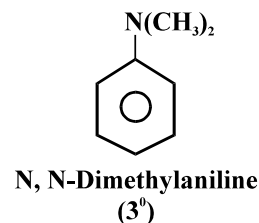
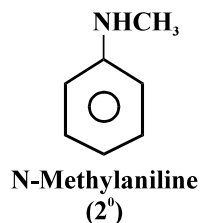
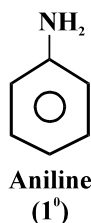
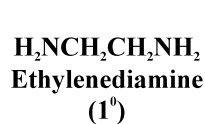


ORGANIC COMPOUND
CONTAINING NITROGEN

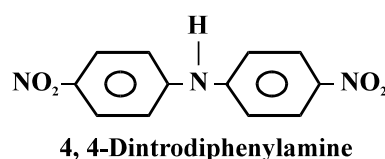
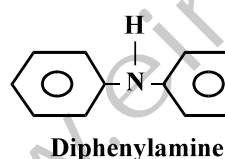
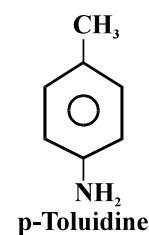
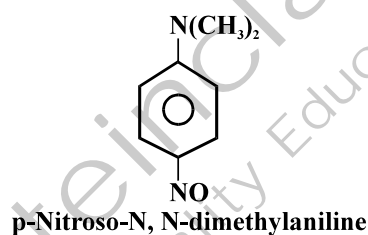
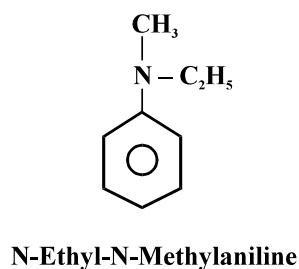
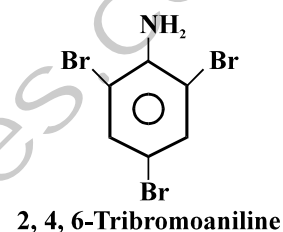
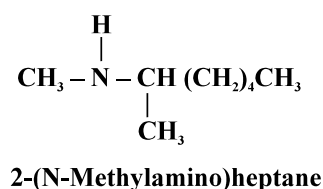
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CONCEPTS

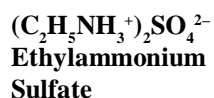
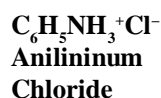
C1A Structure : of the organic compounds that show appreciable basicity (e.g. those strong enough to turn litmus blue), by far the most important are the amines. An amine has the general formulae RNH_2 , R_2NH or R_3N where R is an alkyl or aryl group. For e.g.



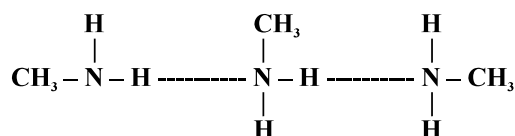
Nomenclature : Aliphatic amines are named by naming the alkyl group or groups attached to nitrogen and following these by the word-amine e.g.



Salts of amine are generally named by replacing amine by ammonium (or aniline by anilinium), and adding the name of the anion (chloride, nitrate, sulfate etc.) e.g.



C1B Physical Properties of amines : Like ammonia, amines are polar compounds and except for tertiary amines, can form intermolecular hydrogen bonds. Amines have higher boiling points than non-polar compounds of same molecular weight, but lower boiling points than alcohols or carboxylic acids.



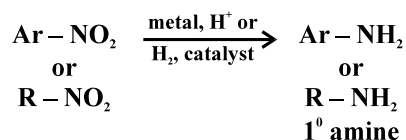
Amines of all three classes are capable of forming hydrogen bonds with water. As a result smaller amines are quite soluble in water, with borderline solubility is reached with six carbon atoms.

Amines are soluble in less polar solvents like ether, alcohol, benzene etc.

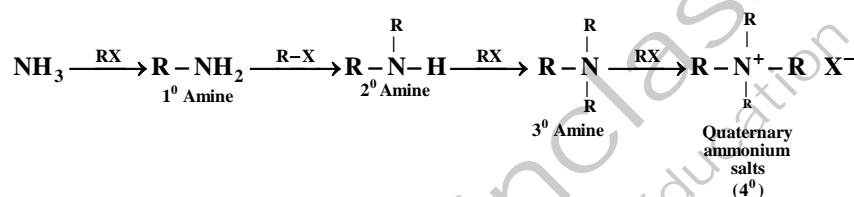
C1C Stereochemistry of Nitrogen : Consider quaternary ammonium salts, compounds in which four alkyl groups are attached to nitrogen. Here all four sp^3 orbitals are used to form bonds and quaternary nitrogen is tetrahedral. Thus quaternary ammonium salts in which nitrogen holds four different groups have been found to exist as configurational enantiomers, capable of showing optical activity.

