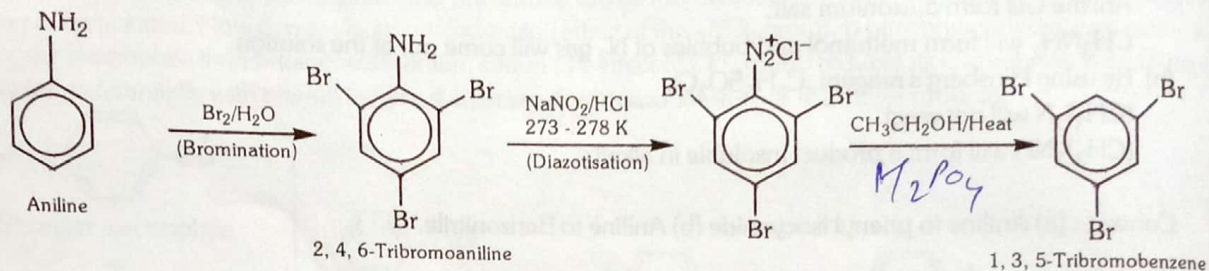
22. Convert :

(i) 3-Methylaniline into 3-nitrotoluene (ii) Aniline into 1, 3, 5-tribromobenzene.

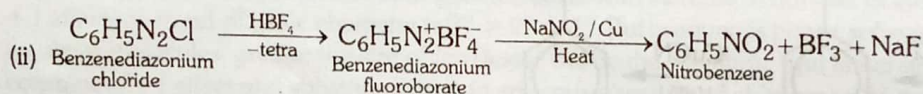
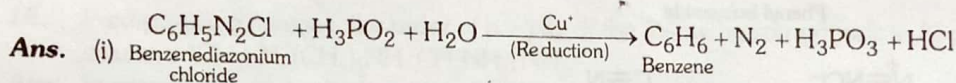
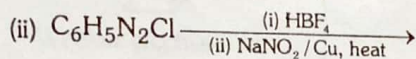
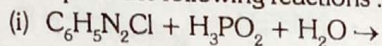
Ans. (i)



(ii)



23. Complete the following reactions :



Short Answer Type Questions (3 mark)

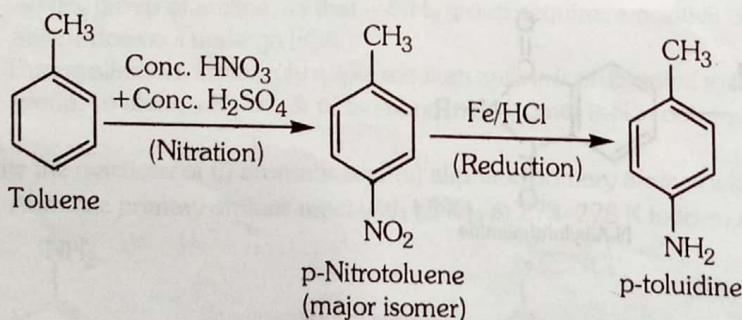
24. How will you carry out the following conversions?

(i) toluene \rightarrow p-toluidine

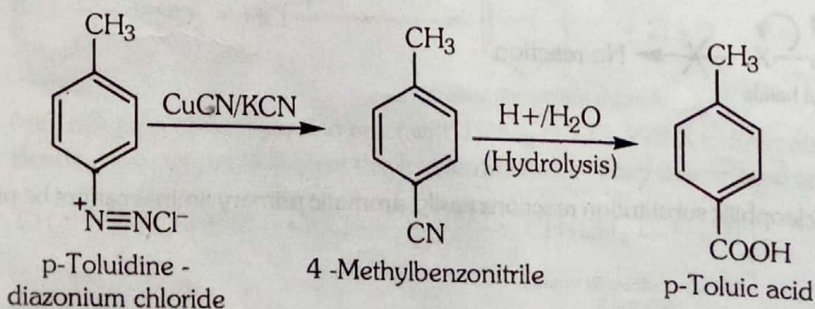
(ii) p-toluidinediazonium chloride \rightarrow p-toluic acid.

