

ST. LAWRENCE HIGH SCHOOL

A JESUIT CHRISTIAN MINORITY INSTITUTION STUDY MATERIAL FOR CHEMISTRY (CLASS-12)



TOPIC-ORGANIC COMPOUNDS CONTAINING NITROGEN

PREPARED BY: MR. ARNAB PAUL CHOWDHURY

SET NUMBER-09 DATE: 23.11.2020

Amines constitute an important class of organic compounds derived by replacing one or more hydrogen atoms of NH 3 molecule by alkyl/aryl group(s).

In the IUPAC system, the amines are regarded as alkanamines, e.g.,

Structure

The nitrogen atom in amine is spa-hybridised. 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.

In arylamines, —NH2 group is directly attached to the benzene ring.

aniline (benzenamine)

(N, N-dimethylbenzenamine)

Methods of Preparation of Amines

(i) Reduction of nitro compounds

$$R$$
—NO₂ $\xrightarrow{\text{Reduction}}$ R —NH₂ + 2H₂O

Reduction can takes place by Sn/HCl, Ni/H2, Zn/NaOH, Pd/H2.

The reduction of nitroalkane or nitrobenzene in neutral medium gives hydroxyl amines.

(ii) Ammonolysis of alkyl halides

Ammonolysis has the disadvantage of yielding a mixture of primary, secondary and tertiary amines and also a quaternary ammonium salt.

However, primary amine is obtained as a major product by taking large excess of NH₃. Order of reactivity of halides 'with amines is RI >RBr> RCI.

Aromatic amines could not be prepared since anyl halides are much less reactive towards nucleophilic substitution reactions.

(iii) Reduction of nitriles or cyanides

$$R$$
—C=N $\xrightarrow{\text{Ni/H}_2}$ R —CH₂NH₂

(iv) Schmidt reaction

$$R$$
COOH + N_3 H $\xrightarrow{\text{Conc H}_2SO_4}$ R — N H $_2$ + N_2 + N_2 + N_3 H alkylamine acid

It is a modification of Curtius degradation.

(v) Reduction of amides

$$R$$
— C — NH_2 $\xrightarrow{\text{(i) LiAlH}_4}$ R — CH_2NH_2

(vi) Gabriel's phthalimide reaction

It only produces 1 0 amines. This method is not suitable for 1° arylamine because aryl halide does not give nucleophilic substitution reaction.

(viii) Hofmann bromamide degradation reaction

$$R$$
— C — $NH_2 + Br_2 + 4NaOH$ \longrightarrow $RNH_2 + Na_2CO_3$ $+ 2NaBr + 2H_2O$

In Hofmann degradation reaction, the amine formed has one carbon less than the parent amide. To obtain primary amine with same number of carbon atoms from primary amide, reduction is done with LiAIH₄/ether.

Physical Properties of Amines

- 1. The lower aliphatic amines are gases with fishy smell.
- 2. Primary amines with three or more carbon atoms are liquid and higher members are all solids.
- 3. Lower aliphatic amines are water suluble because they can form hydrogen bonds with water molecules, however the solubility decreases with increase in hydrophobic alkyl group.
- 4. Boiling points order primary > secondary > tertiary
- 5. Tertiary amines does not have intermolecular association due to the absence of hydrogen atom available for hydrogen bond formation.

Basic Strength of Amines

Amines act as Lewis bases due to the presence of lone pair of electrons on the nitrogen atom.

More the K_b (dissociation constant of base), higher is the basicity of amines.

Lesser the $pK_{{}_{\!b}}$ higher is the basicity of amines.

Aliphatic amines (CH₃NH₂) are stronger bases than NH₃ due to the electron releasing +/ effect of the alkyl group.

Among aliphatic methyl amines, the order of basic strength in aqueous solution is as follows

$$(C_2H_5NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$$

 $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

Aromatic amines are weaker basesthan aliphatic amlnes and NH_3 , due to the fact that the electron pair on the nitrogen atom is involved in resonance with the π -electron pairs of the ring.