C2 Methods of Preparation :

1. **Reduction of Nitro Compounds :**



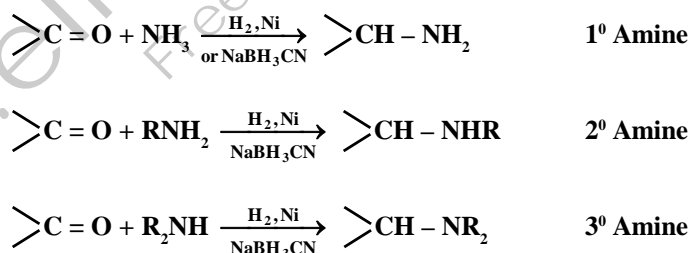
2. **Reaction of halides with ammonia or amines :**



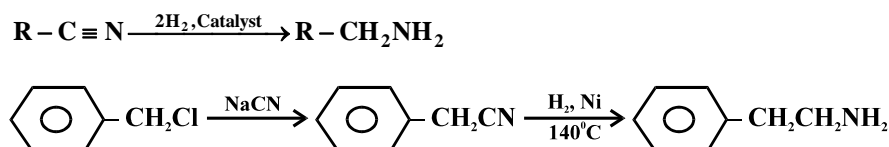
$\text{RX} \rightarrow$ must be alkyl or aryl with electron withdrawing substituents.

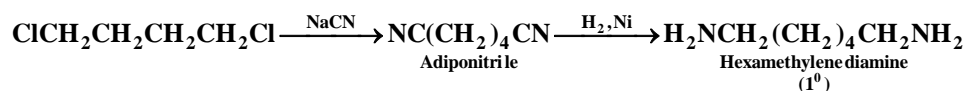
The presence of large excess of ammonia lessens the importance of these last reactions and increases the yield of primary amine.

3. **Reductive Amination :**

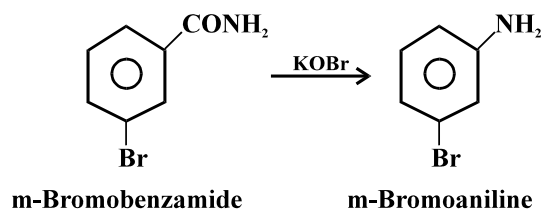
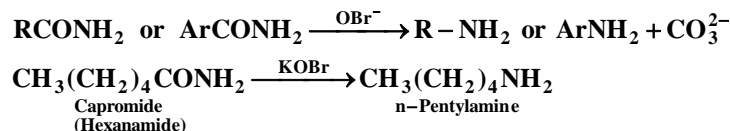


4. **Reduction of nitriles (Higher carbon number is obtained)**





5. Hoffman degradation of amides :

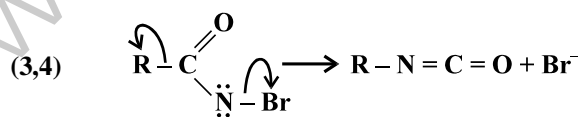


Discussion : From the above reaction it is clear that in this reaction, the rearrangement occurs, since the group joined to carbonyl carbon in the amide is found joined to nitrogen in the product.

The reaction is believed to proceed by the following steps :

1. $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\ddot{\text{N}}\text{H}_2 + \text{OBr}^- \longrightarrow \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\ominus}{\text{N}}(\text{H})-\text{Br} + \text{OH}^-$
2. $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\ominus}{\text{N}}(\text{H})-\text{Br} + \text{OH}^- \longrightarrow \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\ominus}{\text{N}}-\text{Br} + \text{H}_2\text{O}$
3. $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\ominus}{\text{N}}-\text{Br} \longrightarrow \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\ominus}{\text{N}} + \text{Br}^-$
4. $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\ominus}{\text{N}} \longrightarrow \text{R}-\overset{\ominus}{\text{N}}=\text{C}=\text{O}$ } Simultaneously takes place
5. $\text{R}-\overset{\ominus}{\text{N}}=\text{C}=\text{O} + 2\text{OH}^- \xrightarrow{\text{H}_2\text{O}} \text{RNH}_2 + \text{CO}_3^{2-}$

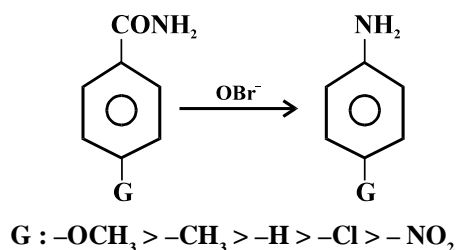
Steps (3) and (4) are generally takes place simultaneously. The attachment of R to nitrogen helps to pushout halide ion.



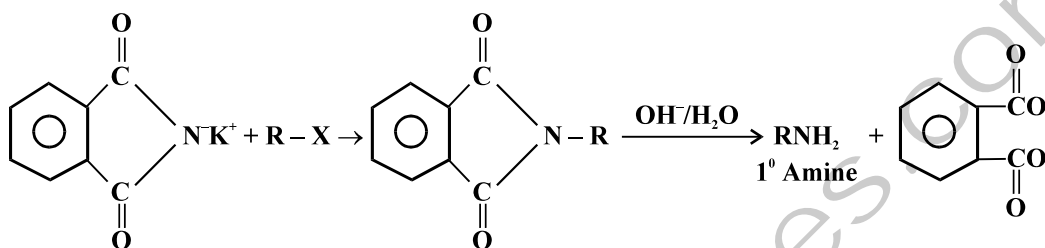
Step (5) is the hydrolysis of an isocyanate ($\text{R}-\overset{\ominus}{\text{N}}=\text{C}=\text{O}$) to form amine and carbonate ion.

