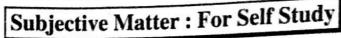
Compounds Containing Nitrogen





Introduction

Derivatives of ammonia obtained by replacing one or more hydrogen atoms by same number of alkyl or aryl groups are called amines.

Mono, di and tri alkyl derivatives of ammonia are respectively primary, secondary and tertiary amines

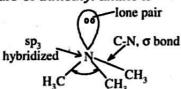
$$\begin{array}{c} NH_{3} \xrightarrow{+R} R-NH_{2} \xrightarrow{+R} R_{2}-NH \xrightarrow{+R} R_{3}-N \\ \text{p-a min e } \text{(A min o)} \text{(Nitrilo)} \end{array}$$

- Classification :
- On the basis of number of alkyl groups attached to nitrogen atom, amines are classified into:
- a) Primary amines: These are monoalkyl derivatives of ammonia. These contain NH₂ Amino group
 - e.g. C₂H₅-NH₂-Ethyl amine
- b) Secondary amines: These are dialkyl derivatives of ammonia. These contain NH– Amino group
 - e.g. CH₃-NH-CH₃ CH₃-NH-C₂H₅
 Dimethyl amine Ethyl methyl amine
 - c) Tertiary amines: These are trialkyl derivatives of ammonia. These contain -N= Amino group.

eg.
$$CH_3$$
 CH_3 CH_3 $CH_3 - N - C_2H_5$

Trimethyl amine Ethyl dimethyl amine

- Structure of amines:
- > N atoms in amine is sp3-hybridized.
- ➤ Three sp³-orbitals contain one electron each, form sigma bonds either with H-atoms or the alkyl or aryl groups while the fourth one contains a lone pair of electrons is not involved in bond formation.
- > The structure of trimethyl amine is



- As lone-pair-bond pair repulsions are much greater than bond pair-bond pair repulsion, therefore the bond angle between any two adjacent H-atoms or alkyl groups decreases from the tetrahedral angle of 1090.28' to 1070 in 10 and 20 amines.
- ISOMERISM IN AMINES:
- > They show chain, position, functional, isomerism.

- Preparation of amines :
- (1) By Ammonolysis of alkyl halides [Hofmann's ammonolysis] :

$$\begin{array}{c} NH_{3} \xrightarrow{RX} R - NH_{2} \xrightarrow{RX} R_{2}NH \xrightarrow{RX} R_{3}N \xrightarrow{RX} R_{4}NX \\ C_{2}H_{5} - Br + NH_{3} \xrightarrow{\Delta} C_{2}H_{5} - NH_{2} + HB_{1} \\ \text{ethyl bromide} \end{array}$$

$$C_2H_5 - NH_2 + C_2H_5 - Br \xrightarrow{\Delta} (C_2H_5)_2 NH + HBr$$

diethylamine

$$(C_2H_5)_2NH + C_2H_5Br \xrightarrow{\Delta} (C_2H_5)_3N + HBr$$

triethylamine

$$(C_2H_5)_3N+C_2H_5Br \xrightarrow{\Delta} (C_2H_5)_4 \overset{*}{N}Br$$

tetraethylammonium bromide

• Limitations:

- (a) This method is not useful for preparation of primary amines because a mixture of primary, secondary and tertiary amines along with quaternary ammonium salt is obtained which is difficult to separate.
- But we can prepare primary amine as a major product if we heated alkyl halide with excess of alcoholic ammonia.
- (b) tert-Butylamine is not prepared by this reaction because tert alkyl halides gives alkene with alcoholic ammonia.

$$CH_{3} \xrightarrow{C} CH_{3} \xrightarrow{CH_{3}} CH_{3} \xrightarrow{C} CH_{2} + NH_{2}Br$$

$$CH_{3} \xrightarrow{C} CH_{3} + NH_{3} \xrightarrow{alcohol} CH_{3} - C = CH_{2} + NH_{2}Br$$

- (2) By reduction of amides, oximes, cyanides, alkylisocyanides and nitroalkanes :
- (a) From RCONH₂:

O

||

$$R-C-NH_2 \xrightarrow{i) \text{ LiAlH}_4/\text{diethylether}} R-CH_2 - NH_2$$

Amides

Amines

(b) With RCN:

RCN + 4H
$$\xrightarrow{Na/C_2H_5OH}$$
 RCH₂NH₂

CH₃-C \equiv N+2H₂ \xrightarrow{Nb} CH₃-CH₂-NH₂

Methyl cyanide Ethyl amine

CH₃-CH₂-C \equiv N + 4[H] $\xrightarrow{Na/alcohol}$ CH₃-CH₂-CH₂-NH₂

Ethyl cyanide n-Propyl amine

(c) Form alky isocyanides:



$$C_2H_5$$
-NC + 4[H] C_2H_5 OH/Na C_2H_5 NHCH₃

(d) Form Oximes:

H

$$R-C=N-OH+4[H]$$
 $R-C=N-OH+4[H]$
 $R-C=N-OH+4[H]$

Acetoxime

$$3Sn + 6HCl \rightarrow 3SnCl_2 + 6(H)$$

isopropylamine

$$R - NO_2 + 6(H) \xrightarrow{Sn/conc.HCl} R - NH_2 + 2H_2O$$

$$CH_3 - CH_2 - NO_2 + 6(H) \xrightarrow{Sn/conc.HCl} CH_3 - CH_2 - NH_2 + 2H_2O$$

nitroethane ethylamine

$$C_6H_5NO_2 \xrightarrow{Sn+HCI} C_6H_5NH_2 + H_2O$$

- > In lab method we use Sn/HCl while in industrial method we use Fe / HCl.
- (3) Gabriel Phthalimide Synthesis (Alkylation of Phthalimide):

Aromatic primary amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

By Hofmann's bromamide reaction (Hofmann's Hypobromite reaction) :

O

$$R - C - NH_2 + Br_2 + 4NaOH \rightarrow R - NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

Armide 1^0 armine

O

$$H_1 - C - NH_2 + Br_2 + 4NaOH \rightarrow CH_3 - NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

Acetamide Methylamine

Physical Properties:

- The lower aliphatic amines are colourless gases having characteristics fishy odour. Aryl amines are i. colourless liquids and toxic in nature.
- The 1^{0} amine having three or more carbon atoms are liquids and the higher ones are solids.
- iii. H-Bonding (weaker as compared to H-O-H).

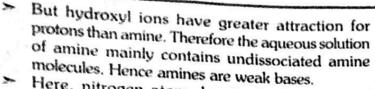
In 3° amine (due to absence of H-atom) Hbonding is not possible.

- (iv) Boiling point: Due to polar nature of amines, they can form hydrogen bonding and hence they have higher boiling point than corresponding moleculer weight of alkanes.
- Boiling point ∝ molecular weight
- > Order of B.P.: 1° amine > 2° amine > 3° amine
- > Order of volatile nature : 3° amine > 2° amine > 1º amine
- (v) Solubility: Low molecular weight amines (< six carbon) are very soluble in water. The water solubility of amines decreases with increasing size of alkyl group.

Order of solubility: p-amine > s-amine > t-amine

- Chemical Properties: Amines are reactive organic compounds due to presence of lone pair of electron with nitrogen
- 1. Basis nature of amines:
- (a) Lewis theory:
- They are basis in nature due to the presence of lone pair on nitrogen atom.
- Amines acts as a base, according to Lewis concept. the species which can donate the lone pair are called as Lewis base.
- Amines are weak bases: In aqueous solution of amines, following equilibrium exists.

$$R - NH_2 + H - O - H \rightarrow R - NH_3 + OH$$



Here, nitrogen atom donate the lone pair of electrons to H+ ion to formed a co-ordinate bond.

Amine also acts as Bronsted-Lowry base as it accepts a proton from acid to form salt.

Aqueous solution of amines are basic and they turn red litmus paper blue.

Amines forms alkyl ammonium hydroxide with water ammonium hydroxides are used for precipitation of IInd and IIIrd group cations in qualitative analysis

$$RNH_2 + H_2O \longrightarrow (RNH_3)OH$$

$$FeCl_3 + 3[RNH_3]OH \xrightarrow{\text{future explosion.com}} Fe(OH)_3 + 3[RNH_3]CI$$
Brown ppt

$$AlCl_3 + 3[RNH_3]OH \longrightarrow Al(OH)_3 + 3[RNH_3]Cl$$
White ppt.

$$CrCl_3 + 3[RNH_3]OH \longrightarrow Cr(OH)_3 + 3[RNH_3]CI$$
Green ppt.