Electron releasing groups (e.g.,- CH_3 ,- OCH_3 ,- NH_2 etc.) increase the basic strength of aromatic amines while electron withdrawing groups (like – NO_2 , -X,-CN etc.) tend to decrease the same.

o-substitutedaromaticamines are usually weaker basesthan aniline irrespective of the nature of substituent whether electron releasing or electron withdrawing. This is called ortho effect and is probably due to sterk and electronic factors.

chemical Properties of Amines

(i) Alkylation All the three types of amines react with alkyl halides to form quaternary ammonium salt as the final product provided alkyl halide is present in excess.

Aromatic amines also undergo alkylation as given below.

triethylanilinium bromide

(ii) Acylation

$$\begin{array}{c} \mathbf{C_2H_5} - \mathbf{NH_2} + \mathbf{CH_3COC1} \xrightarrow{\mathbf{Base}} \mathbf{C_2H_5} - \mathbf{N} - \mathbf{C} - \mathbf{CH_3} + \mathbf{HC1} \\ & \mathbf{H} & \mathbf{O} \\ \\ \mathbf{C_2H_5} - \mathbf{NH_2} + \mathbf{CH_3} - \mathbf{C} - \mathbf{O} - \mathbf{C} - \mathbf{CH_3} & \longrightarrow \\ & \mathbf{O} & \mathbf{O} \\ \\ & \mathbf{C_2H_5} - \mathbf{N} - \mathbf{C} - \mathbf{CH_3} + \mathbf{CH_3COC} \\ \end{array}$$

(iii) Benzoylation

$$CH_3NH_2 + C_6H_6COCl \xrightarrow{Pyridine} CH_3NHCOC_6H_5 + HCl$$

acetanilide

Benzoylation of aniline is known as Schotten Baumann reaction.

(ivii) Carbylamine reaction [only by 1° amines]

$$R$$
—NH₂ + CHCl₃ + 3KOH $\xrightarrow{\text{Heat}}$ R —N $\stackrel{\textstyle \rightharpoonup}{=}$ C + 3KCI + 3H₂O isocyanide (a bad smelling compound)

MIC or methyl isocyanate gas (CH₃—N=C=O) was responsible for Bhopal gas tragedy in December 1984.

(v) Reaction with nitrous acid

$$RNH_2 + HNO_2 \xrightarrow{NaNO_2 + HCl} [RN_2^+Cl] \xrightarrow{H_2O} ROH + N_2 + HCl$$

Quantitative evolution of nitrogen is used in estimation of amino acids and proteins.

$$G_0H_5$$
— NH_2
 $\xrightarrow{NaNO_2 + 2HCl}$
 $\xrightarrow{273-278 \text{ K}}$
 $G_0H_5N_2^+Cl^ + NaCl + 2H_2O$
benzene diazonium
chloride

But secondary and _tertiary amines react with nitrous acid in different manner.

Methyl amine give dimethyl ether with HNO₂.

(vi) Reaction with aryl sulphonyl chloride [Hinsberg reagent] The reaction of benzenesulphonyl chloride with primary amine yield N-ethyl benzenesulphonyl amide.

(soluble in alkali)

The reaction of benzenesulphonyl chloride with secondary amine yields N,N-diethyl benzene sulphonamide.

$$\begin{array}{c|c}
 & O \\
 & S \\
 & Cl + H \\
 & O \\
 & C_2H_5
\end{array} \rightarrow \begin{array}{c}
 & O \\
 & H_3C \\
 & & S \\
 & O \\
 & & C_2H_5 + HCl \\
 & O \\
 & & C_2H_5
\end{array}$$
(insoluble in alkali)

Tertiary amines does not react with benzenesulphonyl chloride.

(vii) Reaction with aldehydes Schiff base is obtained.

$$C_6H_5NH_2 + OHCC_6H_5$$

benzaldehyde $\xrightarrow{\Delta}$ $C_6H_5N = CHC_6H_5$
 $-H_2O$ benzylidene aniline (Schiff base)

(viii) Electrophihe substitution reactions Aniline is ortho and para directing towards electrophilic substitution reaction due to high electron density at ortho and parapositions.

