NITROGEN COMPOUNDS

AMINES

Amines are derivative of ammonia where one or more hydrogen atoms are replaced by alkyl or aryl groups.

CLASSIFICATION

Amines are classified as being primary (1°), secondary tertiary (3°) on the basis of the number of alkyl or aryl groups attached to the nitrogen.

(i) Primary amines:

(ii) Secondary Amine:

(iii) Tertiary Amine:

When all the alkyl or aryl groups are same the amine is called simple", and "mixed" when these are different. Amines are divided into aliphatic amines and aromatic amines. In an aliphatic amines all the carbon bonded directly to nitrogen are derived from alkyl: In an aromatic amines one or more of the group bonded directly to nitrogen are aryl groups.

STRUCTURES

The nitrogen atom of most amines is like that of ammonia; it is approximately sp³ hybridized. The three alkyl groups (or hydrogen atoms) occupy corner of a tetrahedron; the sp³ orbital containing the unshared electron pair is directed towards the other corner. We describe the shape of amines by the location of the atoms as being trigonal pyramidal.

METHODS OF PREPARATION

By the ammonolysis of alkyl halide: This method of preparation of amines involves nucleophilic substitution by ammonia or an amine molecule on an alkyl halide

$$R - X \xrightarrow{\ddot{N}H_1} R - \ddot{N}H_2$$
(1°-Amines)

To obtain the 1°-amine large amount of NH₃ is used. If alkyl halide is taken in to excess then mixture of 1°, 2°, 3° amines of quartnary salt is obtained.

$$\ddot{N}H_{s} \xrightarrow{R-X} R - NH_{2} \xrightarrow{R-X} R_{s}N \xrightarrow{R-X} R_{s}N \xrightarrow{RX} R_{s}N$$

Gabriel Phthalimide synthesis: Pottasium phthalimide can be used to prepare primary amines by the method known as Gabriel synthesis.

By Hofmann Bromamide degradation reaction:

Primary amide react with solution of bromine or chlorine in sodium hydroxide or pottasium hydroxide to yield amines through a reaction known as Hofmann degradation or Hofmann rearrangement.

$$R - C - NH_2 + Br_2 + 4 KOH \xrightarrow{\Delta} R - NH_2 + 2KBr + K_2CO_3 + 2H_2O$$

Mechanism

(I)
$$R - C - \ddot{N} - H \xrightarrow{OH^-} R - C - \ddot{N} + H_{,O} \xrightarrow{Br - Br} R - C - N - Br$$

Amide N -Bromo acid ami

(II)
$$R - C - \ddot{N} - Br \xrightarrow{OH} R - C - \ddot{N} - Br \xrightarrow{OH} O = C = N - R$$

N-Bromo amide

(III)
$$R - \ddot{N} = C = O \xrightarrow{\Theta} R - \ddot{N} = C - O \xrightarrow{\Theta} R - \ddot{N} = C = O \xrightarrow{OH} R - \ddot{N} = C = O \xrightarrow{Intramolecular} R - \ddot{N} + C = O$$

$$R - \ddot{N} = C = O \xrightarrow{\Theta} R - \ddot{N} = C = O \xrightarrow{Intramolecular} R - \ddot{N} + C = O$$

$$R - \ddot{N} = C = O \xrightarrow{\Theta} R - \ddot{N} = C = O \xrightarrow{Intramolecular} R - \ddot{N} + C = O$$

Note:

- (i) Intermediate products of this reaction is R C NH Br & R N = C = O
- (ii) Migration of alkyl group is the r.d.s. (rate determine step) of the reaction. i.e. formation of R-N=C=O is r.d.s.
- (iii) No change takes place in the configuration of chiral carbon during migration of alkyl group.

From Alkanoic acid (Schimdt Reaction):

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Mechanism: -

$$R - C - OH + H^{\oplus} \longrightarrow R - C - OH \longrightarrow R - \stackrel{\oplus}{C} - OH \xrightarrow{HN-N=N} \xrightarrow{R-C} R - COH \xrightarrow{-H_2O} \xrightarrow{R-N} \xrightarrow{R-N}$$

Curtius Rearrangement:

$$R - C_1 \xrightarrow{(i) \text{ NaN}_i} RNH_2$$

Mechanisms

(i)
$$R - C - CI \xrightarrow{0 \atop N = N = N} R \xrightarrow{0 \atop N} R \xrightarrow{0 \atop N = N} R \xrightarrow{0 \atop N} R \xrightarrow{0 \atop N = N} R \xrightarrow{0 \atop N}$$