(iii) nitrobenzene \rightarrow acetanilide

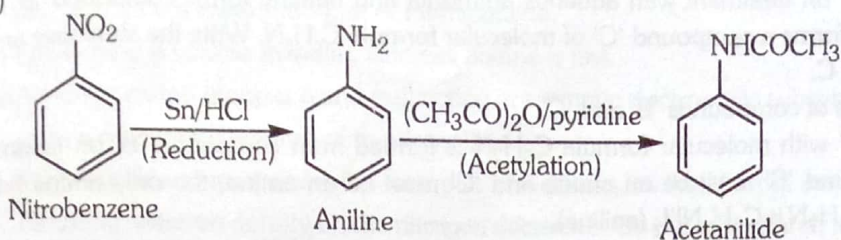
Ans. (i)



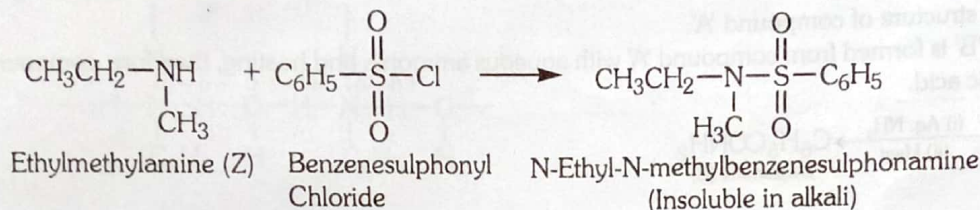
(ii)



(iii)



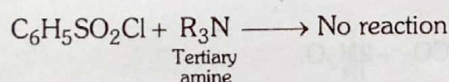
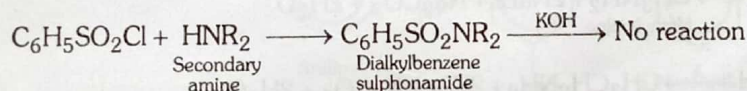
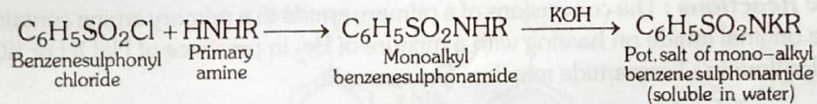
25. A compound Z with molecular formula $\text{C}_3\text{H}_9\text{N}$ reacts with $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$ to give a solid, insoluble in alkali. Identify Z.
Ans. Since the amine Z on treatment with $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$ gives a product which is insoluble in alkali, therefore, the product does not have a replaceable hydrogen on the N-atom. In other words, the amine Z is a 2° amine. The only 2° amine having the M.F. $\text{C}_3\text{H}_9\text{N}$ is ethylmethylamine, i.e., the amine (Z) is ethylmethylamine ($\text{CH}_3\text{CH}_2\text{NHCH}_3$)



26. How can you separate a mixture of primary, secondary and tertiary amines? Write chemical reactions involved in the process.

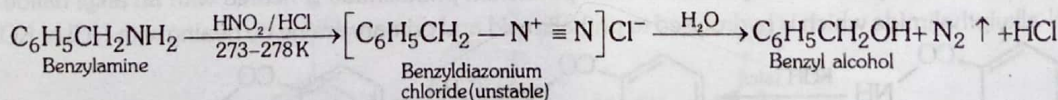
Ans. By Hinsberg's reagent (benzenesulphonyl chloride). The amine is treated with benzenesulphonyl chloride and shaken with alkali solution when the three amines behave in different ways :

- Primary amines form alkylbenzenesulphonamide which dissolves in alkali to form sodium or potassium salt of monoalkyl benzenesulphonamide.
- Secondary amines form dialkyl benzenesulphonamide which does not react with alkali and hence it remains insoluble, i.e., in the form of precipitate.
- Tertiary amines do not react with benzenesulphonyl chloride at all.

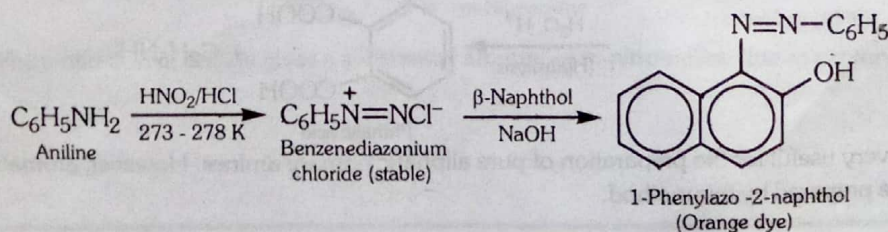


27. Give chemical test to distinguish between $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ and $\text{C}_6\text{H}_5\text{NH}_2$.

Ans. $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ reacts with HNO_2 at 273 – 278 K to give diazonium salt, which, being unstable, decomposes with brisk evolution of N_2 gas.



whereas, $\text{C}_6\text{H}_5\text{NH}_2$ reacts with HNO_2 at 273–278 K to form stable benzenediazonium chloride, which upon treatment with an alkaline solution of β -naphthol, given an orange dye.

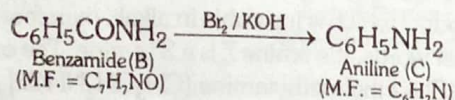


28. An aromatic compound 'A' on treatment with aqueous ammonia and heating forms compound 'B' which on heating with Br₂ and KOH forms a compound 'C' of molecular formula C₆H₇N. Write the structures and IUPAC names of compounds A, B, C.