If the Hoffman degradation is carried in absence of water an isocyanate is actually isolated.

- * When the migrating group is aryl the rate of degradation is increased by the presence of electron releasing substituents in the aromatic ring. Thus substituted benzamide show the following order of reactivity :



6. Gabriel Phthalimide Synthesis :



Practice Problems :

1. Boiling of $\text{C}_2\text{H}_5\text{NCO} + \text{NaOH}$ leads to the formation of

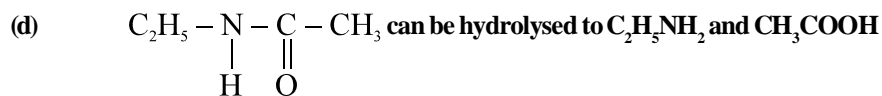
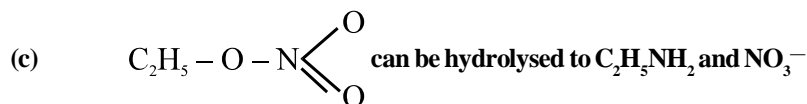
- (a) $\text{C}_2\text{H}_5\text{COOH} + \text{NH}_3$ (b) $\text{C}_2\text{H}_5\text{NH}_2 + \text{Na}_2\text{CO}_3$
 (c) $\text{CH}_3\text{NH}_2 + \text{CH}_3\text{COONa}$ (d) None

2. $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2 + \text{KOH} + \text{Br}_2 \rightarrow$ Intermediates of this reaction are except :

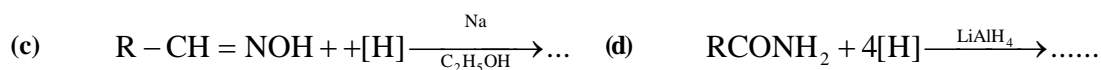
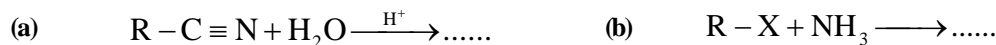
- (a) $\text{R}-\text{N}=\text{C}=\text{O}$ (b) $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\ddot{\text{N}}$
 (c) $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\underset{\text{H}}{\text{N}}-\text{Br}$ (d) a, c

3. Which of the following would you predict as incorrect

- (a) $\text{C}_2\text{H}_5-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2$ can be hydrolysed to $\text{C}_2\text{H}_5\text{COOH}$
 (b) $(\text{CN})_2$ can be hydrolysed to $\begin{array}{c} \text{COOH} \\ | \\ \text{COOH} \end{array}$



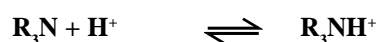
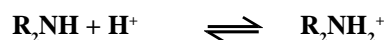
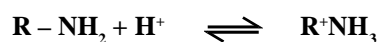
4. Which of the following reactions does not yield an amine



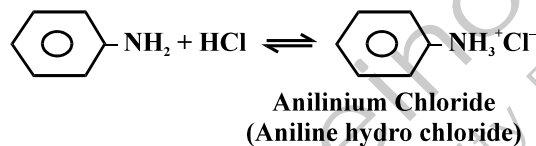
[Answers : (1) b (2) b (3) c (4) a]

C3 Chemical properties of Amines : The tendency of nitrogen to share the unpaired electrons underlines the entire chemical behaviour of amines : their basicity, their action as nucleophiles - in both aliphatic and acyl substitution - and the usually high reactivity of aromatic rings bearing amino or substituted amino groups.

1. Basicity of Amines : Salt formation :



Example :



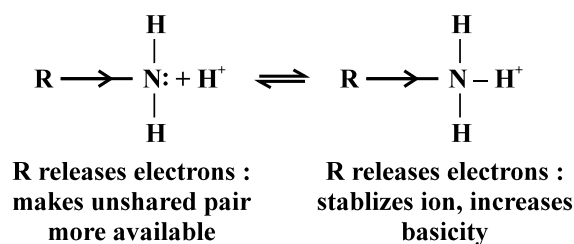
Structure and Basicity :

Let us see how basicities are related to the structure.

We shall compare the stabilities of amines with the stabilities of their ions; the more stable the ion relative to the amine from which it is formed, the more basic the amine.