To prepare monosubstituted derivative, activating effect of -NH₂ group must be controlled. It can be done by protecting the -NH₂ group by acetylation with acetic anhydride.

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

In strongly acidic medium, aniline is protonated as anilinium ion which is meta directing so it gives meta product also.

(c) Sulphonation On sulphonation, aniline gives sulphanilic acid, as the major product.

- (d) Aniline does not undergo Friedel-Crafts reaction due to salt formation with aluminium chloride, the Lewis acid, which is used as a catalyst. Due to this, nitrogen of aniline acquires positive charge and hence. behave like a strong deactivating group for further chemical reaction.
- (ix) Oxidation Use of diffrentoxidising agents gives difTerent products. e.g.,

Oxidising agent	Product
Accidified KMnO ₄ (or Na ₂ Cr ₂ O ₇ + CuSO ₄ + dil acid)	Aniline black (a dye)
Chromic acid (Na ₂ C ₅ O ₇ + Conc H ₂ SO ₄)	p-benzoquinone
Caro's acid (H ₂ SO ₅)	nitrobenzene and nitrosobenzene
Conc. nitric acid	decomposes

Separation of Mixture of Amines (1°, 2° and 3°)

- (a) Fractional distillation This method Is based on the boiling points of amines and is used satIsfactorily in Industry.
- (b) Hofmann's methoOdDiethyloxalate is called Hofmann's reagent with which mixture of amines is treated.
- 1° amine forms solid dialkyloxamide (CONHR)₂

- 2° amine forms liquid dialkyloxamlc ester(CONR₂-COOC₂H₅)
- 3° amlnes do not react
 - (c) HInsberg's method see.chemkal reactions.

Benzene Diazonium Chloride (C₆H₅N₂+;Cl-)

Preparation (Diazotisation reaction)

$$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273 \cdot 278 \text{ K}} C_6H_5N = N - Cl + NaCl + 2H_2O$$

The excess acid in diazotisation reaction is necessary to maintain proper acidic medium for the reaction and to prevent combination of diazonium salt formed with the undiazotised amine.

Diazonium salts are prepared and used in aqueous solutions because in solid state, they explode.

Properties

It is a colourless crystalline solid, soluble in water. It has tendency to explode when dry.

Stability of Arenediazonium salts

It is relatively more stable than the alkyldiazonium salt. The arenediazonium ion is resonance stabilised as is indicated by the following resonating structures:

Various resonating structures of arenediazonium ion

Chemical Reactions

$$\begin{array}{c} \text{Cu}^+, \text{H}_3\text{PO}_2/\text{H}_3\text{O} \\ \text{(Hypophosphorous acid)} \\ \text{CeH}_6\text{N}_2^+\text{Cl}^- \\ \text{CH}_3\text{CH}_2\text{OH} \\ \text{CuBr} / \text{HBr} \\ \text{(bromobenzene)} \\ \end{array} \begin{array}{c} \text{C}_6\text{H}_6+\text{N}_2\uparrow+\text{H}_3\text{PO}_3+\text{HCl} \\ \text{(Hypophosphorous acid)} \\ \text{CH}_3\text{CH}_2\text{OH} \\ \text{CH}_3\text{CH}_2\text{OH} \\ \text{(Deamination)} \\ \text{CuBr} / \text{HBr} \\ \text{(bromobenzene)} \end{array}$$