Ans. 1. To find out the structures of compounds 'B' and 'C'.

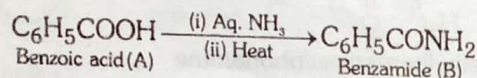
(i) Since compound 'C' with molecular formula C₆H₇N is formed from compound 'B' on treatment with Br₂ + KOH compound 'B' must be an amide and 'C' must be an amine, the only amine having the molecular formula C₆H₇N is C₆H₅NH₂ (aniline).

(ii) Since 'C' is aniline, the amide from which it is formed must be benzamide. Thus, compound 'B' is benzamide. The chemical equation showing the conversion of 'B' to 'C' is



2. To find out the structure of compound 'A'.

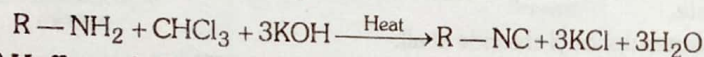
As compound 'B' is formed from compound 'A' with aqueous ammonia and heating, therefore, compound 'A' must be benzoic acid.



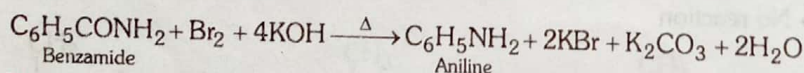
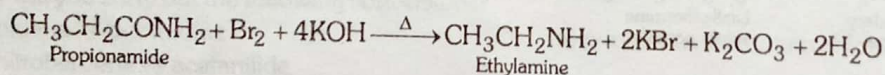
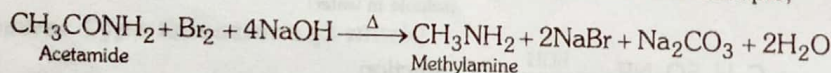
29. Write short notes on the following :

- (i) Carbylamine reaction
- (ii) Hoffmann's-bromamide reaction
- (vii) Gabriel phthalimide synthesis.

Ans. (i) **Carbylamine reaction** : Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamines which are foul smelling substances. Secondary and tertiary amines do not show this reaction. This reaction is known as carbylamine reaction or isocyanide test and is used as a test for primary amines.

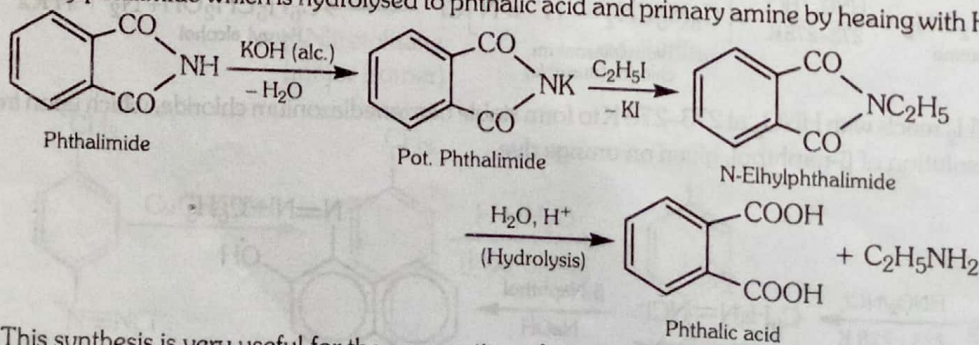


(ii) **Hoffmann's Bromamide Reactions** : The conversions of a primary amide to a primary amine containing one carbon atom less than the original amide on heating with a mixture of Br₂ in presence of NaOH or KOH, i.e., NaOBr or KOBr is called Hoffmann's bromamide reaction. For example,



This reaction is extremely useful for converting a higher homologue to the next lower homologue, i.e., for stepping down a homologous series.

(iii) **Gabriel Phthalimide Synthesis** : In this reaction, phthalimide is converted into its potassium salt by treating it with alcoholic potassium hydroxide. Then potassium phthalimide is heated with an alkyl halide to yield an N-alkylphthalimide which is hydrolysed to phthalic acid and primary amine by heating with HCl or KOH solution.

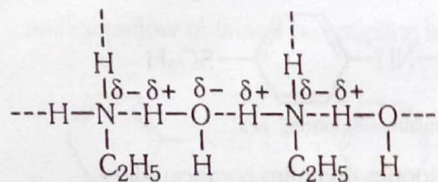


This synthesis is very useful for the preparation of pure aliphatic primary amines. However, aromatic primary amines cannot be prepared by this method.

30. 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) Although amino group is o and p-directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m-nitroaniline.