(iii)
$$R-N=C=O \xrightarrow{H} \xrightarrow{O} R \xrightarrow{R} C \xrightarrow{C} O \xrightarrow{R} \longrightarrow R \xrightarrow{O} C=O \longrightarrow R \xrightarrow{NH} C=O \longrightarrow R \xrightarrow{NH} + CO_2 \xrightarrow{H} \xrightarrow{NH} R \xrightarrow{NH_2} C=O \xrightarrow{NH} + CO_2 \xrightarrow{NH} + CO_2 \xrightarrow{NH} + CO_3 \xrightarrow{NH} C=O \xrightarrow{NH} C=O$$

The Lossen Rearrangment

The thermal, acid or base catalysed, intramolecular conversion of hydroxamic acid and their O-acyl and O-aryl derivatives to isocyanate is called Lossen rearrangement.

$$C_6H_5-C-NH-OH \xrightarrow{(i)} \stackrel{\bigoplus}{H} C_6H_5-NH_2$$

$$C_6H_5 - C - NH - O - C - CH_3 \xrightarrow{\text{(i) OH}} R - NH_2$$

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Mechanism

(i) The base catalysed mechanism

$$\begin{array}{c} O \\ R-C-NH-G \\ R-C-NH-G \\ \end{array} (G=OH,O-C-CH_3,O-C-Ar) \\ R-C \\ OH \\ \longrightarrow R \\ \longrightarrow$$

(ii) The acid catalysed mechanism

$$R - C - NH - O - Z$$
 $(Z = H, -C - CH_{1}, -C - Ar)$

$$R-C-NH-O-Z \xrightarrow{\bigoplus_{H}} R-C-NH-O-Z \xrightarrow{\bigoplus_{H}} R-C-$$

By the Reduction of Nitriles and Iso-Nitriles

$$R-C \equiv N \xrightarrow{H_2, \text{ catalyst}} R \text{ CH}_2 \text{ NH}_2 \qquad (1^{\circ} \text{ amine})$$

$$R-N \stackrel{\stackrel{\longrightarrow}{=}} C \xrightarrow{\text{LiAlH}_4} R \text{ NH CH}_3 \qquad (\text{methyl substituted amine})$$

$$CH_2C1 \xrightarrow{\text{NaCN}} O - CH_2CN \xrightarrow{H_2, \text{Ni}, 140^{\circ}C} O - CH_2CH_2 \text{ NH}_2$$

From Alkylchloride:

$$R-Cl + H-NH_2 \xrightarrow{Cu_2O} R-NH_2 + HCl$$

Note: In the above reaction Cu₂O neutralises the evolved HCl in form of Cu₂Cl₂ + H₂O otherwise HCl forms additional salt with amines.

From Grignard reagent:

$$R-Mg-Cl + Cl-NH_2 \longrightarrow R-NH_2 + MgCl_2$$

From Alcohol:

$$R + OH + H + NH_2 \xrightarrow{300^{\circ}C} R-NH_2 + H_2O$$

By Aldehyde or Ketone (reaction with H, and NH, in presence of catalyst):

Primary amine can be produced by passing a mixture of aldehyde or ketone and large excess of ammonia and hydrogen under pressure (20-150 atm) over raney nickel catalyst at 40-150 °C.

$$R_1R_2C=O + NH_3 \xrightarrow{H_2/N_1} R_1R_2CHNH_2$$

Note: Small amount of secondary and tertiary amines are also produced in this method as by products.

From Alkyl isocyanate (Alkaline Hydrolysis):

$$R-N=C=O + 2KOH \longrightarrow R-NH_2 + K_2CO_3$$

From Aldoxime (By Reduction):

$$\begin{array}{c} H \\ R-C=N-OH + 2H \xrightarrow{\text{LIAIH}_4} & R-C \\ H & H \end{array} - \begin{array}{c} H \\ R-C \\ -N - OH \xrightarrow{2H} R-CH_2-NH_2 \end{array}$$

By reduction of Nitro compounds: Nitro alkanes are reduced catalytically to primary amine.

- (a) By LiAlH₄
- (b) By Metal and acid (commonly used Sn + HCl or Fe + HCl) RNO₂

 reduction → RNH₂ + 2H₂O
- Note: (i) When reduction with metal is carried out in neutral solution e.g. with Zn dust & NH₄Cl solution, nitro compounds are converted into N-alkyl hydroxyl amine.

$$RNO_2 \xrightarrow[+NH_4C1]{Zn} RNHOH + 2H_2O$$

N-alkylhydroxyl amine

(ii) When reduction of nitroalkane is carried out with SnCl₂ and conc. HCl, a mixture of N-alkyl hydroxyl amine and oxime are produced.

$$RCH_2NO_2 \xrightarrow{SnCl_2+} RCH_2NHOH + RCH = NOH$$

N-Alkyl hydroxy amine Oxime

BASIC CHARACTER OF AMINES

Amines are relatively weak bases. They are stronger bases than water but are far weaker bases than hydroxides ions (OH), alkoxide ions (RO) and alkanide (R:) anions. These react with acids to form salts.

