FOCUS

Class XII

NEET/JEE 2019

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UNIT - 7 : Organic Compounds Containing Nitrogen | Biomolecules

ORGANIC COMPOUNDS CONTAINING NITROGEN

Amines

- These are alkyl or aryl derivatives of ammonia formed by the replacement of one or more hydrogen atoms by corresponding number of alkyl on aryl groups.

Classification

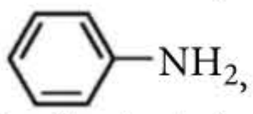
Amines are classified into two categories :

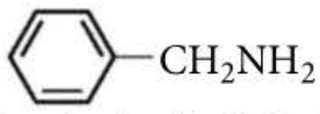
- Aliphatic amines where nitrogen atom is directly bonded to one or more alkyl groups. These may be primary, secondary or tertiary amines.

$C_2H_5—NH_2$, $C_2H_5—NH—C_2H_5$,
1° amine 2° amine

$$C_2H_5—\underset{\displaystyle C_2H_5}{\overset{\displaystyle C_2H_5}{\underset{|}{\overset{|}{N}}}}—C_2H_5$$
3° amine

- Aromatic amines where nitrogen atom is directly bonded to one or more aryl groups. These are arylamines or aralkylamines.


Aniline (Arylamine)

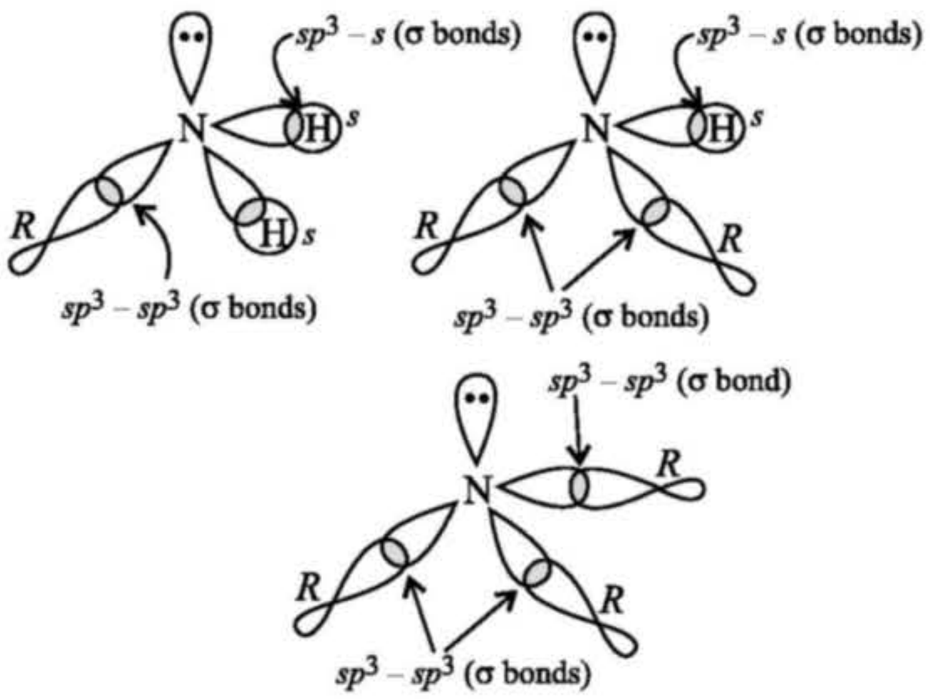

Benzylamine (Aralkylamine)

Nomenclature

- In common system, an aliphatic amine is named by prefixing alkyl group to amine, *i.e.*, alkylamine. In IUPAC system, amines are named as alkanamines. In secondary and tertiary amines, when two or more groups are the same, the prefix di or tri is appended before the name of alkyl group.

Structure

- The amines have a pyramidal shape and the nitrogen atom is sp^3-hybridised. Out of the four hybrid orbitals, three singly filled orbitals form sigma bonds with the C-atom of alkyl group and the hydrogen atom, whereas the fourth hybrid orbital containing an electron pair is not involved in bond formation. Due to the presence of unshared pair of electrons the angle C—N—*E* (where *E* is C or H) is less.