$$\begin{array}{c} \text{Cucl/HCl} & \text{C}_6\text{H}_6\text{Cl} + \text{N}_2 & (\text{Sandmeyer's reaction}) \\ \hline \text{Cu/HCl} & \text{C}_6\text{H}_5\text{Cl} + \text{N}_2 + \text{Cucl} (\text{Gattermann's reaction}) \\ \hline \text{Cu/HBr} & \text{C}_6\text{H}_5\text{Br} + \text{N}_2 + \text{CuBr} \\ \hline \text{KCN/CuCN} & \text{C}_6\text{H}_5\text{CN} (\text{benzonitrile}) + \text{N}_2 \\ \hline \text{KI} & \text{C}_6\text{H}_5\text{I} + \text{N}_2 + \text{KCl} \\ \hline \text{HBF}_4 & \text{C}_6\text{H}_5\text{N}_2 (\text{BF}_4) \\ \hline \text{-HCl} & \text{C}_6\text{H}_5\text{N}_2 (\text{BF}_4) \\ \hline \text{Boiling} & \text{C}_6\text{H}_5\text{OH} + \text{N}_2 + \text{HCl} \\ \hline \text{Boiling} & \text{C}_6\text{H}_5\text{OH} + \text{N}_2 + \text{HCl} \\ \hline \text{phenol} & \text{Phydroxyazobenzene} \\ \hline \text{C}_6\text{H}_6\text{NH}_2 & \text{OH} \\ \hline \text{phydroxyazobenzene} \\ \text{(orange dye)} & \text{OH} \\ \hline \text{P-aminoazobenzene} \\ \text{(yellow dye)} & \text{NH}_2 \\ \hline \end{array}$$

Alkyl Cyanides'

These compound have formula RCN. These are the derivatives of RCN.

According to IUPAC system, cyanides are named as 'alkane nitrile', e.g.,

C₃H₇CN , C₆H₅CN butanenitrile benzenenitrile

Methods of Preparation

(i) From alkyl halides

$$RX + KCN(ale) \xrightarrow{100^{\circ}C} RCN + RNC$$
(major)

ii) From acid amides

$$RCONH_2 \xrightarrow{P_2O_5,\Delta} RC = N$$

Physical properties

- 1. These are neutral compound with pleasentodour, similar to bitter almonds.
- 2. These are soluble in water as well as organic solvents.
- 3. These are poisonous but less than HCN.

Chemical Properties

i) Hydrolysis

$$RCN \xrightarrow{\text{H}_2O} \text{RCONH}_2 \xrightarrow{\text{H}_2O} RCOOH + NH_3$$
(partial hydrolysis)
$$RCOOH_2 \xrightarrow{\text{H}_2O} RCOOH_3 \xrightarrow{\text{H}_2O} RCOOH_4 + NH_3$$

(ii) Reduction

$$RCN + 4[H] \xrightarrow{Na+C_2H_5OH} RCH_2NH_2$$

$$RCN + 4[H] \xrightarrow{LiAlH_4} RCH_2NH_2$$
 (Mendius reduction)

$$RCN \xrightarrow{SnCl_2/HCl} RCH = NH \cdot HCl \xrightarrow{H_2O} RCHO + NH_4Cl$$
imine hydrochloride aldehyde

(iii) Reaction with Grignard reagent

$$RCN + R'MgX \xrightarrow{Ether} R \xrightarrow{R'} C = NMgX \xrightarrow{2H_2O} R \xrightarrow{R'} C = O$$

Alkyl iscoyanides (RNC)

Accordingg to IUPAC system, these are named as 'alkane isonitrile'

e.g., CH₃NC methyl isonitrile C₆H₃NC benzene isonitrile **Methods of Preparation** (a) From alkyl halides

$$R - X + AgCN \xrightarrow{C_2H_5OH} RNC + RCN$$
(major)

(b) Carbylamine reaction

$$RNH_2 + CHCl_3 + 3KOH(alc) \xrightarrow{\Delta} RNC + 3KCl + 3H_2O$$

(c) From N-alkyl formamide

$$R$$
—NH—C—H $\xrightarrow{\text{POCl}_3}$ R —N \rightleftharpoons C+H₂O

Physical Properties

- 1. These are colourlessunpleasent smelling liquids.
- 2. These are soluble in organic solvents but insoluble in water.