(b) Neutralisation with acids :

$$\begin{array}{lll} C_2H_5-NH_2+HCl\rightarrow [C_2H_5N^+H_3]Cl^-\\ & \text{Ethyl amine} & \text{Ethyl ammonium chloride}\\ (C_2H_5)_2\,NH & +HCl\rightarrow [(C_2H_5)_2\,N^+\,H_2]Cl^-\\ & \text{Diethyl amine} & \text{Diethyl ammonium chloride}\\ (C_2H_5)_3\,N & +HCl\rightarrow [(C_2H_5)_3\,N^+\,H\,]\,Cl^-\\ & \text{Triethyl amine} & \text{Triethyl ammonium chloride}\\ C_2H_5NH_2 & +HNO_3\rightarrow [C_2H_5NH_3]^+\,\overline{N}O_3\\ & \text{Ethyl amine} & \text{Ethyl ammonium mitrate}\\ (C_2H_5)_2NH & +H_2SO_4\rightarrow [C_2H_5\,NH_2\,]_2\,SO_4^{-2}\\ & \text{Diethylamine} & \text{Diethylamine} \end{array}$$

 $(C_2H_5)_3N+CH_3COOH \rightarrow [(C_2H_5)_3\stackrel{+}{NH}]CH_3COO^-$ Triethylamine Triethylamine acetate

• Relative basic strenght of amines:

Due to +I effect of alkyl groups the electron density on nitrogen increases and the lone pair of electrons becomes readily available for protonation.

The alkyl ammonium ion gets stabilized due to the dispersal of positive charge by the +l effect of alkyl group. Thus aliphatic amines are stronger base than ammonia.

 Basic strength of amines depends on electron donating tendency.

Order of basic strength: (CH₃)₂NH > CH₃ NH₂ > (CH₃)₃ N > NH₃ $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$ (A) More basic nature of secondary amines then tertiary amine is due to

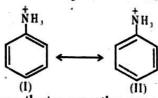
tertiary animes.

(i) Steric hindrance: In case of tertiary amines due to more +I effect lone pair is easily available for donation, but due to more steric hindrence there path is blocked. At the same time tertiary amines show less solvation effect.

(B) Aromatic amines are less basic then aliphatic amines: The lone pair of electron present on N- atom in aromatic amines is involved in resonance hence it less available for donation and they becomes less basic.

> Resonance in aniline.

At the same time if aniline accept a proton it gives anilinium ion has only two resonance structure.



As, we know that more the resonating structure more is the stability. Thus aniline is more stable than anilinium ion.

Hence, aniline or any aryl amine accept proton less radily i.e. they are less basic in nature than ammonium.

In case of substituted aniline, electron releasing group like −OCH₃, −CH₃, −NH₂ increase the basic strength whereas electron withdrawing groups like −NO₂, −C₆H₅, −SO₃, −COOH, −CN, −X decreases the basic strength.

The basic order: Pyridine > Aniline > Pyrider N-methylethanamine > propan-1-amine > aniline Ammonia > benzene-1, 4-diamine > 4-aminobenzoic acid phenylmethylamine > N-Methylaniline > N-phenylaniline

(2) Reaction with HNO₂: Primary, secondary and tertiary amines react differently with nitrous acid and form different visible products hence it is used to distinguish between them.

a. Primary amines :

$$\begin{array}{c} R-NH_2+HO-N=O \xrightarrow{NaNO_2+dil.HCl} R-OH+H_2O+N_2 \\ \hline Primary amine & Primary alcohol \\ \hline C_2H_5-NH_2+HO-N=O \xrightarrow{NaNO_2+dil.HCl} C_2H_5-OH+H_2O+N_2 \\ \hline etyhylamine & ethylalcohol \\ \hline \end{array}$$