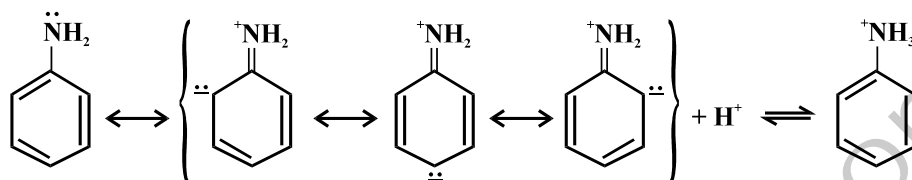
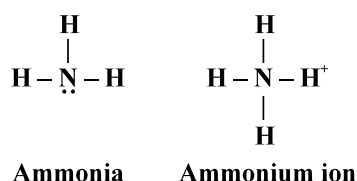
First of all, amines are more basic than alcohols, ethers, esters etc. for the same reason that ammonia is more basic than water, Nitrogen is less electronegative than oxygen and can better accommodate the positive charge of the ion.

An aliphatic amine is more basic than ammonia : because the electron-releasing alkyl groups tend to disperse the positive charge of the substituted ammonium ion;



How can we account for the fact that aromatic amines are weaker bases than ammonia?

Let us compare the structure of aniline with anilinium ion with the structures of ammonia and the ammonium ion.



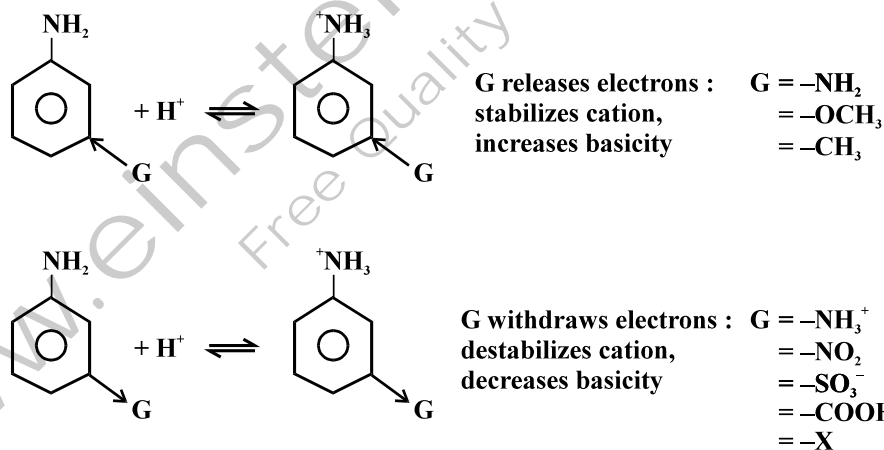
Aniline i.e. Aromatic amines are less basic due to the fact that amine is stabilized by resonance to the greater extent than its ion.

From another point of view we can say that its electron pair is partly shared by ring and is less available for sharing with a hydrogen ion.

Effect of substituents on basicity of aromatic amines :

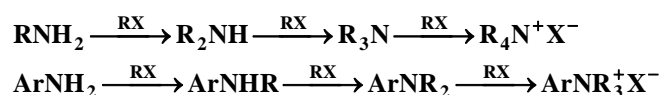
Electron releasing substituents like CH_3 , increases the basicity of aniline, and electron withdrawing substituents like $-\text{X}$, $-\text{NO}_2$ decreases the basicity.

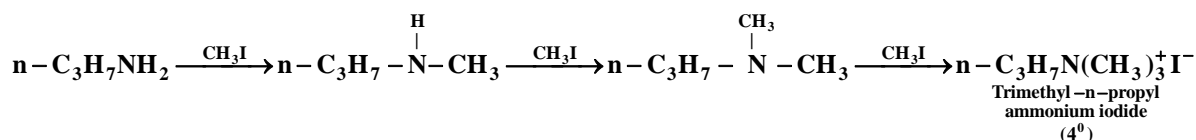
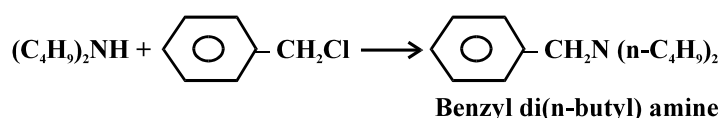
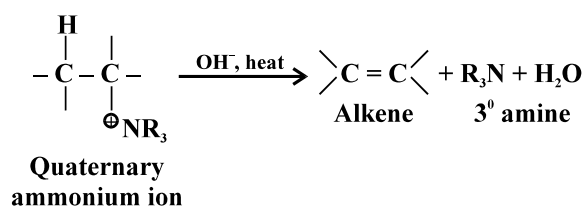
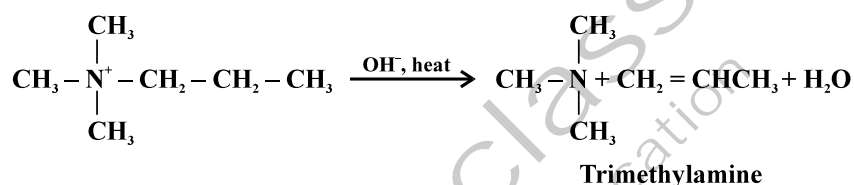
- The electron releasing substituents tends to disperse the positive charge of the anilinium ion, and thus stabilizes the ion relative to amine. The electron withdrawing tends to intensify the positive charge of the anilinium ion, and thus destabilizes the ion relative to the amine.