Chemical Properties

(i) Hydrolysis

$$R-N \stackrel{\textstyle \rightharpoonup}{=} C + 2H_2O \xrightarrow{\textstyle H^+} RNH_2 + HCOOH$$

(ii) Reduction

$$RN \stackrel{\longrightarrow}{=} C + 4[H] \xrightarrow{\text{Na/C}_2H_5OH} RNHCH_3$$
or Ni or Pt
2° amine

(iii) Addition reaction Due to the presence of unshared pair of electrons on C atom, alkyl isocyanides give addition reaction.

$$RNC+S \longrightarrow RNCS$$
 $RNC+HgO \longrightarrow RNCO+Hg$
 $RNC+O_3 \longrightarrow RNCO$

(iv) Isomerisation At 250°C, it isomerises to nitrile.

$$RNC \xrightarrow{\Delta} RCN$$

Nitro Compounds

These are obtained by replacing one H of hydrocarbon by -NO₂ group. These are named according to IUPAC system as 'nitro alkane'.

Methods of Preparation

(i) From alkyl halides

$$RX + AgNO_2 \xrightarrow{\Delta} RNO_2 + AgX$$

(ii) Nitration Nitrating mixture is conc HNO3 + conc H2SO4.

Physical Properties

- 1. These are colourlesspleasent smelling liquids.
- 2. Their boiling point are much higher than isomeric alkyl nitriles.
- 3. These are less soluble in water but readily soluble in organic solvents.

Chemical Properties

(i) **Reduction** With Sn/HCl or catalytic hydrogenation, nitroalkanes are reduced to amines.

$$RNO_2 + 6[H] \xrightarrow{Sn/HCl} R-NH_2 + 2H_2O$$

If neutral reducing agent like Zn dust + NH₄Cl is used, hydroxylamines are obtained as major product.

$$RNO_2 + 4[H] \xrightarrow{Zn + NH_4Cl} R-NHOH + H_2O$$
N-alkylhydroxylamine

In the presence of (NH₄)₂S or Na S, selective reduction takes place.

$$NO_2$$
 + $3(NH_4)_2S$ - NO_2 + $6NH_3 + 2H_2O + 3S$ (Zinin reduction)

Nitrobenzene gives different prociucts with different reagents and in different mediums.

Medium	Reagent	Product
Acid Neutral	Sn/HCl Zn/NH ₄ Cl	N-phenyl hydroxylamine
	19.00	2
	Na ₃ AsO ₃ /NaOH	azoxybenzene (C ₆ H ₅ N == NC ₆ H ₅)
Alkaline	Zn/NaOH, CH ₃ OH	azobeńzene
2004	Zn/NaOH, C2H5OH	hydrazobenzene
Metallic hydride	LIAIH ₄	aniline
Electrolytic	dil H2SO4	p-aminophenol

(ii) Action of HNO2

1° nitroalkane gives nitrolic acid which gives red colour with NaOH.

$$RCH_2NH_2 \xrightarrow{-H_2O} RC(NO_2) = NOH$$
 $\xrightarrow{\text{nitrolic acid}} RC(NO_2) = NONa$
 $\xrightarrow{\text{NaOH}} RC(NO_2) = NONa$
 $\xrightarrow{\text{(red)}}$

2° nitroalkanes give pseudonitrol with HNO2.

$$R_2$$
CH(NO₂) $\xrightarrow{\text{HNO}_2}$ R_2 C—NO $\xrightarrow{\text{NaOH}}$ Blue NO₂ pseudonitrol

- 3° nitroalkanes does not react with HNO2
- (iii) Nef carbonyl synthesis Na or K salt of 1° or 2° nitroalkanes give carbonyl compounds on acidification with 50% H₂SO₄ at room temperature. This reaction is called Nef carbonyl synthesis.

$$R$$
— $CH_2NO_2 \xrightarrow{NaOH} R$ — $CH=N$
 $O^ O^ Na^+$
 SO_4
 R — $CH=O$
aldehyde

(iv) Electrophifie substitution On nitration, nitrobenzene gives m-dinitrobenzene (as - NO₂ is a m-directing group and strongly deactivating).

It does not give Friedel-Craft's alkylation.

(v) **Nucleophilic** substitution reaction -NO₂ group activates the ring towards nucleophilic substitution.

PREPARED BY: MR. ARNAB PAUL CHOWDHURY