N 2 C1futureexplosion.com +NaNO, +2HC1-273-278k O + NaC1 + 2H,0 Diazonium salts

b. Secondary amines :

$$R_1 = NH + HO - N = O \xrightarrow{NaNO_2 + HC1} R_2N - N = O + H_2O$$

$$(C,H_s)$$
 NH + HO - N = O $\xrightarrow{\text{NaNO}_2 + \text{HCI}}$ $(C_2H_5)_2$ N - N = O + H_2 O N - nitroso diethylamine $(C_1,-N-H)$ $(C_2,-N-N) = 0$

$$CH, -N-H$$

$$CH, -N-N=0$$

$$+ HO-N=0 \xrightarrow{SaNO_1+HC_1} O + H_0$$

$$N-aitroso N-methylaniline$$

c. Tertiary amines :

$$R_3N + HNO_2 \xrightarrow{NaNO_2 + HC1} [R_3NH]^+ NO_2^-$$

$$(C_2H_5)_3N + HNO_2 \xrightarrow{NaNO_2 + HCI} [(C_2H_5)_3NH]^{\dagger}NO_2^{-}$$

$$(CH_3)_2N - \bigcirc + HO - N = 0$$

N. N-Dimethylaniline

$$\frac{NaNO_{2} + HC1}{273 - 278K} (CH_{3})_{2} N - N = O + H_{2}O$$

4-Nitroso-N, N-dimethylaniline

(3) Acetylation:

$$RNH_2 + CICOCH_3 \longrightarrow RNHCOCH_3 + HCl$$
(N-alkyl acetamide)

(Acetanilide)

O

O

$$C_2H_4NH_2 + Cl - C - C_6H_5 \xrightarrow{Pyridine} C_2H_5NH - C - C_6H_5 + HCl$$

N - Ethylbenzamide

Tertiary amine does not undergo acetylation.

$$(C_2H_3)_3N + CH_3 - C - C1 \xrightarrow{Pyriding} No reaction$$
Triethyl amine

- (4) Reaction with alkyl halides (Hoffmann's exhaustive alkylation.): The replacement of hydrogen from nitrogen atom of amines by alkyl group to form quaternary ammonium salts is called exhaustive alkylation of amines.
- When primary amine on heating with primary alkyl halide, it gives a mixture of secondary amine, tertiary amine along with tertraalkylammonium halide.

$$RNH_2 + R - X \xrightarrow{-HX} R_2NH \xrightarrow{RX}$$

$$R_3N \xrightarrow{RX} R_4NX$$

$$CHSI + CCH + NIH$$

$$CH_3 - NH_2 + I - CH_3 \xrightarrow{CH3I} (CH_3)_2NH$$

Methyl amine Dimethyl amine

 $\xrightarrow{\text{CH3I}}$ (CH₃)₃N + HI $\xrightarrow{\text{CH3I}}$ [(CH₃)₄N⁺] I⁻ Tetramethyl ammonium iodide Trimethyl amine

(5) Benzoylation (Schotten baumann reaction):

(6) Carbylamine Reaction (Iso cyanide test):

$$R-NH_2 + CHCl_3 + 3 KOH \longrightarrow R-N \equiv C + 3KCl + 3H_2O$$

$$C_2H_5 - NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} C_2H_5 - NC + 3KCl + 3H_2O$$

ethylamine chloroform Ethylisocyanide

$$C_6H_5 - NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} C_6H_5 - NC + 3KCl + 3H_2O$$
Aniline chloroform Phenyl isocyanide

Hoffmann elimination reaction: (7)

$$C_2H_5 - N(CH_3)_3I^- + AgOH \xrightarrow{AgOH/H_2O} C_2H_5 - N(CH_3)_3OH^- + AgI$$

$$C_2H_5 - N(CH_3)_3OH^- \xrightarrow{\Delta} CH_2 = CH_2 + (CH_3)_3N + H_2O$$

Ethylene

In this reaction the major product is least substituted alkene.

- (8) Reaction With Aryl Sulphonyl Chloride: Hinsberg's test: It is used to distinguish primary. secondary and tertiary amines by using benzene sulphonyl chloride i.e. C₆H₅SO₂Cl (Hinsberg's reagent).
- a. Primary amine:

$$R - NH_{2} + C_{6}H_{5}SO_{2}CI \xrightarrow{OH^{-}} C_{6}H_{5}SO_{2}NHR$$

$$\xrightarrow{KOH} C_{6}H_{5}SO_{2}N^{-}RK^{+} \xrightarrow{H^{+}} C_{6}H_{5}SO_{2}NHR$$

$$O \longrightarrow \begin{cases} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{cases}$$

$$O \longrightarrow \begin{cases} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{cases}$$

$$O \longrightarrow \begin{cases} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{cases}$$