$$R - \ddot{N}H_{2} + HX \iff R - \ddot{N}H_{3} + \ddot{X}$$

$$\ddot{N}H_{2} \qquad \qquad \ddot{N}H_{3}CI$$

$$Anilne \qquad \qquad Anilinium$$

On reaction with a base such as NaOH, amine salt regenerate parent amine.

$$\mathbb{R}^{\oplus}$$
 \mathbb{R}^{\ominus} \mathbb{R}^{\ominus}

BASICITY OF ALKANAMINES

Primary alkanamines (RNH₂) are more basic than ammonia (NH₃). Their reactions with proton can be used to compare their basicity.

$$R - \bigvee_{H}^{H} : + \bigvee_{H}^{H} : \longrightarrow R - \bigvee_{H}^{H} - \bigvee_{H}^{H}$$

$$H - \bigvee_{H}^{H} : + \bigvee_{H}^{H} : \longrightarrow H - \bigvee_{H}^{H} - \bigvee_{H}^{H}$$

We can account for this on the basis of the electron-releasing ability of an alkyl group (R). An alkyl group releases electrons towards nitrogen, so the unshared electron pair becomes more available for sharing with proton of the acid. The substituted ammonium ion thus formed, gets stabilized as a result of positive charge dispersal by +I effect of the alkyl group. This makes alkylamines stronger bases than ammonia.

This explanation is supported by measurements showing that in the gas phase, the basicities of the following amines increase with increasing methyl substitution:

This is not the order of basicity of these amines in aqueous phase, however. In aqueous phase, the substituted ammonium cations get stabilized by +I effect of the alkyl group as well as solvation with water molecules. With a larger size of the ion, solvation and stability of the ion will be lesser. The stability order in aqueous phase is as follows:

$$R - N' - H - OH_2$$
 $R - N' - H - OH_2$
 $R - N' - H - OH_2$

When the stability of the substituted ammonium cation is greater, the corresponding amine as a base is stronger. The basicity order in aliphatic amines is $1^{\circ} > 2^{\circ} > 3^{\circ}$. This is the reverse of basicity order based on inductive effect.

There is no steric hindrance to H bonding when the alkyl group is small. There is a difference in the basicity order in methyl and ethyl group and so on. Therefore, in aqueous state, inductive effect, solvation effect and steric hindrance of the alkyl group determine the basicity strength. The following examples show the basicity strength order in ethyl and methyl substituted amines.

$$(C_2H_5)_2$$
 NH > $(C_2H_5)_3$ N > C_2H_5 NH₂ > NH₃
 $(CH_3)_2$ NH > (CH_3) NH₂ > $(CH_3)_3$ N > NH₃

BASICITY OF ARYLAMINES

The pK_b value of aniline is quite high because in aniline, the -NH₂ group is directly attached to the benzene ring. The following contributors make aniline a resonance hybrid:

$$\stackrel{\text{NH}_1}{\longleftrightarrow} \longleftrightarrow \stackrel{\text{NH}_2}{\longleftrightarrow} \longleftrightarrow \stackrel{\text{HH}_3}{\longleftrightarrow} \longleftrightarrow \stackrel{\text{HH}_2}{\longleftrightarrow} \longleftrightarrow \stackrel{\text{HH}_2}{\longleftrightarrow} \longleftrightarrow \stackrel{\text{HH}_3}{\longleftrightarrow} \longleftrightarrow \stackrel{\text{HH}_2}{\longleftrightarrow} \longleftrightarrow \stackrel{\text{HH}_3}{\longleftrightarrow} \longleftrightarrow \stackrel{\text{HH}_3}{$$

Structure 1 and 2 are the Kekule structures that contribute to any benzene derivative. Structures 3-5, however, delocalize the unshared electron pair of the nitrogen over the ortho and para position of the ring. This delocalization of the electron pair make it less available to a proton, and delocalization of the electron pair stabilizes aniline. When aniline accepts a proton it becomes an anilinium ion:

The higher the number of resonating structures, the greater is the stability. This makes aniline with five resonating structures more stable than the anilinium ion. Therefore, the basic nature of aniline or other arylamines is less than that of ammonia.

PHYSICAL PROPERTIES

(a) Like ammonia, amines are polar compounds and except 3° amines can form intermolecular H- bonds that's why they have higher boiling points.

Boiling points of 1°, 2° and 3° amines follow the order.

$$1^{\circ} > 2^{\circ} > 3^{\circ}$$
 amine.

- (b) Unlike other organic compounds, amines are much more soluble in water. Because All amines form a stronger H- bond with water.
- (c) Solubility in water follow the order.

$$1^{\circ} > 2^{\circ} > 3^{\circ}$$
 amine.