- Ans.** (i) In aniline due to resonance, the lone pair of electrons on the N-atom are delocalized over the benzene ring. Resulting, electron density on the nitrogen decreases. On the other hand, in CH_3NH_2 , positive-I-effect of CH_3 increases the electron density on the N-atom. Thus, aniline is a weaker base than methylamine and hence its pK_b value is higher than that of methylamine.
- (ii) Ethylamine dissolves in water because it forms H-bonds with water molecule as shown below :

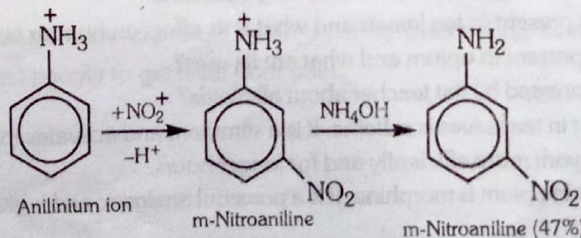
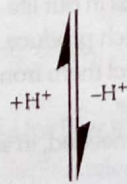
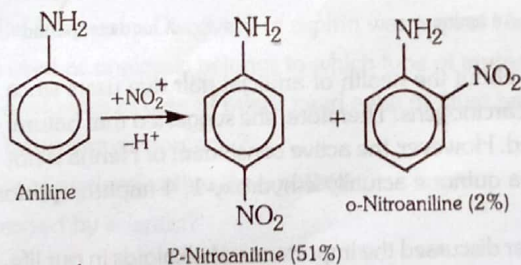


In aniline, due to the large, hydrocarbon part, the extent of H-bonding decreases considerably and hence aniline is insoluble in water.

- (iii) Nitration is usually carried out with a mixture of conc. HNO_3 and conc. H_2SO_4 .

In presence of these acids, most of aniline gets protonated to form anilinium ion. Thus, in presence of acids, the reaction mixture consists of aniline and anilinium ion. Now $-NH_2$ group in aniline is o, p-directing and activating while the $^+NH_3$ group in anilinium ion is m-directing and deactivating.

On the other hand, nitration of aniline mainly gives p-nitroaniline, the nitration of anilinium ion gives m-nitroaniline.



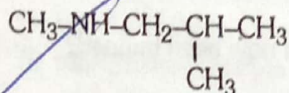
Thus, nitration of aniline gives a substantial amount of m-nitroaniline due to protonation of the amino group.

EXERCISE-1

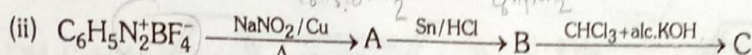
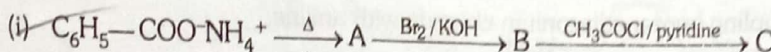
PREVIOUS YEARS BOARD PROBLEMS

CBSE 2016

1. Write the IUPAC name of the given compound:

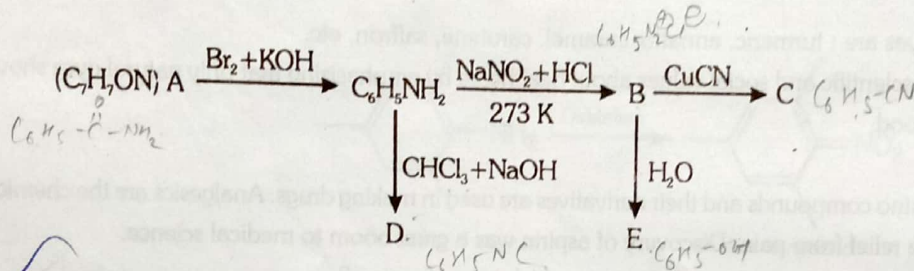


2. Write the structures of A, B and C in the following reactions:



CBSE 2015

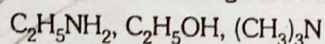
1. An aromatic compound 'A' of molecular formula $\text{C}_7\text{H}_7\text{ON}$ undergoes a series of reactions as shown below. Write the structures of A, B, C, D and E in the following reactions :



2. (a) Write the structures of the main products when aniline reacts with the following reagents :

- (i) Br_2 water (ii) HCl (iii) $(\text{CH}_3\text{CO})_2\text{O/pyridine}$

(b) Arrange the following in the increase order of their boiling point :



(c) Give a simple chemical test distinguish between the following pair of compounds $(\text{CH}_3)_2\text{-NH}$ and $(\text{CH}_3)_3\text{N}$

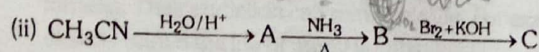
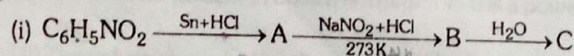
CBSE 2014