- We notice that base strengthening substituents are the ones that activate an aromatic ring towards electrophilic substitution; the base-weakening substituents are the ones that deactivate an aromatic ring towards electrophilic substitution.

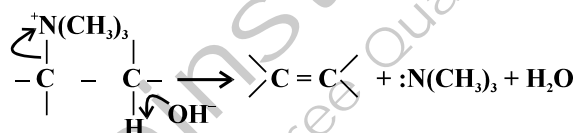
2. Alkylation :



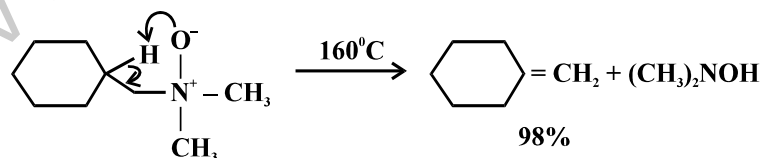
Example :**3. Hoffmann elimination from quaternary Ammonium Salts :****Example :**

This reaction is called Hoffmann elimination, is quite analogous to the dehydrohalogenation of an alkyl halide. Most commonly reaction is E₂ :

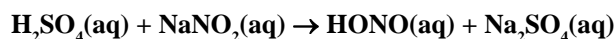
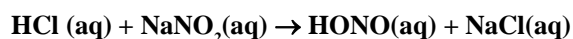
Hydroxide ion abstracts a proton from carbon; a molecule of tertiary amine is expelled.

**4. The Cope Elimination :**

Tertiary amine oxide are prepared easily by treating tertiary amines with H₂O₂.

**5. Reactions of Amines with Nitrous acid :**

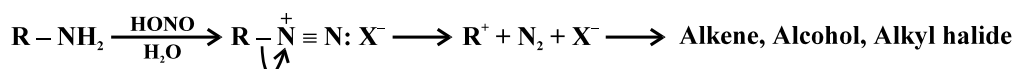
Nitrous acid is a weak acid & is unstable also. It is prepared by treating sodium nitrite (NaNO₂) with an aqueous solution of a strong acid :



Nitrous acid reacts with all kinds of amines. The products that we obtain from these reactions depends on whether the amine is primary, secondary or tertiary and whether the amine is aliphatic or aromatic.

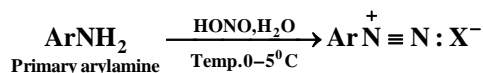
Reactions of primary aliphatic amines with nitrous acid :

- Primary aliphatic amines react with nitrous acid through diazotisation reaction giving high yield of unstable diazonium salts.
- Even at low temperature they decompose to form nitrogen (N_2) and carbocation (R^+)
- R^+ reacts with H_2O to form ROH, or alkene or $R - X$. It means mixture of products produced.



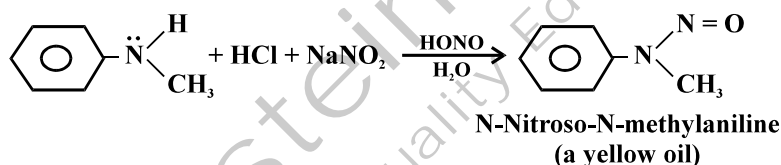
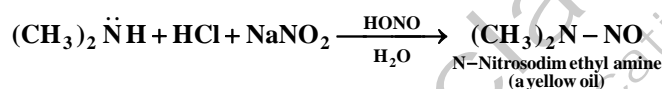
Reactions of Primary Arylamines with Nitrous acid :

Primary arylamine react with HONO acid to give arenediazonium salts. These salts are although unstable but are more stable than the diazonium salt of aliphatic primary amine.



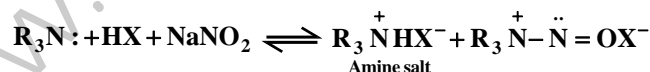
Reaction of Secondary amine with Nitrous acid :

Secondary amines both aliphatic and aromatic react with nitrous acid to yield N-nitroamines usually separate from reaction mixture as oily yellow liquid. **Specific Examples :**



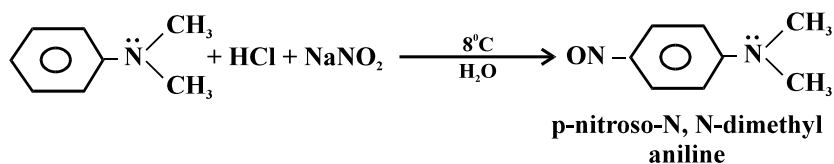
Reaction of Tertiary amine with nitrous acid :

