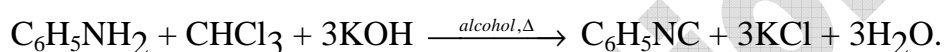
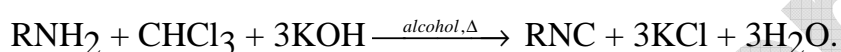


Organic compounds containing Nitrogen

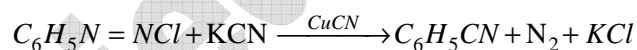
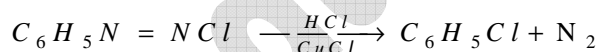
****1. Write short notes on the following:**

(i) Carbylamine reaction(ii) Sandmeyer reaction

Ans. (i) Carbyl amine Reaction: When aliphatic and aromatic primary amines are heated with chloroform and ethanolic potassium hydroxide, carbylamines or isocyanides are formed. These substances produced have foul smell. Secondary and tertiary amines do not give this reaction. This reaction is used to detect primary amines and to distinguish primary amines from Secondary and tertiary amines.



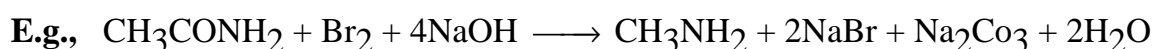
ii. sandmeyer Reaction: Benzene diazonium chloride is converted to chlorobenzene when treated with cuprous chloride and hydrogen chloride, bromobenzene is formed with cuprous bromide and hydrogen bromide and benzonitrile with potassium cyanide and cuprous cyanide. These reactions are called Sandmeyer reactions.



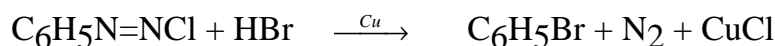
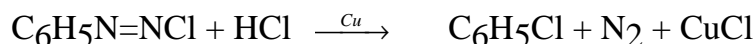
****2. Write short notes on the following**

(i) Hoffmann bromamide degradation reaction (ii) Gattermann reaction

Ans. (i) Hoffmann bromamide degradation reaction: This is a method used for converting primary amide into primary amine. An amide is treated with bromine in an aqueous or ethanolic solution of sodium hydroxide. The amine so formed contains one carbon less than that present in the amide.



(ii) Gattermann Reaction: Benzene diazonium chloride is converted to chlorobenzene when treated with HCl and Cu, bromobenzene is formed with HBr and Cu. This reaction is known as Gattermann reaction.



The yield in Gatterman reaction is lower than that in Sandmeyer reaction.

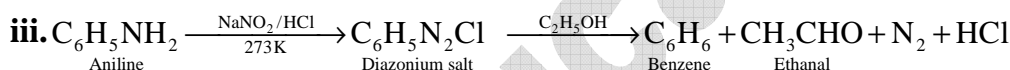
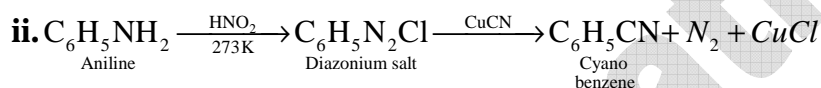
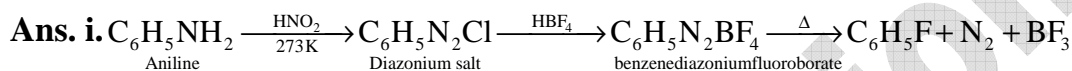
****3. Complete the following conversions: Aniline to**

i. Fluoro benzene

ii. cyanobenzene

iii. Benzene

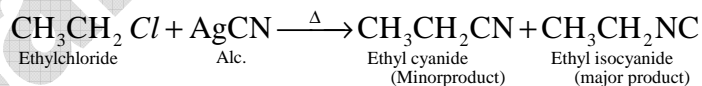
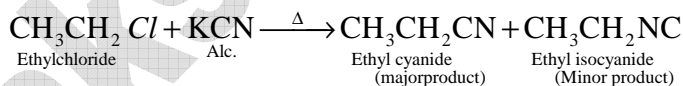
IV. Phenol



***4. How do you prepare Ethyl cyanide and Ethyl isocyanide from a common alkyl halide?**

Ans. Alkyl halides with ethanoic potassium cyanide forms alkyl cyanide as major product while

With ethanoic silver cyanide alkyl isocyanide as major product.