Benzene sulphonyl chloride N-ethylbenzenesulphonyl amide

b. Secondary amines :

$$R_2NH + C_6H_5SO_2C1 \xrightarrow{GH} C_9H_5SO_2NR_2 \xrightarrow{H^2/OH}$$
 no reaction insoluble

CHEMISTRY - II /



N, N-diethylbenzenesulphonyl amide

Tertiary amines :

$$R_1N+C_6H_5SO_2CI \longrightarrow C_6H_5SO_7\hat{N}R_7CI \xrightarrow{GH} C_6H_5SO_7+R_7N+CI$$

$$(C_2H_3)_{j}N+C_5H_5SO_{j}CI\longrightarrow C_4H_5SO_{j}N(C_2H_3)_{j}CI \xrightarrow{\otimes g} C_6H_5SO_{j}+\{C_2H_3\}_{j}N+CI$$

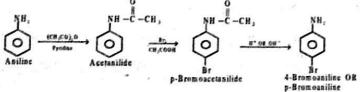
(9) Aromatic Electrophilic Substitution :-NH2 group in aniline is activating ortho-para directing group hence it undergo electrophilic substitution reactions.

(a) Bromination:

2,4,6-Tribromoaniline

o-and p-Bromoaniline

Formation of monobromo aniline: To prepare monobromo derivatives -NH2 group is deactivatetd by acetyl group.



(b) Nitration:

In strong acidic medium -NH2 group is converting to -NH3+ group which is acts as a meta directing and hence m-nitroantline is also obtained.

$$\begin{array}{c|c}
NH_2 & NH_2 \\
\hline
O & H_2SO_4 \\
\hline
HNO_1 & O \\
\hline
O & H_2SO_4
\end{array}$$

$$\begin{array}{c}
NH_2 \\
+NO_2 \\
\hline
O \\
NO_2
\end{array}$$

$$\begin{array}{c}
NH_2 \\
\hline
O \\
NO_2
\end{array}$$

Formation of paranitro aniline:

(c) Sulphonation:

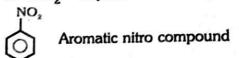
Sulphanilic acid exists as a salt, called dipolar ion or Zwitter ion. This is due to reaction between acidic.

Catalytic hydrogenation: (17)

Aniline is used in the Uses of Aniline manufacture of dyes, accelerators, antioxidants. acetanilide, indigo and sulpha drugs.

Nitro Compounds:

R-NO₂ Aliphatic nitro compound



$$CH_3$$
 NO_2
 $CH_3 - C - NO_2$
 $CH_3 - CH - CH_3$
 CH_3
 CH_3
 CH_3
 CH_3
 CH_3
 CH_3
 CH_3
 CH_3
 CH_3

CH₃ - CH - CH₂ - NO₂ 2 - Methyl - 1 - nitropropane **Isomerism**: Nitroalkanes shows chain, position functional isomerism and Tautomerism.

Preparation of nitroalkanes:

1. By Nitration of alkanes:

$$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}_3 & \xrightarrow{\text{F HNO}_3} & \text{CH}_3\text{CH}_2\text{CH}_2\text{NO}_2 + \\ \text{CH}_3\text{-CH--CH}_3 & + & \text{CH}_3\text{CH}_2\text{NO}_2 + & \text{CH}_3\text{NO}_2 \\ \text{NO}_2 & & \text{NO}_2 \end{array}$$

The hydrocarbon is heated with conc. HNO3 under pressure at 413 K. Nitration under these conditions is always slow and a large number of polynitro compounds are formed.

2. From alkyl halides:

$$R - X + AgNO_2 \longrightarrow R - NO_2 + AgX$$

 $R - Br + NaNO_2 \rightarrow R - NO_2 + NaBr$

$$\begin{array}{c} CH_3 - CH_3 + HO - NO_2 \xrightarrow{423K-698K} CH_3 - CH_2 - NO_2 + H_2O \\ Ethane & conc. \end{array}$$
 Nitroethane



$$CH_1 - CH_2 - Br + NaNO_2 \xrightarrow{DMSO} CH_1 - CH_2 - NO_2 + NaBr$$
 $CH_1 - CH_2 - Br + NaNO_3 \xrightarrow{DMSO} CH_1 - CH_2 - NO_2 + NaBr$