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

2. Account for the following.

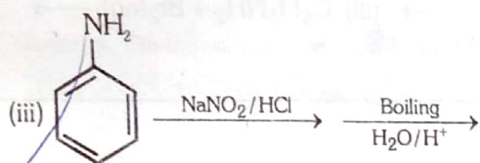
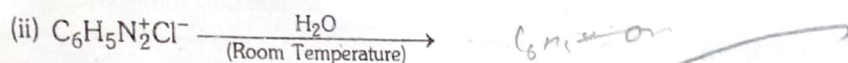
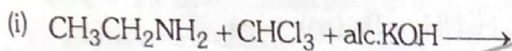
- (i) Primary amines (R-NH_2) have higher boiling point than tertiary amines (R_3N).
 (ii) Aniline does not undergo Friedel - Crafts reaction.
 (iii) $(\text{CH}_3)_2\text{NH}$ is more basic than $(\text{CH}_3)_3\text{N}$ in an aqueous solution.

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

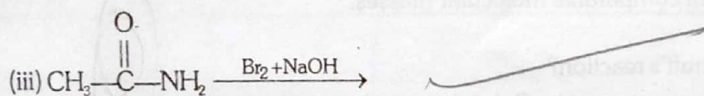
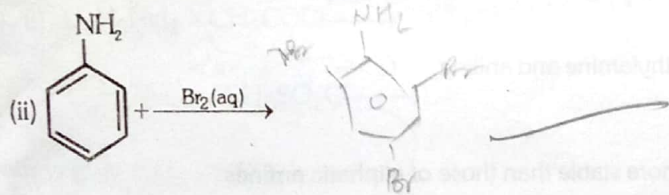
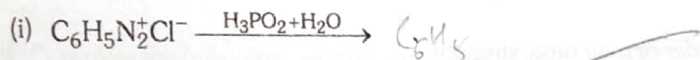


CBSE 2013

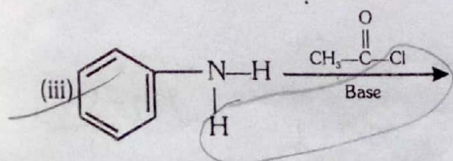
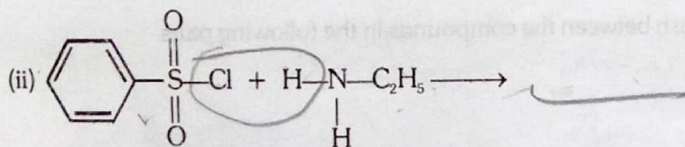
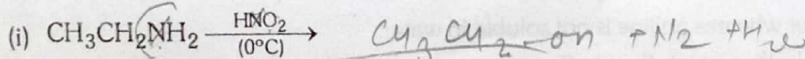
- Write the structure of prop-2-en-1-amine.
- Write the structure of N-methylethanamine.
- Write the structure of 2-aminotoluene.
- Complete the following reactions



- Write the main products of the following reactions.



- Write the main products of the following reactions

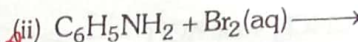
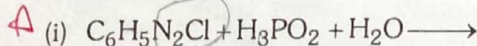


CBSE 2012

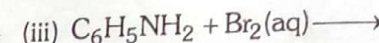
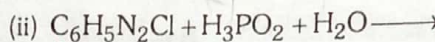
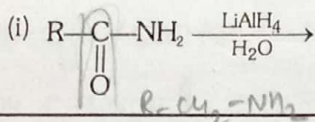
1. Describe the following giving the relevant chemical equation in each case.

- (i) Carbylamine reaction
- (ii) Hoffmann's bromamide reaction

2. Complete the following reaction equations,

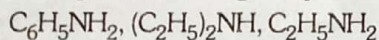


3. Complete the following reaction equations.

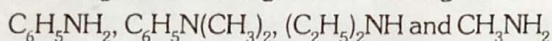


CBSE 2011

1. Arrange the following compounds in an increasing order of their solubility in water.



2. Rearrange the following in an increasing order of their basic strength.



3. Give a chemical test to distinguish between ethylamine and aniline.

4. Account for the following

- (i) Diazonium salts of aromatic amines are more stable than those of aliphatic amines.
- (ii) Amines are more basic than alcohols of comparable molecular masses.

- 5. (i) Why Aniline does not undergo Friedel-Craft's reaction?
- (ii) Why can primary aromatic amines be not prepared by Gabriel phthalimide synthesis?

6. State reasons for the following.

- (i) pK_b value for aniline is more than that for methylamine.
- (ii) Ethylamine is soluble in water whereas aniline is not soluble in water.
- (iii) Primary amines have higher boiling points than tertiary amines.