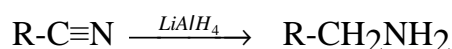
5. Account for the following:

(i) pK_b of aniline is more than that of methyl amine.

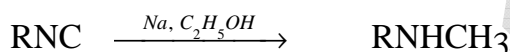
ii) Reduction of alkyl cyanides forms primary amines while alkyl isocyanides form secondary amines.

Ans. i) In aniline, the electron pair on nitrogen atom is involved in conjugation with ring and is less available for protonation than in methyl amine. Therefore aniline is less basic and pK_b value of aniline is more than that of methylamine. Higher the pK_b value, less is the basicity.

ii. **Alkyl cyanides** on complete reduction using $LiAlH_4$, hydrogen and nickel or sodium and ethyl alcohol as reducing agents gives primary amines



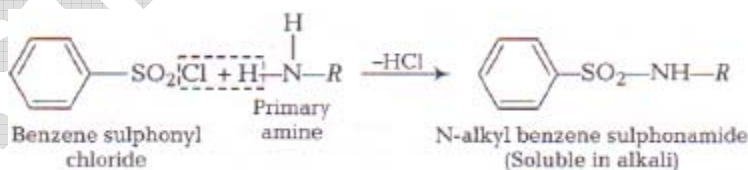
On reduction with hydrogen and platinum or sodium and ethanol, isocyanides form secondary methyl amines.



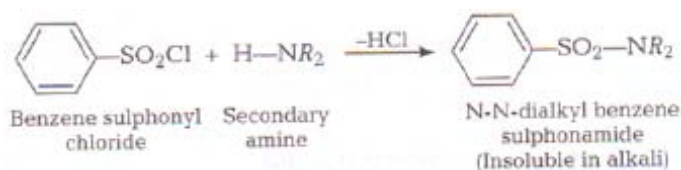
**6. Explain with suitable example how benzene sulphonyl chloride can distinguish primary, secondary and tertiary amines?

Ans. Hinsberg's reagent i.e. benzene sulphonyl chloride ($C_6H_5SO_2Cl$) reacts with primary, secondary and tertiary amines in a different manner. This is used for the distinction of three types of amines.

(i) **Primary Amine:** The reaction of benzene sulphonyl chloride with primary amine produces N-alkyl benzene sulphonamide. Hydrogen attached to nitrogen in the product is acidic so it is soluble in alkali.



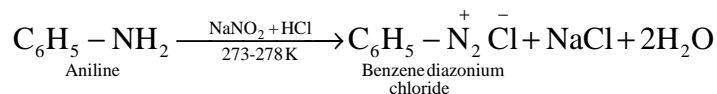
(ii) **A secondary Amine:** reacts with Hinsberg's reagent to form N, N-dialkyl benzene sulphonamide which remains insoluble in alkali.



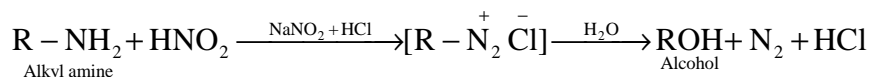
(iii) **A tertiary amine:** does not react with benzene sulphonyl chloride.

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

Ans. (i) Aromatic primary amines react with nitrous acid at low temperatures (273 - 278 K) to form diazonium salts. Nitrous acid is produced by the reaction of NaNO₂ and HCl.



(ii) Aliphatic primary amines react with nitrous acid to form aliphatic diazonium salts (unstable), which produce nitrogen gas and alcohols after decomposition.