Orbital Structures of 1°, 2° and 3° Amines

Preparation

Reduction of nitro compounds :

$$RNO_2 \xrightarrow[\text{or } H_2/Pd \text{ or } LiAlH_4/\text{ether}]{Sn/HCl \text{ or } Fe/HCl}$$

Hofmann's ammonolysis method :

$$RX \xrightarrow[373\ K]{NH_3}$$

Mendius reduction :

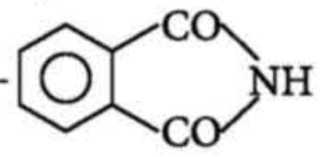
$$RCN \xrightarrow[\text{or } Na(Hg)/C_2H_5OH]{H_2/Ni \text{ or } LiAlH_4/\text{ether}}$$

Reduction of amides :

$$RCONH_2 \xrightarrow[\text{or } Na/C_2H_5OH]{LiAlH_4/\text{ether}}$$

RNH_2

Gabriel phthalimide synthesis :



$$\xleftarrow[\text{(ii) } RX,\ \Delta \\ \text{(iii) } H^+/H_2O/\Delta]{\text{(i) KOH(alc.)}}$$

Hofmann bromamide degradation :

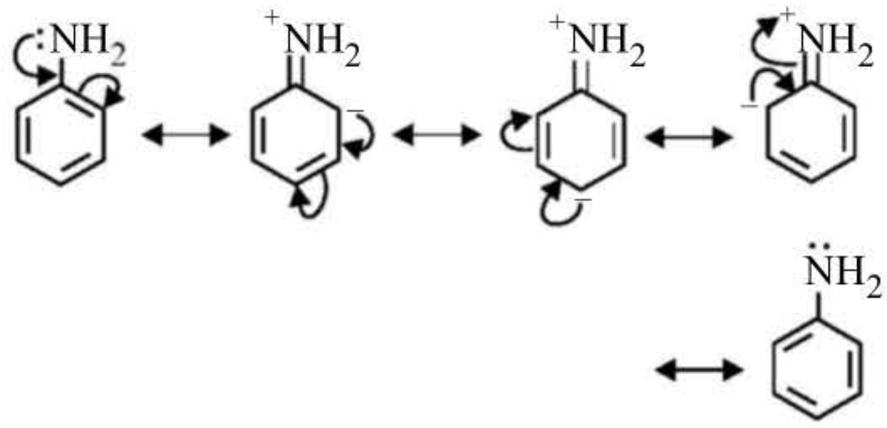
$$RCONH_2 \xrightarrow[KOH,\ \Delta]{Br_2}$$

Basic Character

- The amines are basic in nature due to the presence of a lone pair of electron on N-atom of the $-NH_2$ group, which it can donate to electron deficient compounds. Aliphatic amines are stronger bases than NH_3 because of the $+I$ effect of the alkyl groups. Greater the number of alkyl groups attached to N-atom, higher is the electron density on it and more will be the basicity. Thus, the order of basic nature of amines is expected to be $3° > 2° > 1°$, however the observed order of basicity in aqueous solution is $2° > 1° > 3°$. In aqueous solution, despite of inductive effect, solvation effect and steric hindrance also play an important role. The order of basicity varies with the nature of alkyl group.

Alkyl group	Basic strength
CH_3-	$R_2NH > RNH_2 > R_3N > NH_3$
C_2H_5-	$R_2NH > R_3N > RNH_2 > NH_3$

- Aniline is a weaker base compared to ammonia. This is because the lone pair of electrons on N-atom of aniline is less available for protonation due to its involvement in conjugation with the π-electrons of the benzene ring.



Further the presence of electron withdrawing groups like $-NO_2$, $-CN$, $-X$, etc., decreases the basicity while, the presence of electron donating groups like $-OCH_3$, $-CH_3$, $-NH_2$, etc., activates the benzene ring and also increases the basicity.

Chemical Properties of Aliphatic Amines

RNH_2

$$RNH_2 \xleftarrow{NaOH} RNH_3^+Cl^- \xleftarrow{HCl}$$

$$RNH_2 \xrightarrow[-R'COOH]{(R'CO)_2O} RNHCOR'$$

$$RNH_2 \xleftarrow{R'X} \underset{\text{Quaternary salt}}{RNR_3'^+} \xleftarrow[-HX]{R'X} RNR_2' \xleftarrow[-HX]{R'X} RNHR'$$

$$RNH_2 \xrightarrow[-KCl,\ -H_2O]{CHCl_3/alc.KOH} RNC \text{ (Carbylamine reaction)}$$