7. Give one the chemical test each to distinguish between the compounds in the following pairs

(i) Methylamine and dimethylamine

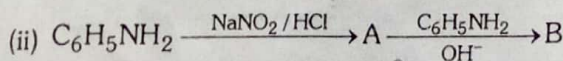
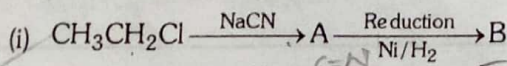
(ii) Aniline and benzylamine

(iii) Ethylamine and aniline

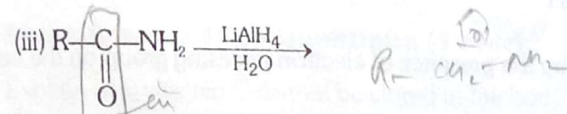
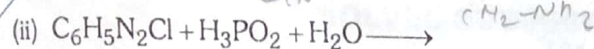
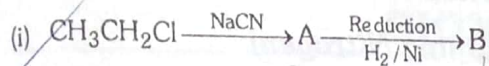
CBSE 2010

1. Give chemical test to distinguish between aniline and N-methyl aniline.

2. Identify A and B in each of the following processes



3. Complete the following reactions.



4. Give one the chemical test each to distinguish between the compounds in the following pairs

(i) Methylamine and dimethylamine

(ii) Aniline and benzylamine

(iii) Ethylamine and aniline

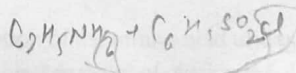
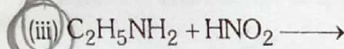
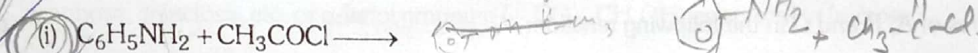
CBSE 2009

1. Arrange the following compound in an increasing order of basic strengths in their aqueous solutions
 $\text{NH}_3, \text{CH}_3\text{NH}_2, (\text{CH}_3)_2\text{NH}, (\text{CH}_3)_3\text{N}$

2. Assign reason for

- (i) amines are less acidic than alcohols of comparable molecular masses.
- (ii) Aliphatic amines are stronger bases than aromatic amines.

3. Complete the following reaction equations.



Nucleus (BIOG-11) Kota (Raj.) (Advanced) Edition (2008) 'Chemistry' Stream (Board: National) Eng. Sheet 3 (OC) (Date: Organic Compounds Containing Nitrogen) p.45

EXERCISE-1

SOLUTION PREVIOUS YEARS BOARD PROBLEMS

ALIPHATIC & AROMATIC AMINES

CBSE 2016

Sol.1 N-methyl-2-methylpropanamine / 2-methyl-N-methylpropanamine

Sol.2 (i) A : $C_6H_5CONH_2$

B : $C_6H_5NH_2$

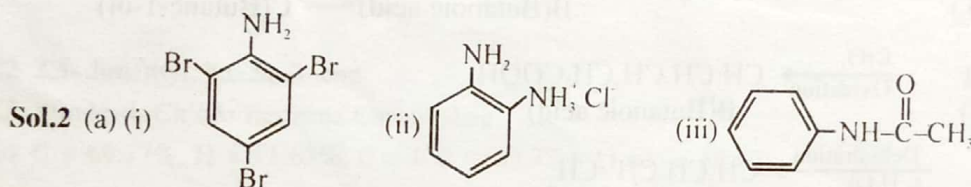
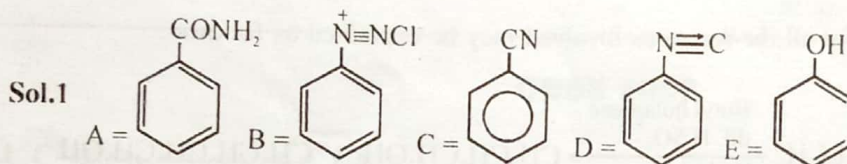
C : $C_6H_5NHCOCH_3$

(ii) A : $C_6H_5NO_2$

B : $C_6H_5NH_2$

C : C_6H_5NC

CBSE 2015



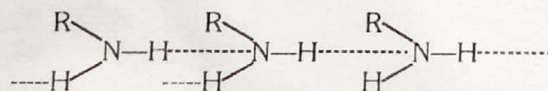
(b) $(CH_3)_3N < C_2H_5NH_2 < C_2H_5OH$

(c) By Hinsberg test - Add Hinsberg reagent (Benzene sulphonyl chloride) in both compounds $(CH_3)_2NH$ forms ppt insoluble in KOH while $(CH_3)_3N$ does not react (or any other correct test)

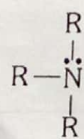
CBSE 2014

Sol.1 Diazotization

Sol.2 (i) Due to the presence of two H-atoms on N-atoms of 1° amines, they undergo extensive intermolecular H-bonding while 3° amines due to the absence of H-atoms on N-atom there is no hydrogen bonding takes place. So primary amines have higher b.p. than tertiary amines of comparable molecular mass.



