SENIOR SECONDARY COURSE: CHEMISTRY (313)

28

Compounds of Carbon Containing Nitrogen

AMINES

Amines constitute an important class of organic compounds derived by replacing one or more hydrogen atoms of NH₃ molecule by alkyl/aryl group(s).



If four alkyl groups are attached to the nitrogen atom, then the quaternary ammonium ion or salt is formed.

_		
	R R - N - R R	x-
_		
quat	ernary am	nonium s

Structure of Amines

The nitrogen atom in amine is spahybridised. The three hybrid orbitals are involved in bond formation and one hybrid atomic orbital contains the lone pair of electrons, giving the pyramidal geometry of amines.



IUPAC Nomenclature of Amines

- The ending –e in the name of the corresponding alkane is changed to amine.
- Secondary and tertiary amines are named by using the prefix N for each substituent on the nitrogen atom.

Compounds	IUPAC name	Common name
CH ₃ NH ₂	Methanamine	Methyl amine
CH ₃ CH ₂ NH ₂	Ethanamine	Ethyl amine
CH ₃ CH ₂ CH ₂ NH ₂	Propan-1-amine	Propyl amine
CH ₃ CHCH ₂ NH ₂ CH ₃	2-Methyl propan-l-amine	_
NH ₂	Benzenamine	Aniline

Preparation of Amines

(i) From alkyl halides

Alkyl halides react with ammonia to form primary amines.

 $R - X + 2 NH_3 \longrightarrow R NH_2 + NH_4X$

(ii) By reduction of nitriles (cyanides), amides and nitro compounds





(iii) By Hofmann bromamide reaction



Physical Properties of Amines

- The lower aliphatic amines are gaseous in nature. They have a fishy smell.
- Primary amines with three or four carbon atoms are liquids at room temperature whereas higher ones are solids.
- Aniline and other arylamines are generally colorless. However, they get

SENIOR SECONDARY COURSE: CHEMISTRY (313)

coloured when we store them in open due to atmospheric oxidation.

- Lower aliphatic amines can form hydrogen bonds with water molecules. Therefore, such amines are soluble in water.
- Increase in the size of hydrophobic alkyl part increases the molar mass of amines. This usually results in a decrease in its solubility in water.

Chemical Properties of Amines

(i) Basic Character

- Amines act as Lewis bases due to the presence of lone pair of electrons on the nitrogen atom. More the Kb (dissociation constant of base), higher is the basicity of amines. Lesser the pKb'higher is the basicity of amines.
- Aliphatic amines (CH₃NH₂) are stronger bases than NH₃ due to the electron releasing +I effect of the alkyl group.
- Among aliphatic methyl amines, the order of basic strength in aqueous solution is as follows (C₂H₅NH > (C₂H₅)₃N > C₂H₅NH₂ > NH₃(CH₃)₂NH > CH₃NH₂ > (CH₃)₃N > NH₃

(ii) Alkylation

Primary amines react with alkyl halides to give secondary amines.



(iii) Acylation

Primary amines on reaction with acid chlorides or acid anhydrides give Nsubstituted amides.



(iv) Carbylamine reaction

(v) Reaction with nitrous acid

Primary aromatic amines react with nitrous acid to give diazonium salts and this reaction is known as diazotisation.



 Primary amines undergo condesnsation
with aldehydes or ketones to form imines. These products are also called
Schiff's bases.



(vii) Ring substitution in aromatic amines:

 -NH₂ group is a strong activating and ortho-, para- directing group for electrophilic aromatic substitution reactions.



LEARNER'S GUIDE

SENIOR SECONDARY COURSE: CHEMISTRY (313)

 (a) Halogenation: Aniline on treatment with an aqueous solution of bromine gives
2,4,6 - tribromoaniline.



(b) Nitration: Nitration Direct nitration of aniline is not possible as it is susceptible to oxidation, thus amino group is first protected by *acetylation*.



(c) Sulphonation: Sulphonation is carried out in the presence of sulphuric acid.



Uses of Amines

- Amines are used in making azo-dyes and nylon apart from medicines and drugs.
- They are widely used in developing chemicals for crop protection, medication and water purification.
- They also find use in products of personal care.
- Ethanol amines are the most common type of amine used in the global market.

Identification of Primary, Secondary and Tertiary amines





DIAZONIUM SALTS: REACTIONS AND IMPORTANCE IN SYNTHETIC CHEMISTRY

(i) The Sandmeyer reaction

In this reaction, the arene diazonium salts are reacted with cuprous bromide, cuprous chloride and cuprous cyanide in the presence of HBr, HCI and HCN, respectively.



Replacement of diazonium group by a hydrogen atom



Coupling Reactions of Arenediazonium Salts

Arene diazonium salts react with phenols and tertiary aryl amines to give azo compounds which are known azo dyes.

N2 ⁺ Cl ⁻ +	ОН	$\xrightarrow{O^{\circ}C}$ NaOH, H ₂ O	Ň	NOH
Benzane liazoniaum chloride	Phenol		P -Hydroz	yazobenzene

NITRO COMPOUNDS

Nitro compounds are those derivatives of hydrocarbons in which a hydrogen atom

SENIOR SECONDARY COURSE: CHEMISTRY (313)



LEARNER'S GUIDE

SENIOR SECONDARY COURSE: CHEMISTRY (313)

Check Yourself

1. Nitrogen atom of amino group is hybridised.

(D) sp³d

- (A) sp (B) sp^2 (C) sp^3
- 2. C₃H₈N cannot represent
- (A) 1° ammine
- (B) 2° ammine
- (C) 3° ammine
- (D) quartemary ammonium salt
- 3. When excess of ethyl iodide is treated with ammonia, the product is
- (A) Ethylamine
- (B) Diethylamine
- (C) Triethylamine
- (D) Tetrathylammonium iodide
- 4. Amides may be converted into amines by a reaction named after
- (A) Hofmann Bromide
- (B) Claisen
- (C) Perkin
- (D) Kekule
- 5. Reduction of CH₃CH₂NC with hydrogen in presence of Ni or Pt as catalyst gives
- (A) CH₃CH₂NH₂
- (B) CH₃CH₂NHCH₃
- (C) CH₃CH₂NHCH₂CH₃
- (D) (CH₃)₃N

Stretch Yourself

- Arrange the following compounds in an increasing order of basic strengths in their aqueous solutions: NH₃, CH₃NH₂, (CH₃)₂NH, (CH₃)₃N
- 2. Give the IUPAC name of $H_2N CH_2 CH_2 CH_2 = CH_2$.
- Give a chemical test to distinguish between ethylamine and aniline.
- 4. How may methyl bromide be preferentially converted to methyl isocyanide?
- 5. The conversion of primary aromatic amines into diazonium salts is known as?

र्वधर्म प्रधानम्

LEARNER'S GUIDE

SENIOR SECONDARY COURSE: CHEMISTRY (313)