$$RNH_2 \xrightarrow{HNO_2} ROH + N_2\uparrow + H_2O$$

$$RNH_2 \xrightarrow[-HCl]{RCHO} \underset{\text{Schiff's base}}{RN{=}CHR}$$

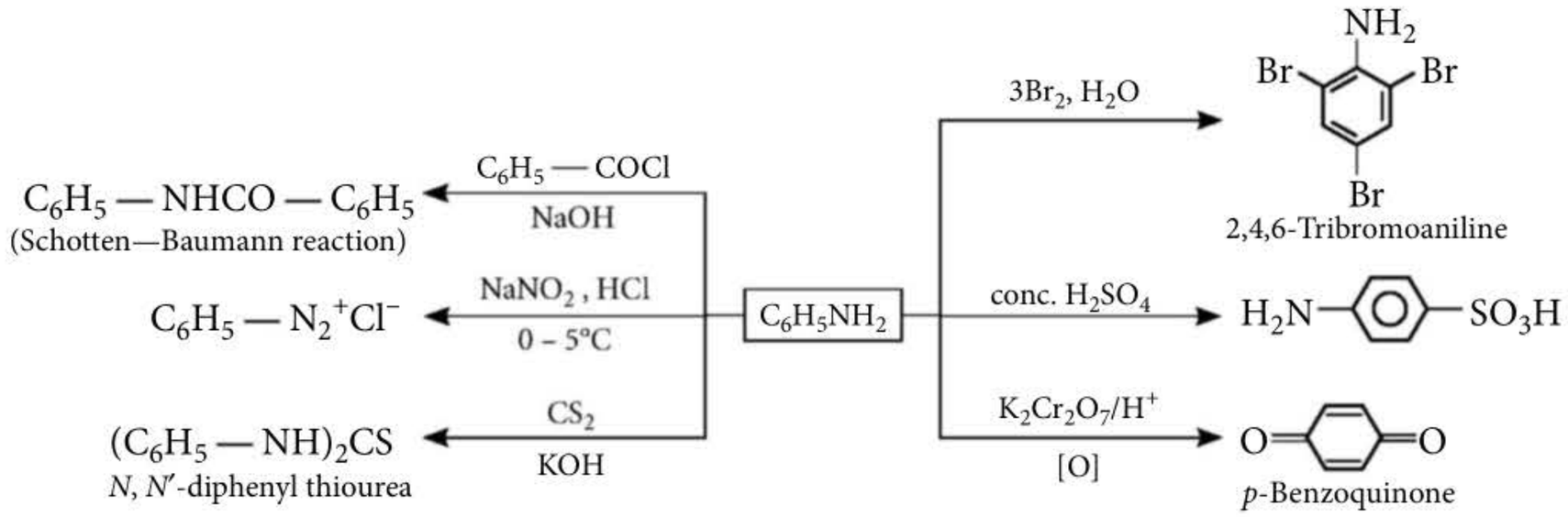
$$RNH_2 \xrightarrow[-HCl]{C_6H_5SO_2Cl} RNHSO_2C_6H_5 \text{ (Hinsberg's test)}$$

(Soluble in NaOH)

$$RNH_2 \xleftarrow[-HCl]{R'COCl} RNHCOR'$$

Chemical Properties of Aniline

- Aniline undergoes electrophilic substitution reactions. $-NH_2$ group is *ortho* and *para* directing and a powerful activating group.



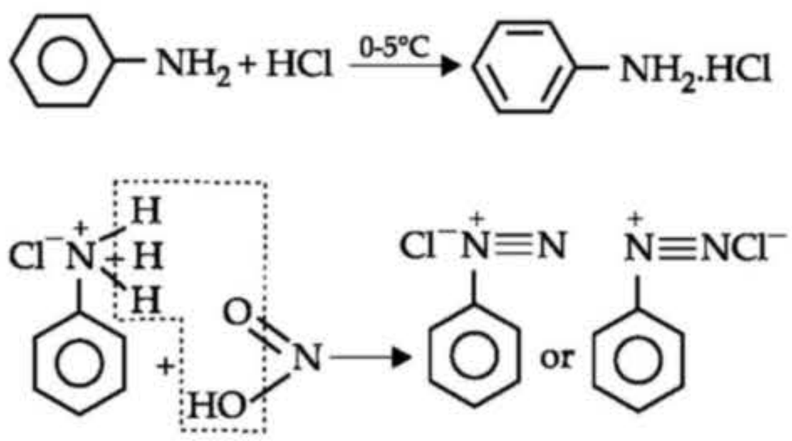
Identification of Primary, Secondary and Tertiary Amines