It is all due to H- Bonding.

(d) Boiling points of amines are lesser than alcohols and acids of comparable mol. weight. Because H-bonding in amines is less pronounced in 1° and 2° than that in alcohols and carboxylic acids. Because nitrogen is less electronegative than oxygen.

Thus every question regarding boiling point can be answered on the basis of H - bonding.

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CHEMICAL PROPERTIES

 Alkylation reaction: Aliphatic amines undergo alkylation on treatment with an alkyl halide in a basic medium such as ammonia.

$$R - \stackrel{\leftarrow}{NH}_1 + \stackrel{\leftarrow}{R} \stackrel{\frown}{X} \longrightarrow R - \stackrel{\oplus}{NH}_1 - R + \stackrel{\ominus}{X}$$
Dialkyl ammonium cation

$$\begin{array}{c|c}
R & R & R & R & R \\
R - N - H & NH_{s} & R - NH + NH_{s}
\end{array}$$

Note: - If alkyl halide is taken into excess then quarternary ammonium salt is obtained.

Ex.
$$CH_3 - \ddot{N}H_2 + CH_3 - Br \longrightarrow CH_3 - \ddot{N}H - CH_3 + HBr$$

Methylamine
(I-amine)

$$CH_3 - \ddot{N}H - CH_3 + CH_3 - Br \longrightarrow CH_3 - \ddot{N} - CH_3 + HBr$$

$$CH_3 - \ddot{N} - CH_3 + CH_3 - Br \longrightarrow \begin{bmatrix} CH_3 & \\ \\ CH_3 & \\ \end{bmatrix} \xrightarrow{CH_3 - N - CH_3} \xrightarrow{Br}$$

Tatramthyl ammonium bromide

Quarternary ammonium halides are converted into their corresponding hydroxides on treatment with moist oxide or methanolic KOH.

$$[R, N]$$
 $X + AgOH \longrightarrow [R, N] OH + AgX \downarrow$

When a quaternary ammonium hydroxide is heated strongly, it decomposes to yield water, a tertiary amine and an alkene. For example Trimethyl-n-propylammonium hydroxide yields trimethylamine and propylene.

$$\begin{bmatrix} CH_{3} \\ CH_{3} - CH_{2} - CH_{3} - CH_{4} - CH_{5} \end{bmatrix} OH^{-} \xrightarrow{\Delta} CH_{3} - CH_{3} - CH_{4} - CH_{5} + H_{4}O$$

$$CH_{3} - CH_{5} - CH_{$$

The reaction is called Hafmann elimination reaction.

Reaction with Grignard reagent: Since primary and secondary amines have active hydrogen, they on reaction with Grignard reagent give alkanes

$$RNH_2 + CH_3MgBr \xrightarrow{\text{ether}} CH_4 + RNH.MgBr$$

 $R_2NH + CH_3MgBr \xrightarrow{\text{ether}} CH_4 + R_2N.Mg Br$

Note: Tertiary do not react because of absence of active hydrogen.

Reaction with Aldehydes and Ketone:

$$RNH_2 + CH_3CHO \longrightarrow RN = CHCH_3 + H_2O$$

(schiff's base or anil's base)

Acylation: 1° and 2° amines react with acetyl chloride or acetic anhydride to form acetyl derivatives.

$$R-NH_2 + CH_3COCI \longrightarrow RNHCOCH_3 + HCI$$

 $R-NH_2 + (CH_3CO)_2O \longrightarrow RNHCOCH_3 + CH_3COOH$
 $(CH_3)_2NH + CH_3COCI \longrightarrow (CH_3)_2N - COCH_3 + HCI$

- Note: (a) Tertiary amines donot undergo this reaction because of absence of replacable H- atom.
 - (b) When Benzoyl chloride is used in place of acetyl chloride reaction is called 'Schotten Baumann' reaction.

Oxidation: All three are oxidised in different ways depending upon conditions of oxidation.

(a) Primary Amine : Oxidised to aldehydes and ketones.

$$RCH_2NH_2 \xrightarrow{[O]} R-CH = NH \xrightarrow{H_2O} R-CHO + NH_3$$

$$aldimine \qquad aldehyde$$
 $R_2CHNH_2 \xrightarrow{[O]} R_2C = NH \xrightarrow{H_2O} R_2C = O + NH_3$

$$ketimine \qquad ketone$$

(b) Secondary Amine :

$$2R_2NH \xrightarrow{[0]} R_2N-NR_2$$

(tetra-alkyl hydrazine)

 $R_2NH \xrightarrow{caro's acid} R_2N-OH$

(dialkyl hydroxylamine)

(c) Tertiary Amine: Resistant to KMnO₄ but oxidised by neutral and aqueous H₂O₂ in cold to form trialkyl amine oxide.