Inter molecular Hydrogen bonding in 1° amines.



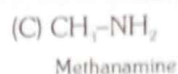
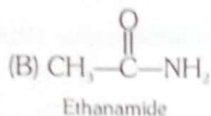
No hydrogen bonding

(ii) Aniline being a Lewis base, reacts with lewis acid $AlCl_3$ to form a salt.

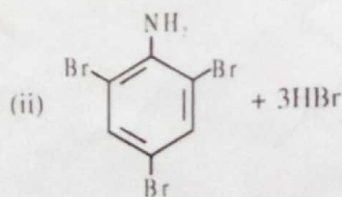
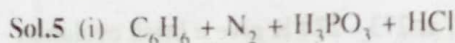
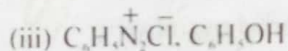
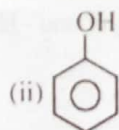
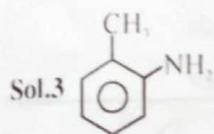


As a result, N of aniline acquires positive charge and hence it acts as a strong deactivating group for electrophilic substitution reaction, consequently, aniline does not undergo Friedel - Crafts reaction.

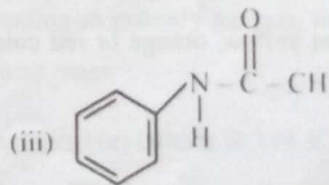
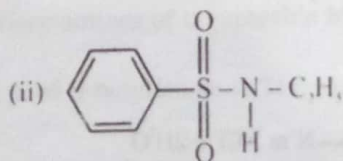
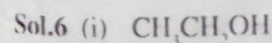
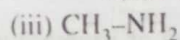
(iii) It is the combination of electron releasing nature of alkyl group, H-bonding and steric factors determine the stability of ammonium cations formed in solution therefore $Et_3NH^+ > Et_3N^+ > EtNH_3^+$ is order of K_b .



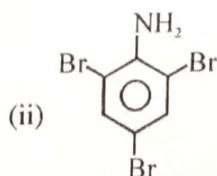
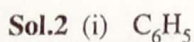
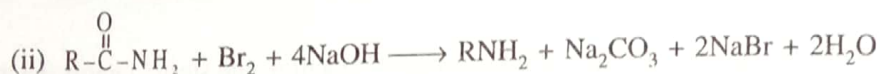
CBSE 2013



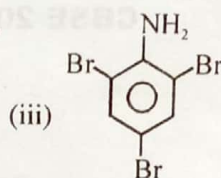
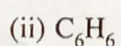
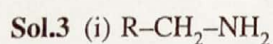
2,4,6 Tribromoaniline



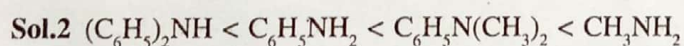
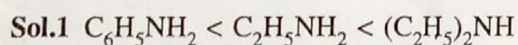
CBSE 2012



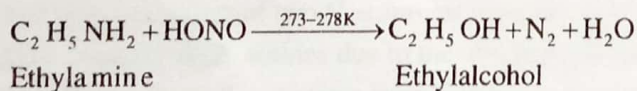
Alcohol →



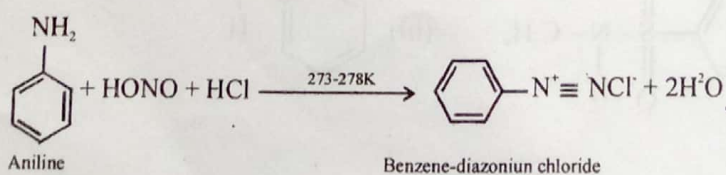
CBSE 2011



Sol.3 **Ethylamine and Aniline:** Ethylamine with HNO_2 ($NaNO_2 + \text{dil HCl}$) at 273 - 278 K give a brisk evolution of N_2 gas with the formation of primary alcohols.



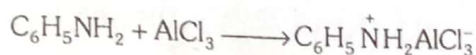
Aniline with HNO_2 at 273-278 K followed by treatment with an alkaline solution of naphthol when a brilliant yellow, orange or red coloured dye is obtained.



Sol.4 (i) Diazonium salts of aromatic amines are more stable than of aliphatic amines due to the delocalisation of the positive charge on the benzene ring as shown below by the resonating structures.

(ii) Amines are less acidic than alcohols of comparable molecular masses because N-H bond in amines is less polar than O-H bond in alcohols. Hence, amines release H^+ ion with more difficulty as compared to alcohol.

Sol.5 (i) Aniline being a Lewis base, reacts with Lewis acid $AlCl_3$ to form a salt.