	Test	Primary amine	Secondary amine	Tertiary amine
1.	Reaction with nitrous acid.	Gives alcohol with effervescence of N_2 gas.	Gives yellow oily compound nitrosoamine.	Forms nitrite in cold which is soluble in water and on heating gives nitrosoamine.
2.	Reaction with benzene sulphonyl chloride (Hinsberg's reagent).	Gives *N*-alkylbenzene-sulphonamide which is soluble in alkali.	Gives *N*,*N*-dialkylbenzene sulphonamide which is insoluble in alkali.	No reaction
3.	Carbylamine test : Reaction with chloroform and alcoholic KOH.	Forms carbylamine or isocyanide (*R*NC) with characteristic unpleasant odour.	No reaction	No reaction
4.	Hofmann's mustard oil reaction : Reaction with CS_2 and $HgCl_2$.	Forms *N*-substituted isothiocyante with characteristic unpleasant smell of mustard oil.	No reaction	No reaction

Diazonium Salts

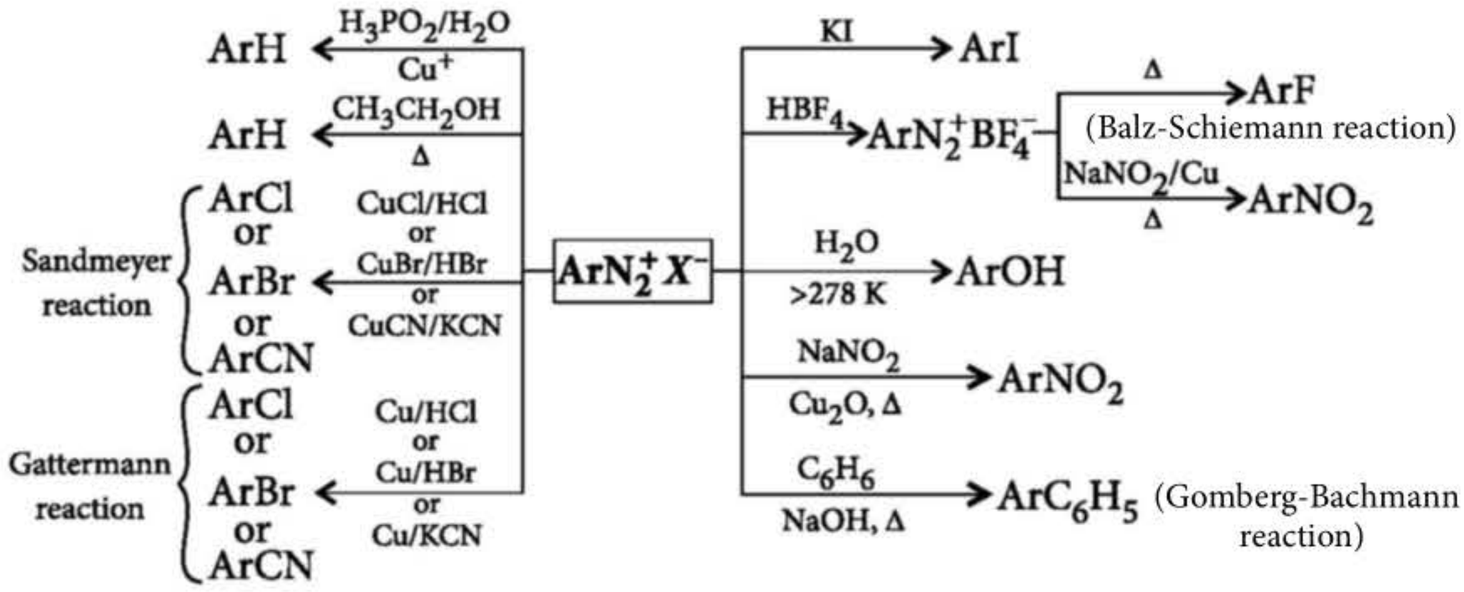
- The diazonium salts have the general formula $ArN_2^+X^-$ where X^- may be an anion like Cl^-, Br^-, etc. and the group N_2^+ is called diazonium ion group.