Salt formation: Amine forms salt with mineral acids

$$\begin{array}{ccc} RNH_2 & \xrightarrow{_{+}HCI} & [RNH_3] + CI^- \\ R_2NH + HCI & \longrightarrow & [R_2NH_2] + CI^- \\ R_3N + HCI & \longrightarrow & [R_3NH] + CI^- \end{array}$$

These salts may undergo dealkylation at higher temp.

For example:
$$C_2H_5NH_3^+Cl^-\xrightarrow{\Delta} C_2H_5Cl + NH_3$$

Reaction with HNO₂: This reaction distinguishes 1°, 2° and 3° alcohols.

(a) Primary Amine: Except methyl amine, reaction happens at ordinary temp. to evolve N₂ Gas. CH₃CH₂NH₂ + HNO₂ → CH₃CH₂OH + N₂ + H₂O

Methylamine reacts in different way:

$$CH_3NH_2 + 2HNO_2$$
 $\longrightarrow CH_3-O-N = O + N_2 + H_2O$
 $methyl nitrite$
 $2CH_3NH_2 + 2HNO_2$ $\longrightarrow CH_3-O-CH_3 + 2N_2 + 3H_2O$
 $dimethyl ether$

(b) Secondary Amine: Form nitroso amines with HNO₂ (No N₂ gas is evolved)
R₂NH + HNO₂ → R₂ − N − N = O + H₂O
(yellow)

Note: These nitroso amines formed, on warming with phenol and conc. H₂SO₄ give a brown or red colour changing to blue or green on further addition of an alkali, colour changes to red. This test is called Libermann's nitroso test and used for identification of 2° amines.

(c) Tertiary Amine: These are inert to HNO₂ but being basic in nature forms salts with it.

$$(CH_3)_3N + HNO_2 \longrightarrow (CH_3)_3NHNO_2$$

Reaction with water: Amine gives alkyl ammonium hydroxides which dissociate into ions-RNH₂ +H₂O RNH₃OH RNH₃++ OH

Isocyanide test or Carbylamine reaction:

Primary amines when heated with chloroform and ethanolic KOH solution, alkyl isocyanides is produced which have characteristic foul smell. This reaction is characteristic to the primary amine. This test is known as carbyl amine test or isocyanide test.

$$RNH_2 + CHCl_3 + 3KOH \longrightarrow RNC + 3KCl + 3H_2O$$

Mechanisms

The reaction proceeds via the formation of dichloro carbene (:CCl₂).

(I)
$$OH + H - C - CI \longrightarrow H,O + C - CI \longrightarrow CCI,$$

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(II)
$$R - NH_2 + DC$$
 (Electron deficient species) $\longrightarrow Vacant \ orbital$

$$R - NH_2 - CCI \longrightarrow R - NH - CC - CI + CI$$

$$R - NH = CC - CI$$

$$R - NH = CC - CI$$

$$R - NH = CC - CI$$

Reaction with Hinsberg reagent: This is a method for separation of 1°, 2° and 3° amines Hinsberg Reagent is

$$C_6H_5$$
-SO₂-Cl. (Benzene sulphonyl chloride)
 $RNH_2 + Cl - SO_2$ - $C_6H_5 \longrightarrow R$ -NH-SO₂- $C_6H_5 + HCl$

(a) Primary amines form N-Alkyl benzene sulphonamide

(b) Secondary amines form N, N-dialkyl benzene sulphonamide

(c) Tertiary amines do not react because they do not possess a replacable Hydrogen atom.

Hofmann Mustard oil reaction: A 1° amine reacts with CS₂ and then with HgCl₂ to form iso thiocyanate having pungent smell of mustard oil.

$$2RNH_2 + S = C = S \longrightarrow S = C \stackrel{NHR}{\underset{SH}{\longleftarrow}} R - N = C = S + RNH_2 + HgS + 2HCI$$
alkyl isothiocyanate

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Reaction with Nitrosyl chloride (TILDEN'S REAGENT)

$$R-NH_2 + NOCI \longrightarrow R-CI + N_2 + H_2O$$

Reaction with Caro's acid [H,SO5]:

With caro's acid, the oxidation products of primary amine are also dependent on the nature of the alkyl group present in the amine.

RCH₂NH₂
$$\xrightarrow{[o]}$$
 RCH₂NHOH + RCH = NOH + R - C $\xrightarrow{\text{OH}}$ NOH

(N-alkyl (aldoxime) (hydroxamic acid) hydroxyl amine)

R₂CHNH₂ $\xrightarrow{[o]}$ R₂C = NOH (ketoxime)

R₃CNH₂ $\xrightarrow{[o]}$ R₃CNO (nitrosoalkane)

SEPARATION OF MIXTURES OF AMINES

Hinsberg method

This involves the treatment of the mixture with benzene sulphonyl chloride (Hinsberg Reagent) and KOH.