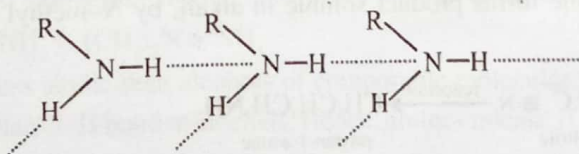
As a result, N of aniline acquires positive charge and hence it acts as a strong deactivating group for electrophilic substitution reaction, consequently, aniline does not undergo Friedel-Crafts reaction.

(ii) In aryl halides, nucleophilic substitution reaction does not occur easily due to the resonance in $Ar-X$. That is why, aromatic primary amines can not be prepared by Gabriel phthalimide reaction.

Sol.6 (i) In aniline, the lone pair of electrons on the N-atom are delocalized over the benzene ring. Resulting, electron density on the nitrogen decreases. On the other hand, in CH_3NH_2 , +I effect of CH_3 increases the electron density on the N-atom. Thus, aniline is a weaker base than methylamine and hence its pK_b value is higher than that of methylamine.

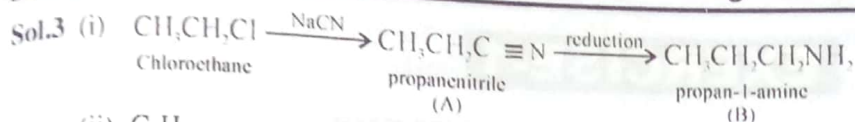
(ii) Ethylamine dissolves in water because it forms hydrogen bonds with water molecules. In aniline due to large, hydrocarbon part, the extent of H-bonding decreases considerably and hence aniline is insoluble in water.

(iii) Primary amines (RNH_2) have two hydrogen atoms on the N atom and therefore, form intermolecular hydrogen bonding.



Tertiary amines (R_3N) do not have hydrogen atoms on the nitrogen atom and therefore, these do not form hydrogen bonds. As a result of hydrogen bonding in primary amines, they have higher boiling points than tertiary amines of comparable molecular mass.

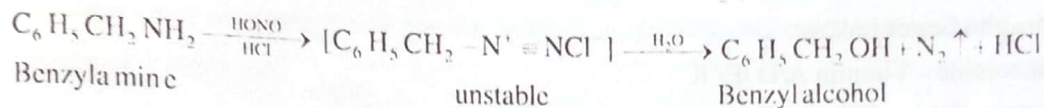
For example b.p. of n-butylamine is 351 while that tert-butylamine is 319 K.



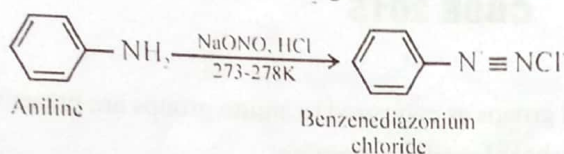
- (ii) C_6H_5
(iii) $\text{R}-\text{CH}_2-\text{NH}_2$

Sol.4 (i) **Methylamine and dimethylamine** : By using the Hinsberg test methyl amine forms product soluble in alkali, by dimethyl amine forms product insoluble in alkali.

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



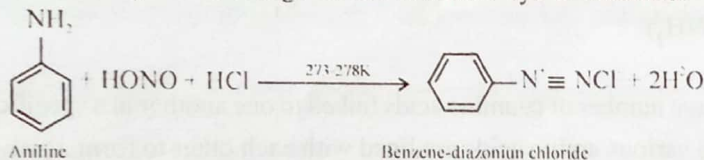
Aniline reacts with HNO_2 to form benzene diazonium Chloride which is stable at 273-278K and hence does not decompose to evolve N_2 gas.



(iii) **Ethylamine and Aniline**: Ethylamine with HNO_2 ($\text{NaNO}_2 + \text{dil HCl}$) at 273 - 278 K give a brisk evolution of N_2 gas with the formation of primary alcohols.

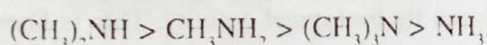


Aniline with HNO_2 at 273-278 K followed by treatment with an alkaline solution of naphthol when a brilliant yellow, orange or red coloured dye is obtained.



CBSE 2009

Sol.1 The order of basic strength of methyl substituted amines in aqueous solution is.



Sol.2 (i) Amines are less acidic than alcohols of comparable molecular masses because N-H bond in amines is less polar than O-H bond in alcohols. Hence, amines release H^+ ion with more difficulty as compared to alcohol.

(ii) In aniline, the lonepair of electrons on the N-atom are delocalized over the benzene ring. Resulting, electron density on the nitrogen decreases. On the other hand, in CH_3NH_2 , +I effect of CH_3 increases the electron density on the N-atom. Thus, aniline is a weaker base than methylamine and hence its pK_b value is higher than that of methylamine.