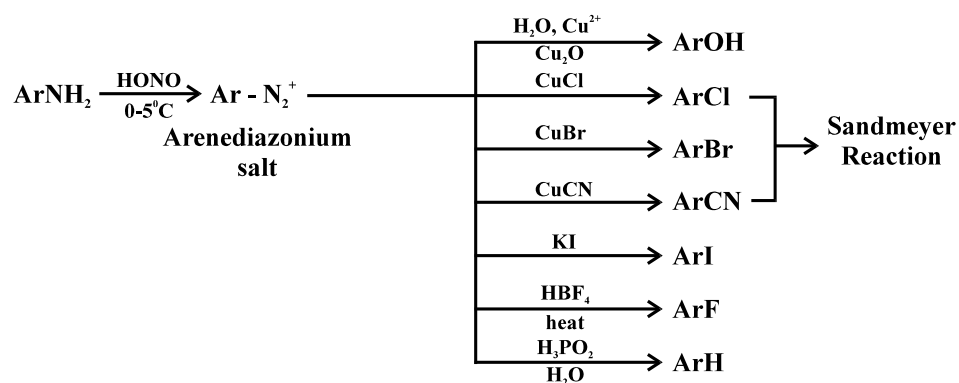
When tertiary aliphatic amine is mixed with nitrous acid an equilibrium is established among the tertiary amine, its salt and an N-nitrosoammonium ion compound



Tertiary aryl amine react with nitrous acid to form p-nitroso aromatic compound.

Nitrosation exclusively takes place at para position.

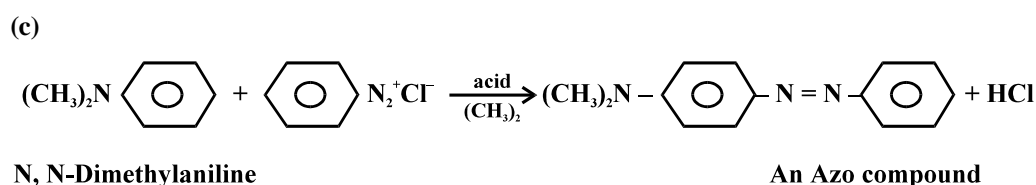
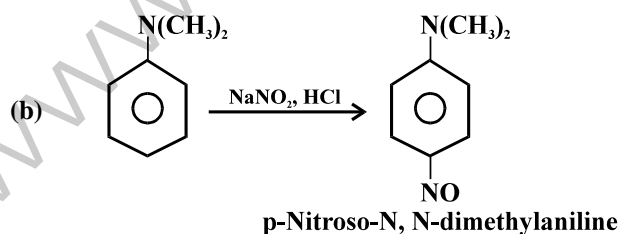
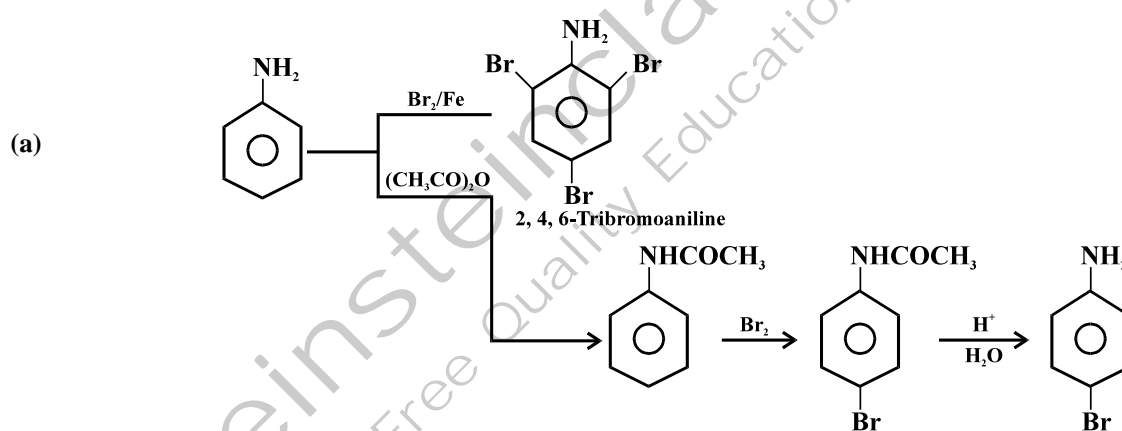


Replacement Reactions of Arene Diazonium Salts :

[H_3PO_2 is known as hypophosphorous acid]

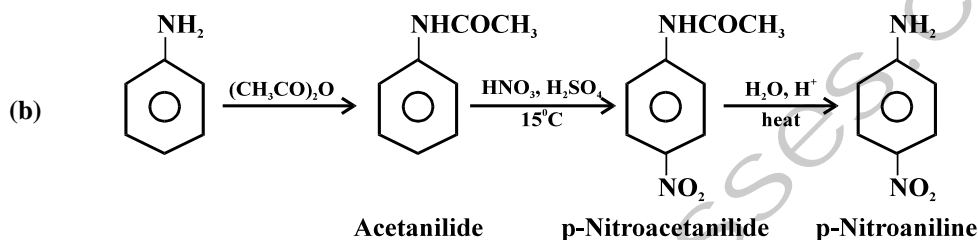
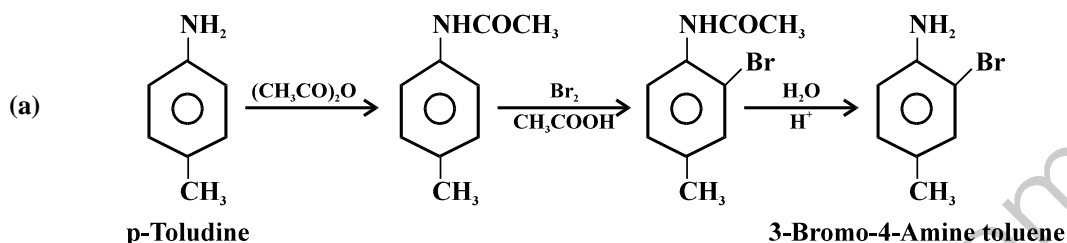
6. Ring Substitution in Aromatic Amines :