(a) The primary amine forms N-alkyl benzene sulphonamide which forms a salt with KOH, which is soluble in water.

- (b) The secondary amine gives N, N- dialkyl benzene sulphonamide which is insoluble in KOH solution
- (c) The tertiary amine does not react at all.

Hofmann method: This involves the treatment of the mixture with diethyl oxalate.

- (a) The primary amine forms a dialkyloxamide, which is a solid
- (b) The secondary amine forms a dialkyl oxamic ester, which is an oily liquid.
- (c) The tertiary amine does not react at all.

Fractional distillation: The mixture of primary, secondary and tertiary amines, may be separated by fractional distillation because their B.P's. are quite different. This method is extensively used in industry.

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Nitrens:
$$\left(R - \stackrel{..}{N}\right)$$

These are defined as 'the electron deficient species in which nitrogen has a sextet of electrons' (six electrons in the outermost shell). They are highly reactive and act as strong electrophiles as they need a pair of electrons to complete the octet. The parent species is \ddot{N} -H, known as nitrene or imidogene or azene or imine.

- (1) The nitrogen analogs of carbenes are called nitrenes.
- (2) There is posibility of two spin states for nitrenes depending on whether the two non-bonding electrons (the normal nitrogen lone pair remains paired) have their spins paired or parallel.

$$R - N$$
 These two are lone pair of electrons

These two may be paired or unpaired

(3) In general nitrenes obey Hunds rule and are ground state triplet with two degenerate sp-orbitals containing a single electron each.

sp-Triplet nitrene

Preparation of nitrene: The simplest nitrene (NH) is formed when hydrozoic acid (N₃H) is irradiated with UV liquid in aromatic solvent.

Reactions - Nitrene are highly reactive unstable compound and give the following

Addition to alkenes: Nitrenes add on alkenes to form corresponding alkeneimine, a cyclic product.

$$CH_3CH = CH_2 + H - N \longrightarrow CH_3 - CH - CH - CH_2$$
Propene Nitrene
$$H$$
Propeneimine

Addition to alkanes: Acetyl nitrene reacts with isobutane to form acetyl tert, butylamine.

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Also photolysis of phenyl nitrene (on dimerization) forms azobenzene.

$$2C_6H_5 - N \xrightarrow{\text{Light}} C_6H_5 - N = N - C_6H_5$$
Phenyl nitrene Azobenzene

Applications: Nitrene have important synthetic applications particularly acyl nitrene (R - C - N), has been proposed as possible intermediate in the Hofmann, Curtius and Lossen rearrangements.

Name of Reaction	Reactant	Reagent	Intermediate	Product
Hofmann bromamide	Amide	Br ₂ /KOH	R-N=C=O	R-NH ₂
Schmidt Reaction	Carboxylic acid	N₃H/H ⁺	R-N=C=O	R-NH ₂
Lossen Rearrangement	Oxamic acid & Oxamic Ester	H ⁺ or OH [−]	R-N=C=O	R-NH ₂
Curtius Rearrangement	Acyl chloride	NaN ₃	R - N = C = O	R-NH ₂

The beckmann Rearrangement

The acid catalysed conversion of ketoximes to N-substituted amides is called Beckmann rearrangement. Acid catalysts used are proton acids (H₂SO₄, HCl, H₃PO₄) and Lewis acids (PCl₅, SOCl₂, PhSO₂Cl, RCOCl, SO₃, BF₃ etc.)

$$C_bH_5 - C_c - CH_5 \xrightarrow{(i) PCI_c} CH_3 - C_c - NH - C_bH_5$$

 $N - OH$

$$C_{e}H_{5}$$
 $C = N$
 OH
 H
 $CH_{3} - C - NH - C_{e}H_{5}$

Mechanism

$$C_{e}H_{s}$$

$$CH_{s} = N$$

$$CH_{s} = C = N - C_{s}H_{s}$$

$$CH_{s} = C - NH - C_{s}H_{s}$$

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Fritsch Reaction:

Monohalogen derivatives of alkene in presence of strong base give the product containing carboncarbon ≡ bond & known as Fritsch reaction.

$$C = C$$

$$CH_3$$

$$C = C$$

$$H$$

$$Or LDA$$

$$CH_3 - C = C - Ph$$

Note: LDA is a very strong base.



Mechanisms

CYANIDES, ISOCYANIDES, ALKYL NITRITES AND NITRO ALKANES

General Characteristics

- (a) Compounds having the formula RCN are called alkyl cyanides or as nitriles of the acid which they produce on hydrolysis.
- (b) According to IUPAC system, cyanides are named as alkane nitriles, i.e., in the name of parent hydrocarbon 'nitrile' is suffixed. In naming the hydrocarbon part, carbon of the — CN group is also counted.