*8. i. Why are amines less acidic than alcohols of comparable molecular masses?

ii. Compare the basicity of the following in gaseous and aqueous state and arrange then in increasing order of basicity. CH₃NH₂, (CH₃)₂NH, (CH₃)₃N and NH₃

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

ii. Alkyl amines are more basic than ammonia, as their conjugate acids become more stable due to the +Inductive effect of the alkyl groups. In gaseous state, order of Basic strength:



In aqueous solution, in addition to +I effect of -R groups, hydrogen bonding with water also stabilises the conjugate acid. As the extent of hydrogen bonding in water and order of stability of ions by solvation decreases with the decrease in number of Hydrogen atoms around N-atom the order of basic strength of aliphatic amines is

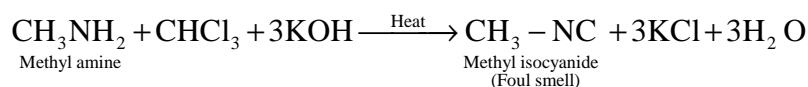


*9. Give one chemical test to distinguish between the following pairs of compounds:

(i) Methylamine and dimethylamine (ii) Ethylamine and aniline

(iii) Aniline and N-methylaniline.

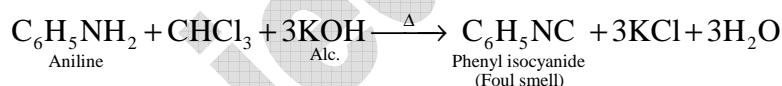
Ans. i) Methylamine and dimethyl amine by isocyanide test: Methyl amine (primary) responds to carbyl amine reaction. When heated with chloroform and KOH, it produces foul smell. Dimethyl amine (secondary) does not respond to this test.



ii) Ethyl amine and aniline: Ethyl amine (primary aliphatic amine) and aniline (primary aromatic amine) can be distinguished by **diazotisation reaction**. **Aniline responds to this test** whereas ethyl amine does not.



iii. Aniline and N-methylaniline (carbylamine test): Aniline gives carbylamine test because it is a primary amine whereas N-methyl aniline (secondary amine) does not give this test.

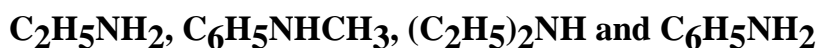


Very Short Answer Questions

1. Aniline does not undergo Friedal-Craft's reaction. Justify?

Ans. Aniline forms salt with Friedal-Craft's catalyst $AlCl_3$. In this salt 'N' atom acquires positive charge and acts as strong deactivating group. Hence, the reactivity is decreased.

2. Arrange the following in the decreasing order of the K_b values:



Ans. Presence of electron donating R group increases the basicity of amines. However, 3° amines in aqueous solution are less basic due to steric hindrance. Aliphatic amines are more basic than aromatic bases because in later lone pair takes part in delocalization, so less available for donation. **The decreasing order of the K_b values is**



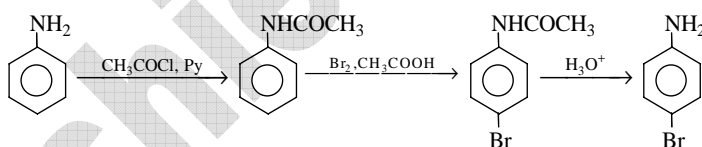
3. Accomplish the following conversions

i. Benzoic acid to Benzamide ii. Aniline to P- bromo aniline

Ans. i. Benzoic acid on heating with ammonia gives benzamide



ii.



4. Arrange the following in increasing order of their basic strength

Aniline, P-nitro aniline and P-toludine.

Ans. The Presence of an electron withdrawing group [$-NO_2$] in aromatic amines generally decreases the basic strength, whereas electron releasing group [$-CH_3$] increases the strength of a base. Thus the decreasing order of basic strength is, P-toludine > Aniline > P-nitro aniline.