Nitroethane

From salt of α-halogeno carboxylic acids :

O
$$CH_{2}-C-ONa + NaNO_{2}$$

$$\begin{array}{c}
O \\
-NaCl \\
O_{2}N-CH_{2}-C-ONa
\end{array}$$

$$\begin{array}{c}
O \\
-NaCl \\
O_{2}N-CH_{2}-C-ONa
\end{array}$$

$$\begin{array}{c}
H_{2}O \\
-NaCl \\
O_{2}N-CH_{2}-C-ONa
\end{array}$$
Nitromethane

$$CH_3$$
 $C = CH - NO_2 + H_2O \xrightarrow{H^4} CH_3 - NO_2 + CH_3 - C - CH_3$
 CH_3
 $C = CH - NO_2 + H_2O \xrightarrow{H^4} CH_3 - NO_2 + CH_3 - C - CH_3$

Nitromethane

By oxidation of primary amines :

$$\begin{array}{c} R & R \\ | & CH_3 \\ |$$

From α-nitroalkenes:

$$CH_3$$

$$CH_3$$

$$CH_1 - C = CH - NO_2 + H_2O \xrightarrow{H^*} CH_3 - NO_2 + CH_3 - C = O$$

$$CH_3 - CH_3 - NO_2 + CH_3 - C = O$$
Nitromethane

By oxidation of oximes:

$$\begin{array}{c|c} H & \\ R-C=N-OH+[O] & \\ \hline \\ R-C=N^+-OH & \\ \hline \\ R-C=N^+-OH & \\ \hline \\ R-C=N^+-OH+[O] & \\ \hline \\ R-C=N-OH+[O] & \\ \hline \\ R-C=N^+-OH & \\ \hline \\ R-C=N^+-OH & \\ \hline \\ R-C=N^+-OH & \\ \hline \end{array}$$

Chemical properties:

Acidic Nature: Primary and secondary nitroalkanes undergo tautomerism and their aciforms are weakly acidic in nature.

$$H$$
 CH_2-N
 O
 CH_2-N
 O
 CH_2-N
 O

The primary and secondary nitroalkanes behave as acids in the presence of strong alkalies.

Reduction: Nitro alkanes can be reduced as

 $R-NO_2 \longrightarrow R-NO \longrightarrow R-NHOH \longrightarrow R-NH_2$ Nature of final product depends on nature of reduction medium and reducing agent.

(a) Reduction in acidic medium:

R - NO₂ + 6[H]
$$\xrightarrow{\text{Sn/conc. HCl.}}$$
 R - NH₂ + 2H₂O

CH₃CH₂NO₂ + 6H $\xrightarrow{\text{Sn+HCl or Zn+HCl or SnCl2+HCl or }}$

CH₃CH₂NH₂ + H₂O

(b) Reduction in neutral medium:

$$\begin{array}{c} R-NO_2+4[H] \xrightarrow{Z_B/NH_4Cl} R-NH-OH+H_2O \\ CH_3-CH_2-NO_2+4H \xrightarrow{Z_B/NH_4Cl \text{ or } CaCl_2} \\ CH_3-CH_2-NHOH \\ N-ethylhydroxylamine. \end{array}$$

> With stannous chloride and hydrochloric acid are used as reducing agent, nitroalkanes are converted into N-alkylhydroxylamine and oxime.

3. Hydrolysis:

R-CH₂-NO₂+H₂O
$$\xrightarrow{H^*}$$
R-C-OH+H₂N-OH

R
R
R
R
R
R
R
R
R
P
Tertiary nirtoalkanes does not undergo hydrolysis.

Tertiary nirtoalkanes does not undergo hydrolysis.

Primary and secondary nitroalkanes i.e. those containing α - hydrogen atom, exhibit tautomerism.

$$R - CH_2 - N + \longrightarrow R - CH = N$$

Isonitro form. (pseudo-acid form) (acid - form or nitronic acid)

4. Nef carbonyl synthesis:

This reaction is known as Nef carbonyl synthesis.