Formula	As cyanide	IUPAC name	
CH ₃ CN	Methyl cyanide	Ethane nitrile	
C ₂ H ₅ CN	Ethyl cyanide	Propane nitrile	
C ₃ H ₇ CN	Propyl cyanide	Butane nitrile	
C ₄ H ₉ CN	Butyl cyanide	Pentane nitrile	

(c) The compounds having the formula RNC are called isocyanide or isonitriles. The nomenclature of isocyanides is similar to cyanides.

Formula	As isocyanides (Common name)	IUPAC names
CH ₃ NC	Methyl isocyanide	Methylcarbylamine
*	(Methyl isonitrile)	(Carbylamino methane)
C ₂ H ₅ NC	Ethyl isocyanide	Ethyl carbylamine
	(Ethyl isonitrile)	(Carbylamino ethane)
C ₃ H ₇ NC	Propyl isocyanide	Propyl carbylamine
	(Propyl isonitrile)	(Carbylamino propane)

(d) Isocyanides are also named as alkane isonitrile.

CH₃NC Methane isonitrile C₂H₅NC Ethane isonitrile C₃H₇NC Propane isonitrile

(e) Hydrogen cyanide is known to exist as a tautomeric mixture. (Diad forms)

$$H - C \equiv N \Longrightarrow H - N \Longrightarrow C$$

Hence, it forms two types of alkyl derivatives which are known as alkyl cyanides and alkyl isocyanides.

 $R - C \equiv N$ $R - N \Longrightarrow C$ Alkyl cyanide Alkyl isocyanide

ALKYL CYANIDES

Methods of Preparation

(i) From alkyl halides: The alkyl cyanides are prepared by refluxing an alcoholic solution of an alkyl halide with potassium cyanide. The disadvantage of this method is that a mixture of nitrile and isonitrile is formed.

RX + KCN (or NaCN) → RCN + RNC
Alkyl halide Nitrile Isonitrile
(Major product) (Minor product)

(ii) From Grignard reagent: Grignard reagent reacts with cyanogen chloride to form alkyl cyanides.

RMgX + CICN \rightarrow RCN + Mg $\stackrel{\times}{\sim}$ CI Grignard Alkyl Cyanide

reagent

 CH_3MgBr + CICN \rightarrow CH_3CN + Mg < CI

Methyl Cyanogen Methylcyanide magnesium chloride

bromide

(iii) From acid amides: Pure nitriles are obtained by dehydration of acid amides with phosphorus pentoxide. Amides are distilled with phosphorus pentoxide, P₂O₅.

 $RCONH_2 \xrightarrow{P_2O_5} RCN$

CH₃CONH₂ P₂O₅ CH₃CN + H₂O Acetamide Methyl evanide

Industrially, alkyl cyanides are prepared by passing a mixture of carboxylic acid and ammonia over alumina at 500°C.

(iv) From primary amines: Primary amines are dehydrogenated when passed over copper or nickel at high temperature to form alkyl cyanides. This is also a commercial method.

$$RCH_2NH_2 \xrightarrow{Cu \text{ or } Ni} RCN + 2H_2$$

Primary amine

Methyl cyanide Ethylamine

From oximes: Aldoximes are converted into alkyl cyanides when distilled with phosphorus (v) pentoxide or acetic anhydride. The dehydration of aldoximes occurs.

$$\begin{array}{c} H \\ R - C = NOH \xrightarrow{P_2O_5} R - CN + H_2O \end{array}$$
Alkyl cyanid

PHYSICAL PROPERTIES

- Lower members containing upto 15 carbon atoms are liquids, while higher members of carbon atoms in (a) the molecule.
- Alkyl cyanides are neutral substances with pleasant odour, similar to bitter almonds. (b)
- They are soluble in water. The solubility decreases with the increase in number of carbon atoms in the (c) molecule are solid.
- They are soluble in organic solvents. (d)
- They are poisonous but less poisonous than HCN. (e)

CHEMICAL PROPERTIES

(i) Reaction with Grignard reagent: With Grignard's reagent, an alkyl cyanide forms a ketone which further reacts to form a tertiary alcohol.

$$R-C \equiv N + R'MgX \rightarrow R - \stackrel{R'}{C} = NMgX \xrightarrow{2H_2O} R - \stackrel{R'}{C} = O + NH_3 + Mg \xrightarrow{OH}_X$$

$$R-\stackrel{R'}{C} = O + R''MgX \rightarrow R - \stackrel{R'}{C} - OMgX \xrightarrow{H_2O} R - \stackrel{R'}{C} - OH + Mg \xrightarrow{OH}_X$$

Tertiary alcohol

Reduction: When reduced with hydrogen in presence of Pt or Ni, or LiAlH4 (Lithium aluminium (ii) hydride) or sodium and alcohol, alkyl cyanides yield primary amines.