$-\text{NH}_2$ } Active powerfully and direct ortho,
 $-\text{NHR}$ } para in electrophilic aromatic
 $-\text{NR}_3$ } substitution
 $-\text{NHCOR}$ \rightarrow Less powerfull than $-\text{NH}_2$

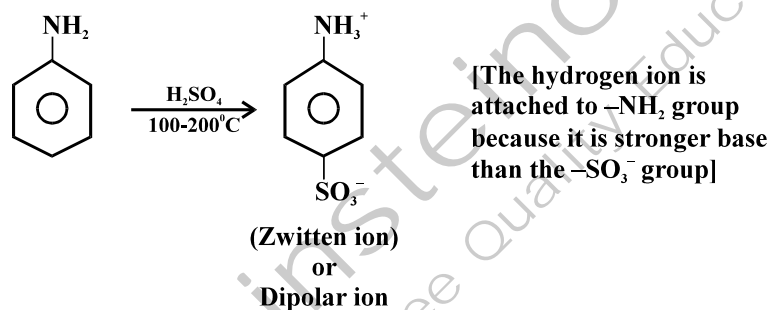
Example :

- Nitric acid not only nitrates but also oxidizes the highly reactive ring as well.
- In the strongly acidic condition aniline is converted into anilinium ion ($-\text{NH}_3^+$) because of its positive charge it directs substitution to the meta position.
- To overcome this difficulty, we protect the amino group : we acetylate the amine, then carry out the substitution and finally hydrolyze the amide to the desired substituted amine

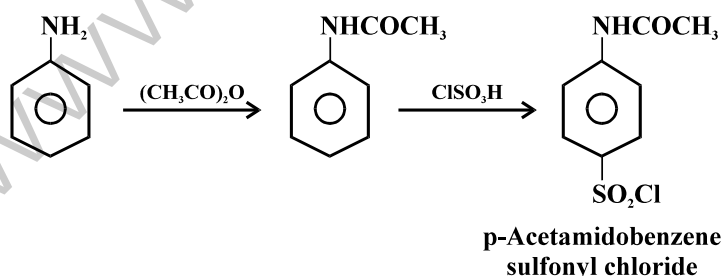
For Example :

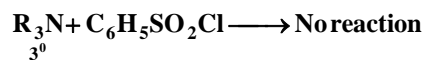
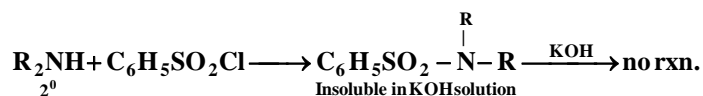
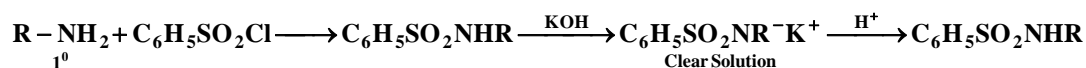
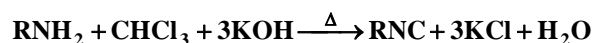


7. Sulfonation of Aromatic Amines :



Sulphanilamide. The Sulfa drug :

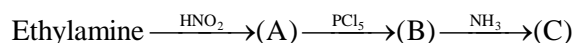


8. Analysis of Amines : Hinsberg Test :9. Carbyl amine test : It is given by 1^o alkyl amine and aryl amine.

unpleasant smell of alkyl isocyanide is obtained. 2^o amine and 3^o amine does not give this test.