Preparation



Chemical Properties

- **Reactions involving displacement of nitrogen (diazo group) :**



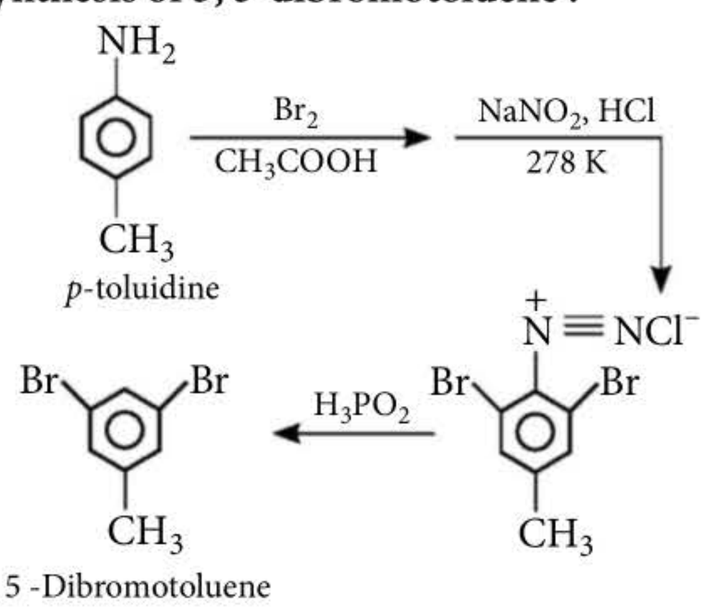
- **Reactions involving retention of diazo group (coupling reactions) :**

$$ArN{=}NC_6H_4NH_2 \xleftarrow[pH = 4\text{-}5,\ 0\text{-}5°C]{C_6H_5NH_2/H^+} \boxed{ArN_2^+X^-} \xrightarrow[pH = 9\text{-}10,\ 0\text{-}5°C]{C_6H_5OH/OH^-} ArN{=}NC_6H_4OH$$

Importance in Synthetic Organic Chemistry

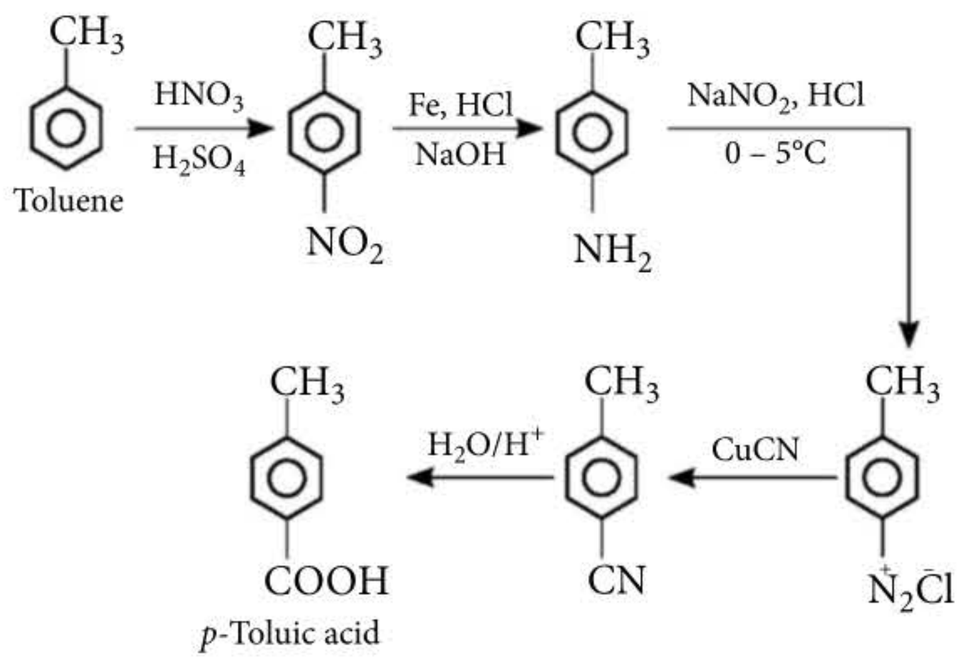
- Diazonium salts are highly useful intermediates in the synthesis of large variety of aromatic compounds. These are used for the preparation of many organic compounds especially aryl halides.

➢ **Synthesis of 3, 5-dibromotoluene :**



3, 5 -Dibromotoluene

➢ **Synthesis of *p*-toluic acid :**



p-Toluic acid

Similarly diazonium salts are used for the manufacture of azo dyes.

BIOMOLECULES

Carbohydrates

- Carbohydrates are defined as polyhydroxy aldehydes or ketones or substances that generally give these on hydrolysis and contain at least one chiral carbon, hence are optically active.
  Their general formula is $C_x(H_2O)_y$ where x and y can be 3, 4, 5, …, etc.

Classification of Carbohydrates

- Based on molecular size :

On the basis of the molecular size, carbohydrates have been classified into three types :

Monosaccharides

Oligosaccharides

Polysaccharides