However, when a solution of alkyl cyanides in ether is reduced with stannous chloride and hydrochloric acid and then steam distilled, an aldehyde is formed (Stephen's reaction).

$$R - C \equiv N \xrightarrow{\frac{SnCl_2/HCl}{[2H]}} RCH = NH.HCl \xrightarrow{H_2O} RCHO + NH_4Cl$$
Aldehyde

(iii) Hydrolysis: Alkyl cyanides are hydrolysed by both acid and alkalies. On partial hydrolysis amides are formed while on complete hydrolysis acids are obtained.

RCN
$$\xrightarrow{H_2O}$$
 RCONH₂ $\xrightarrow{H_2O}$ RCOOH + NH₃

Alkyl cyanide Amide Acid

CH₃CN $\xrightarrow{H_2O}$ CH₃CONH₂ $\xrightarrow{H_2O}$ CH₃COOH + NH₃

Methyl cyanide Acetamide Acetic aci

(iv) Alcoholysis: When an alkyl cyanide is refluxed with an anhydrous alcohol in presence of dry HCl, an imido ester is formed, which on hydrolysis with water forms ester.

$$RCN + R'OH + HCI \rightarrow \begin{bmatrix} \dot{N}H_2 \\ II \\ R-C-OR' \end{bmatrix} CI \xrightarrow{H_2O} RCOOR' + \dot{N}H_2CI$$
Ester

Uses: Alkyl cyanides are important intermediates in the laboratory synthesis of a large number of compounds like acids, amides, ester, amines, etc.

ALKYL ISOCYANIDES

Methods of Preparation

(i) From alkyl halides: The isocyanides are prepared by refluxing an alkyl halide solution in alcohol with silver cyanide. The isonitrile is the main product but small amount of nitrile is also formed.

$$R - X + AgCN \longrightarrow RNC + RCN$$
Alkyl halide Isocyanide Cyanide
(Isonitrile) (Nitrile)

Main product Minor product

 $CH_3CI + AgCN \longrightarrow CH_3NC + CH_3CN$

Methyl chloride Methyl isocyanide
(Main product)

This method is, thus, suitable for preparing isocyanides.

(ii) From Primary Amines: (Carbylamine reaction): Alkyl isocyanides may be prepared by heating primary amines with chloroform and alcoholic potash.

(iii) From N-alkyl formamides: N-alkyl formamides when dehydrated with POCl₃ in presence of pyridine give isocyanides.

$$R - NH - \stackrel{O}{C} - H \xrightarrow{POCl_3} R - N \equiv C$$
N-alkyl formamide Isocyanide

PHYSICAL PROPERTIES

- (a) Alkyl isocyanides are colourless, unpleasant smelling liquids.
- (b) They are insoluble in water but freely soluble in organic solvents.
- (c) The boiling points of isonitiriles are lower than corresponding alkyl cyanides.
- (d) Isonitriles are much more poisonous than isomeric cyanides.

CHEMICAL PROPERTIES

 Hydrolysis: Alkyl isocyanides are hydrolysed by dilute mineral acids (but not by alkalies) to form primary amines.

RN
$$\rightleftharpoons$$
C + 2H₂O $\xrightarrow{H^+}$ RNH₂ + HCOOH
Alkyl isocyanide Primary amine Formic acid

(ii) Reduction: When reduced with nascent hydrogen or hydrogen in presence of nickel, isocyanides form secondary amines containing methyl as one of the alkyl groups.

$$R - N \equiv C + 4H \longrightarrow RNHCH_3$$
Alkyl isocyanide Secondary amine

(iii) Action of heat: When heated for sometime at 250°C, a small amount of isonitrile changes into isomeric nitrile.

(iv) Addition reaction: Alkyl isocyanide give addition reactions due to presence of unshared electron pair on carbon atom.

$$R:N:::C: or R - \overset{+}{N} \equiv \overset{-}{C}$$

The following are some of the addition reactions shown by alkyl isocyanides.

Distinction between Ethyl Cyanide and Ethyl Isocyanide

S.No.	Test	Ethyl Cyanide (C ₂ H ₅ CN)	Ethyl isocyanide (C2H5NC)
1	Odour	Not unpleasant	Extremely unpleasant
2	Solublity in water	Soluble	Insoluble
3	Hydrolysis	Yields propionic acid	Produces ethyl amine
4	Reduction	Gives propylamine (Primary amine)	Gives ethylmethylamine (Secondary amine)
5	Heating at 250°C	No effect	Changes to ethyl cyanide