Practice Problems :

1. Which compound is obtained at the end of the following reaction,



(a) ethyl cyanide (b) ethyl amine (c) methyl amine (d) acetamide

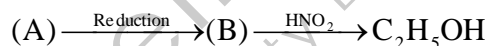
2. When ethyl amine is heated with chloroform and alcoholic KOH, a bad odour compound is formed. The compound is

(a) a secondary amine (b) an acid
(c) a cyanide (d) an isocyanide

3. $\text{CH}_3\text{NH}_2 + \text{CHCl}_3 + 3\text{KOH} \rightarrow \text{X} + \text{Y} + 3\text{H}_2\text{O}$; compounds X and Y are

(a) $\text{CH}_3\text{CN} + 3\text{KCl}$ (b) $\text{CH}_3\text{NC} + 2\text{KCl}$
(c) $\text{CH}_3\text{CONH}_2 + 3\text{KCl}$ (d) $\text{CH}_3\text{NC} + \text{K}_2\text{CO}_3$

4. In the following series of reaction, A is



(a) CH_3CN (b) CH_3NC (c) $\text{C}_2\text{H}_5\text{CN}$ (d) CH_3NO_2

5. Which one of the following is least basic

(a) $\text{C}_2\text{H}_5\text{NH}_2$ (b) NH_3 (c) $(\text{C}_2\text{H}_5)_2\text{NH}$ (d) $\text{C}_6\text{H}_5\text{NH}_2$

6. Which of the following is least basic

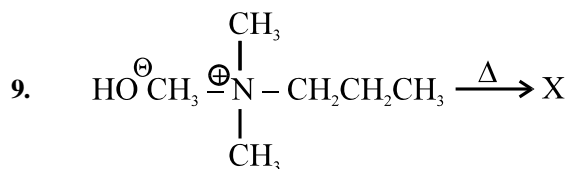
(a) aniline (b) p-methylaniline
(c) diphenylamine (d) triphenylamine

7. A positive carbylamine test is given by

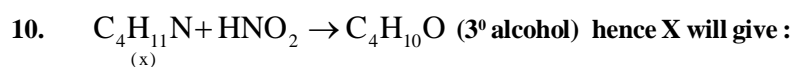
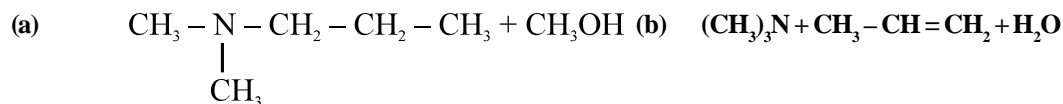
(a) N, N-dimethyl aniline (b) 2, 4-dimethyl aniline
(c) N-methyl-o-methylaniline (d) p-methyl benzylamine

8. A nitrogenous substance X is treated with HNO_2 and the product so formed is further treated with NaOH solution, which produces blue colouration. X can be

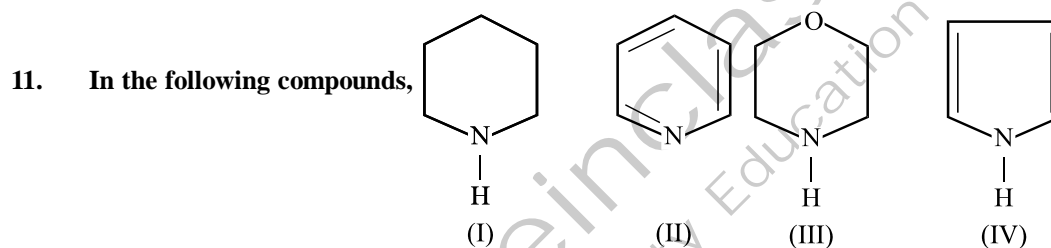
(a) $\text{CH}_3\text{CH}_2\text{NH}_2$ (b) $\text{CH}_3\text{CH}_2\text{NO}_2$
(c) $\text{CH}_3\text{CH}_2\text{ONO}$ (d) $(\text{CH}_3)_2\text{CHNO}_2$



X is :

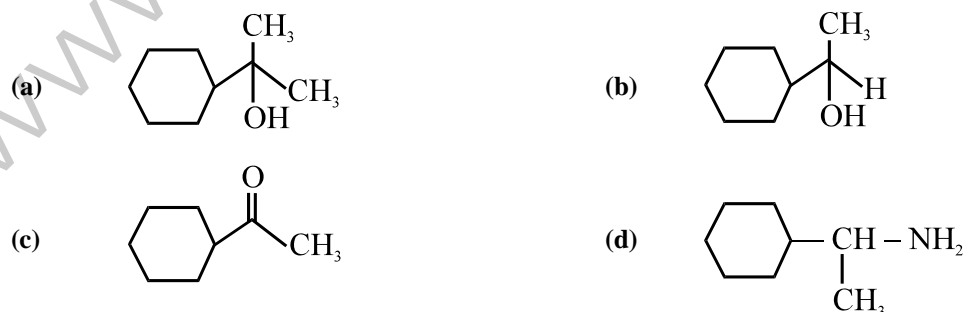


- (a) carbyl amine reaction
 (b) Hofmann mustard oil reaction
 (c) diazonium salt (as the intermediate) with HNO_2
 (d) all are correct



the order of basicity is

- (a) $\text{IV} > \text{I} > \text{III} > \text{II}$ (b) $\text{III} > \text{I} > \text{IV} > \text{II}$
 (c) $\text{II} > \text{I} > \text{III} > \text{IV}$ (d) $\text{I} > \text{III} > \text{II} > \text{IV}$



[Answers : (1) b (2) d (3) b (4) a (5) d (6) d (7) b (8) d (9) b (10) d (11) d (12) a]