5. Halogenation:

$$\begin{array}{ccc} & & & & & Br \\ R - C - NO_2 + 2Br_2 + 2NaOH & \longrightarrow & R - C - NO_2 + 2NaBr + 2H_2O \\ & & & & Br \\ I^a \ Nitroalkanes & & Dibromo derivatives \end{array}$$



- 6. Action of nitrous acid: Test used to distinguish primary, secondary and tertiary nitroalkanes.
- (a) Primary nitroalkane:

$$R - CH_2 + O = N - OH \xrightarrow{-H,O} R - C = NOH$$

$$NO_2$$

$$NO_2$$

$$NO_2$$

$$NO_3$$

$$R - C = NOH$$

$$R - C = NONa$$

$$R - C = NONa$$

$$NO_3$$

Red coloured sodium salt (b) Secondary nitroalkane:

 $R_2CH+ HON=O \xrightarrow{-H_2O} R_2C- NO \xrightarrow{NaOH}$ Blue coloration NO, ·

- (c) Tertiary nitroalkane: These compounds do not react with nitrous acid.
- 7. Condensation with aldehydes and ketones:

$$C_6H_5 - C = O + CH_3NO_2 \xrightarrow{KOH/C_2H_5OH}$$

$$C_6H_5 - C - CH_2 - NO_2 \xrightarrow{-H_2O} C_6H_5 - CH = CH - NO_2$$
OH

p and s nitroalkane condense with aldehyde in presence of alkali forming nitro alcohols.

 $CH_3NO_2 + CH_3CHO \longrightarrow CH_3CH(OH)CH_2NO_2$ β -hudroxy nitropropage β -hydroxy nitropropane

$$CH_3-C=O+CH_3-CH_2-NO_2\rightarrow CH_3-C-CH-NO_2$$

OH β-hydroxy-2-nitrobutane

8. Reaction with Grignard reagent :

$$R-CH=N$$
O
 $+ CH_3Mgl \longrightarrow CH_4 + RCH=N$
O
O
O

USES: Used as solvents for oils, fats, resin dyes, rubbers, explosive and intermediates for the synthesis of many organic comounds.

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Diazonium salts:

Stability of arenediazonium ion can be explained on the basis of resonance.

- Chemical properties:
- A. Reactions Involving Replacement of Diazonium Group
- 1. Replacement by -Cl, -Br and -CN: Sandmeyer reaction:

$$Ar \stackrel{+}{N_2} Cl^{-} \xrightarrow{CuCl/HCl} Ar - Cl + N_2 \uparrow$$

$$Ar \stackrel{+}{N_2} Cl^{-} \xrightarrow{CuBr/HBr} Ar - Br + N_2 \uparrow$$

$$Ar \stackrel{+}{N_2} Cl^{-} \xrightarrow{CuCN/HCN} Ar - CN + N_2 \uparrow$$

2. Gattermann reaction:

$$Ar \stackrel{+}{N_2} Cl^- \xrightarrow{Cu/HCl} Ar - Cl + N_2 \uparrow$$

$$Ar \stackrel{+}{N_2} Cl^- \xrightarrow{Cu/Br} Ar - Br + N_2 \uparrow$$

The yield obtained in Gattermann reaction is poor as compare to Sandmeyer's reaction.

3. Replacement by -I:

$$Ar - N_2 X^- + KI \xrightarrow{\Delta} Ar - I + N_2 \uparrow + KX$$

4. Replacement by -F/Balz-Schiemann reaction:

Ar
$$-N_2$$
 X⁻ $\xrightarrow{HBF_4}$ Ar $-N_2$ BF $_4$ $\xrightarrow{\Delta}$ Ar $-F + BF_3 + N_2$ \uparrow
5. Replacement by $-H/P_2$ \xrightarrow{A}

5. Replacement by -H/ Reduction:

Ar
$$-N_2 X^- + H_3 PO_2 + H_2 O \xrightarrow{Cucl} ArH + N_2 \uparrow + H_3 PO_3 + HX$$

Ar $-N_2 X^- + CH_3 - CH_3 -$

Ar
$$-N_2X^- + CH_3 - CH_2 - OH \longrightarrow ArH + N_2 \uparrow + CH_3 - CHO + HX$$

6. Replacement by $-NO$

6. Replacement by -NO₂:

$$C_6H_5N_2X \xrightarrow{HBF_4} C_6H_5N_2BF_4 \xrightarrow{N_6NO_2/C_8} C_6H_5NO_2 + N_2 \uparrow + NaBF_4$$

Reaction involving returns

B. Reaction involving retention of diazonium group /Coupling reaction:

