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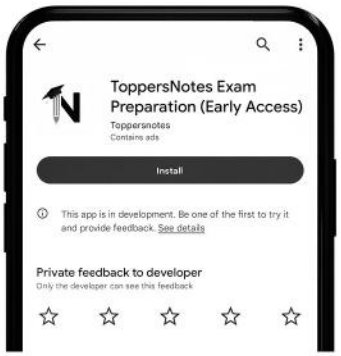

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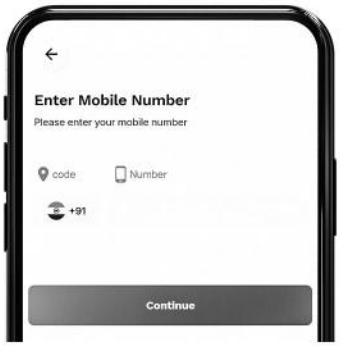

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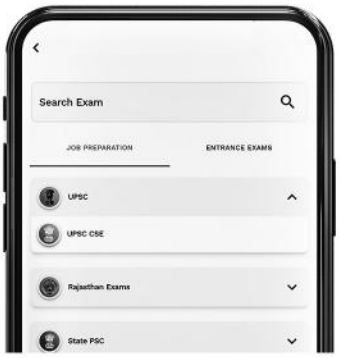

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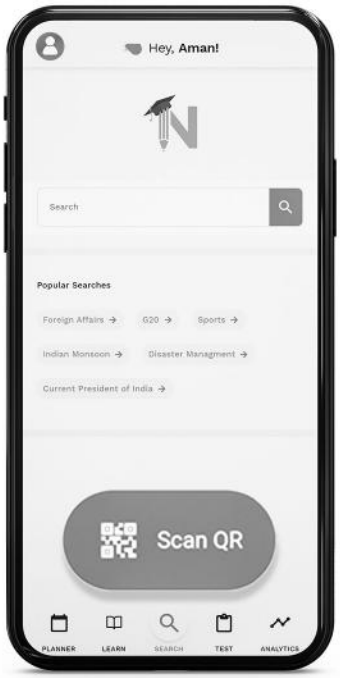

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CHAPTER 1

Amines

CHAPTER OUTLINE

- Some Nitro Compounds – Alkyl nitrites, Nitro alkanes, Nitrobenzene, Amine, Aniline
- Cyanides
- Isocyanides

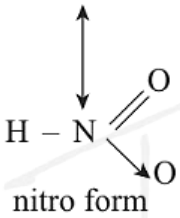
SOME NITRO COMPOUNDS

Alkyl Nitrites and Nitro Alkanes

- HNO_2 exists in the following two tautomeric forms-

$H-O-N=O$

nitrite form



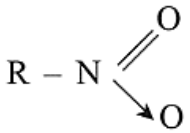
nitro form

- Alkyl nitrites are alkyl derivatives of the nitrite form, whereas nitroalkanes are alkyl derivatives of the nitro form.

Alkyl Nitrite $(\mathbf{R-O-N=O})$

$(R-O-N=O)$

alkyl nitrite

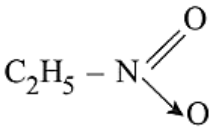


nitroalkane

Example:

$(C_2H_5-O-N=0)$

ethyl nitrite



nitroalkane

Methods of preparation

- To make alkyl nitrite, combine concentrated H_2SO_4 with an aqueous solution of sodium nitrite and alcohol.

$$NaNO_2 + H_2SO_4 \longrightarrow NaHSO_4 + HONO$$

$$ROH + HONO \longrightarrow RONO + H_2O$$

Example:

$$NaNO_2 + H_2SO_4 \longrightarrow NaHSO_4 + HONO$$

$$C_2H_5OH + HONO \longrightarrow C_2H_5ONO + H_2O$$

- Alkyl nitrite can also be produced by the chemical reaction of alkyl iodide with potassium nitrite.

$$RI + KNO_2 \longrightarrow RONO + KI$$

Example:

$$C_2H_2I + KNO_2 \longrightarrow C_2H_5ONO + KI$$

- Alkyl nitrite can also be produced by the action of nitrogen trioxide on alcohol.

Example:

$$2C_2H_5OH + N_2O_3 \longrightarrow C_2H_5ONO + H_2O$$

Physical properties

- At room temperature, ethyl nitrite is a gas that, when cooled, transforms into a colourless liquid with an apple-like odour (boiling point 290K).
- It is water insoluble but soluble in alcohol and ether.
- It has the critical ability of dilating blood arteries, which decreases hypertension and severe angina pectoris pain.

Chemical properties

Hydrolysis: Water, diluted alkali, or diluted acid can hydrolyze alkyl nitrite to form alcohol.

$$RONO + 2H_2O \longrightarrow ROH + NH_3 + H_2O$$

Example:

$$C_2H_5ONO + 2H_2O \longrightarrow C_2H_5OH + NH_3 + H_2O$$

Reduction: It yields alcohol, ammonia, and hydroxylamine upon reduction with Sn/HCl.

$$RONO + 6[H] \xrightarrow{Sn + HCl} ROH + NH_3 + H_2O$$

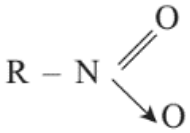
$$RONO + 4[H] \xrightarrow{Sn + HCl} ROH + NH_2OH$$

Example:

$$C_2H_5ONO + 6[H] \xrightarrow{Sn + HCl} C_2H_5OH + NH_3 + H_2O$$

$$C_2H_5ONO + 4[H] \xrightarrow{Sn + HCl} C_2H_5OH + NH_2OH$$

Nitro Alkanes



Method of preparation

1. **From alkyl halide:** Nitroalkanes are produced when alkyl halides and alcoholic silver nitrate solution react.

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

   Example:

   $$C_2H_5Br + AgNO_2 \longrightarrow C_2H_5NO_2 + AgBr$$

2. **From α-Halo substituted acids**

   $$\underset{\text{Chloroacetic acid}}{ClCH_2COOH} + NaNO_2 \xrightarrow{\Delta} \underset{\text{Nitroacetic acid}}{O_2NCH_2COOH} + NaCl$$

   $$O_2NCH_2COOH \xrightarrow{\Delta} CH_3NO_2 + CO_2$$

3. **By nitration of paraffin:** As the nitration of paraffins (alkanes) is more challenging than that of aromatic hydrocarbons, they can only be nitrated with fuming HNO_3 in the vapour phase at a temperature between 423-673K and under pressure. The cleavage of C-C bonds results in the formation of a mixture of Nitro alkanes. It occurs as an outcome of free radicals mechanism.

   $$R - CH_3 + HONO_2 \xrightarrow{400^\circ C} RCH_2NO_2 + H_2O$$

   Example:

   $$CH_3 - CH_3 + HONO_2 \xrightarrow{400^\circ C} CH_3CH_2NO_2 + H_2O + CH_3NO_2$$

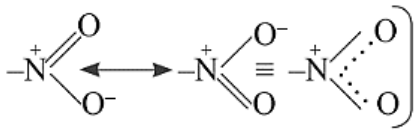
   $$CH_3 - CH_2 - CH_3 \xrightarrow[\substack{\text{fuming} \\ HNO_3 \\ 673\ K}]{\Delta} CH_3 - \underset{\displaystyle NO_2}{\underset{|}{CH}} - CH_3 + CH_3 - CH_2 - CH_2NO_2 + CH_3NO_2 + C_2H_5NO_2$$

Physical properties

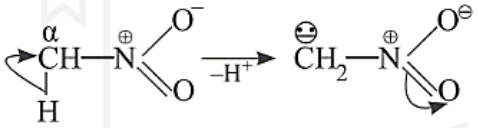
- Nitroalkanes are odourless, colourless liquids that are partially soluble in water but readily soluble in organic solvents.
- Their boiling point is high due to their polar nature.

Chemical properties

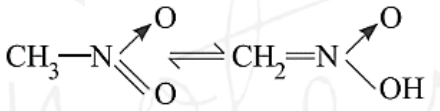
- The NO_2 group is a hybrid resonance of the structures listed below. Its resonance is demonstrated by the fact that the bond length of both N-O bonds is identical.



- Acidic character: Due to the presence of α -hydrogen atom, these react with strong alkali such as aqueous NaOH to form salts.

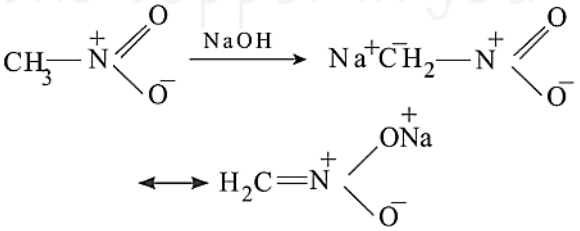


Due to α-H-atom Tautomerism exists

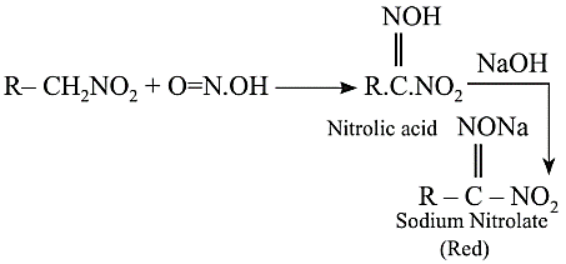


Nitro-form Aci-form

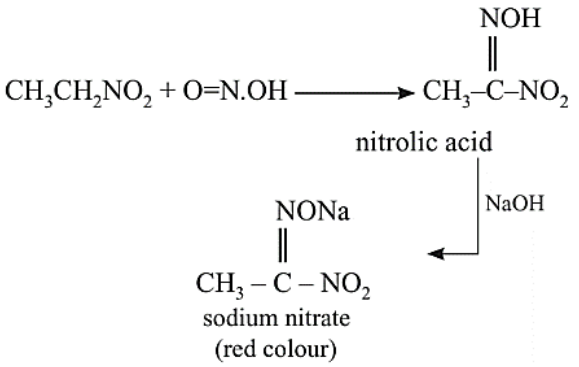
In presence of an alkali, mainly aci-form dominates.



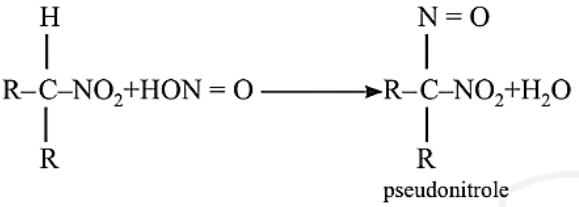
- Reaction with nitrous acid: Primary nitroalkanes react with nitrous acid to produce nitrolic acid, which dissolves in NaOH to produce a red sodium nitrolate solution.



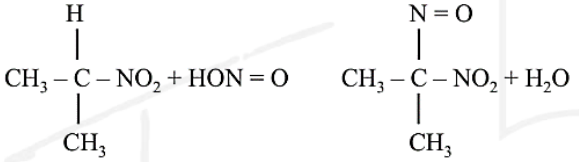
Example:



- Secondary nitroalkanes react with HNO_2 to form pseudonitroles, which impart a blue colour to a NaOH solution.



Example:



- Due to the absence of α-hydrogen, tertiary nitroalkanes do not exhibit this reaction. This interaction between HNO_2 and p°, s°, t°, and R-NO_2 is the basis for the Victor Meyer Test for alcohols.
- Hydrolysis: Primary nitroalkanes undergo acidic hydrolysis to give acids.

  Example:

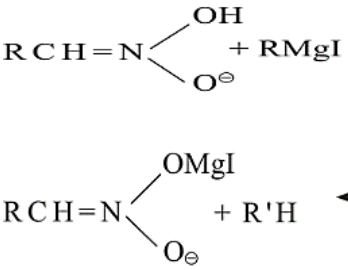
  $CH_3CH_2NO_2 + H_2O \xrightarrow{HCl} CH_3COOH + NH_2OH$

  - Secondary nitroalkanes on hydrolysis give ketones.

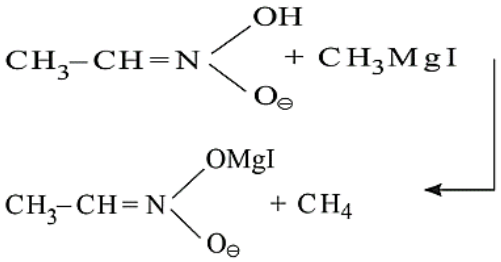
    $2R_2CHNO_2 \xrightarrow{HCl} 2R_2CO + N_2O + H_2O$

    Example:

    $2(CH_3)_2CHNO_2 \xrightarrow{HCl} 2(CH_3)_2CO + N_2O + H_2O$
  - Tertiary nitroalkanes do not show this reaction.
- Reaction with Grignard reagent: Nitroalkane in Aci-form gives alkanes with Grignard reagent.



Example:



- Halogenation: Nitroalkanes undergo halogenation at α-position.

  Example:

  $CH_3CH_2NO_2 \xrightarrow{Cl_2-NaOH} CH_3\underset{Cl}{\underset{|}{C}}HNO_2 + CH_3-\underset{Cl}{\underset{|}{C}}-NO_2$

  Nitroethane

  $CH_3NO_2 \xrightarrow{Cl_2+NaOH} CCl_3.NO_2$

  Nitroethane — Chloropicrin

  $CH_3-\underset{CH_3}{\underset{|}{CH}}-NO_2 \xrightarrow{Cl_2+NaOH} CH_3-\underset{Cl}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-NO_2$

  2 – Nitroethane
- Reduction: Nitroalkanes undergo reduction as follows:

  $R-NO_2 \xrightarrow[-H_2O]{2[H]} \underset{\text{Nitroso Compound}}{R-N=O} \xrightarrow{2[H]} \underset{\text{Hydroxyl amine derivative}}{R-NHOH} \xrightarrow{2[H]} \underset{\text{p°-Amine}}{R-NH_2}$

  - Reduction by $\mathbf{Sn + HCl}$ **or** $\mathbf{Zn/HCl}$ **or** $\mathbf{Fe + H_2O + HCl}$ **or** $\mathbf{LiAlH_4}$ gives **primary amine**.

    $RNO_2 + 6[H] \xrightarrow{Sn+HCl} RNH_2 + 2H_2O$

    Example:

    $\underset{\text{nitroethane}}{C_2H_5NO_2} + 6[H] \xrightarrow{Sn+HCl} \underset{\text{ethyl amine}}{C_2H_5NH_2} + 2H_2O$
  - Reduction with **zinc dust** and $\mathbf{NH_4Cl}$ gives **hydroxylamines**.

    $RNO_2 + 4[H] \xrightarrow{Zn+NH_4Cl} RNHOH + H_2O$

Example:

$$C_2H_5NO_2 + 4[H] \xrightarrow{Zn + NH_4Cl} \underset{\text{ethyl hydroxyl amine}}{C_2H_5NHOH} + H_2O$$

- Reduction with $\mathbf{SnCl_2/HCl}$ gives a mixture of **oxime** and **hydroxyl amine**.

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

Example:

$$CH_3CH_2NO_2 \xrightarrow{SnCl_2/HCl} CH_3CH_2NHOH + CH_3CH=NOH$$

- Mannich reaction: It involves the **condensation** of nitroalkane, formaldehyde, primary amine and hydrogen chloride.

$$R_2CHNO_2 + HCHO + RNH_2.HCl \longrightarrow R_2\underset{\displaystyle NO_2}{\underset{|}{C}}\underset{\displaystyle R}{\underset{|}{C}}H_2.NH.HCl + H_2O$$

Example:

$$(CH_3)_2CHNO_2 + HCHO + C_2H_5NH_2.HCl \longrightarrow (CH_3)_2\underset{\displaystyle NO_2}{\underset{|}{C}}\underset{\displaystyle C_2H_5}{\underset{|}{C}}H_2.NH.HCl + H_2O$$

Effect of heat

- On moderate heating below $300^\circ C$, nitroalkanes form alkenes.

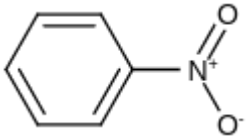
$$RCH_2CH_2NO_2 \xrightarrow{300^\circ C} R.CH=CH_2 + HNO_2$$

- On heating rapidly, explosion takes place.

Example:

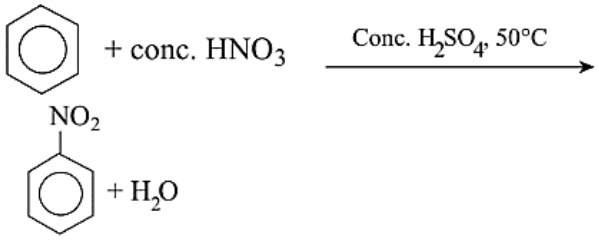
$$CH_3NO_2 \xrightarrow{\Delta} CO_2 + \frac{1}{2}N_2 + \frac{3}{2}H_2$$

Nitrobenzene

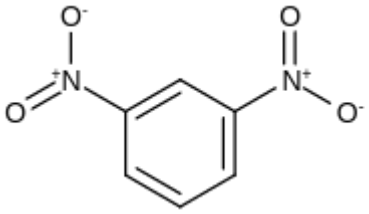


- It is also known as **Oil of Mirbane** and has a bitter, almond like odour.

Methods of preparation



- If temperature is above $100^\circ C$, nitration takes place and the product is **m-dinitrobenzene**.



Physical properties

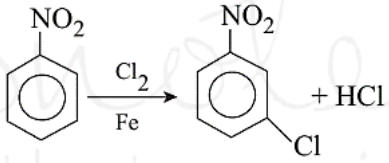
- It is a light brown, oily liquid with a boiling point of 210 degrees Celsius.
- It is water-insoluble and volatile in steam.
- It can be purified by distillation with steam.

Chemical properties

- *Due to benzene ring:*

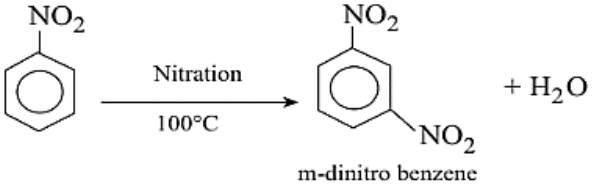
  The nitro group deactivates the benzene ring; consequently, further substitution occurs only at the meta-position, and the rate of electrophilic substitution is considerably slower than that of benzene.

- **Halogenation:**

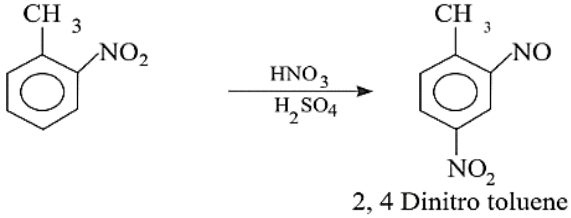


m-chloronitro benzene

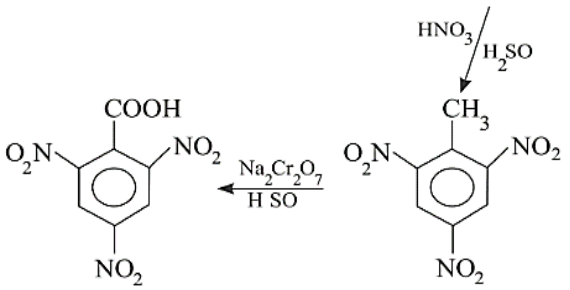
- **Nitration:**



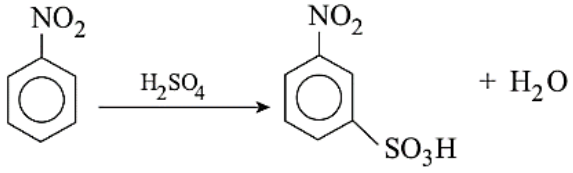
m-dinitro benzene



2, 4 Dinitro toluene



- **Sulphonation:**

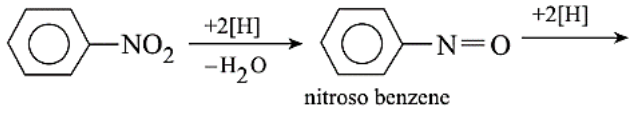


m-nitro benzene sulphonic acid

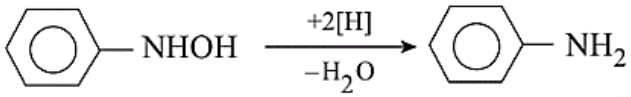
Friedel crafts reaction

Friedel Crafts reaction **does not occur** in any of the meta (m) directing groups like $-NO_2, -CHO, -COOH, -CX_3, -SO_3H$, -COX etc.

Reduction of nitro benzene



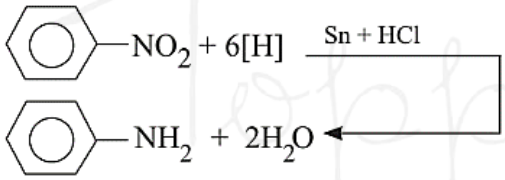
nitroso benzene



phenylhydroxy amine aniline

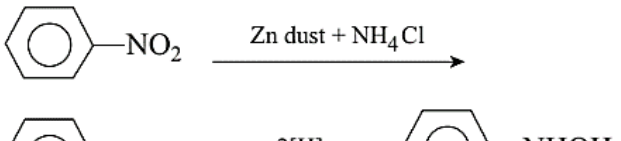
- Nitrobenzene can be reduced to a variety of products, the nature of which depends on the reducing agent employed.

In a strong acidic medium



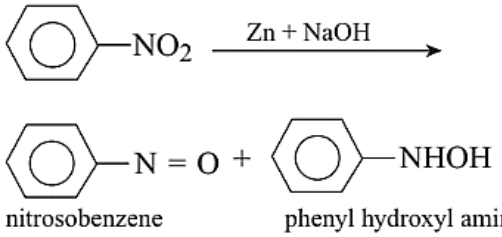
aniline

In a neutral medium



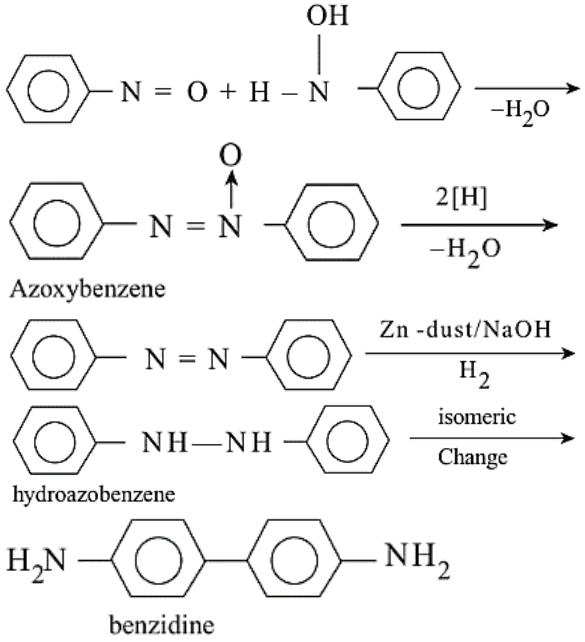
nitrosobenzene phenyl hydroxyl amine

In basic medium



nitrosobenzene phenyl hydroxyl amine

- Nitrosobenzene and phenylhydroxylamine react further to produce the following compounds, depending on the reagent employed.

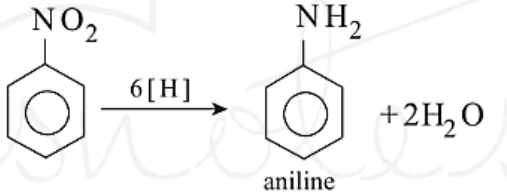


benzidine

- Zinc dust/NaOH or sodium amalgam produces azobenzene and hydrazobenzene.
- Together, sodium arsenite and NaOH produce azoxybenzene.

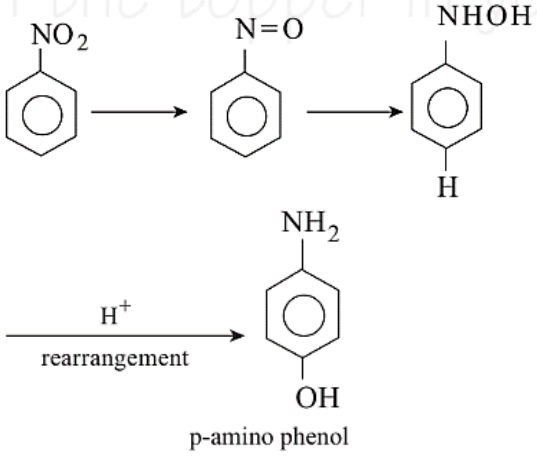
Electrolytic reduction:

In a weak acidic medium



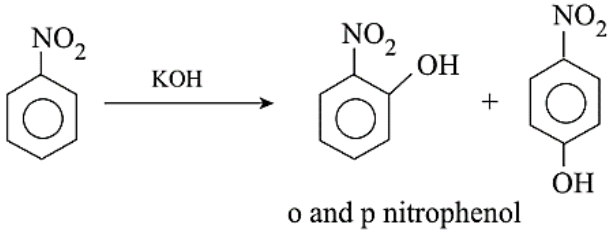
aniline

In a strong acidic medium



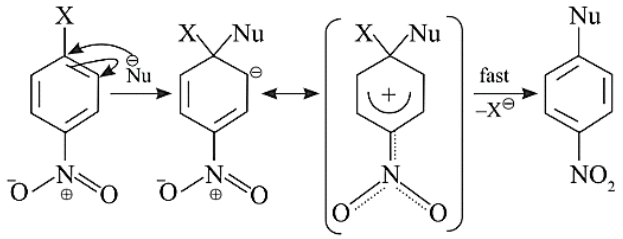
p-amino phenol

Reaction with solid KOH : It is an illustration of **nuclephilic substitution reaction**.



o and p nitrophenol

- The -NO_2 group is strongly bonded to the benzene nucleus, and partial double bond character develops as a result of resonance, leaving nitrobenzene inert and preventing displacement reactions.
- If any group, such as -X, is present at the o and p positions of the -NO_2 group, the chance of nucleophilic substitution increases.



Uses

- Nitrobenzene is utilised in the production of azodyes, aniline, and as a fragrance component in shoe polish and detergents.

Amines

Structure

- Amines are the alkyl or aryl derivatives of ammonia (NH_3).
- Amines have a general formula $\mathbf{C_nH_{2n+3}\ N}$.
- N is **sp^3-hybridized** in amines, and their geometry is **pyramidal.**
- Due to the presence of an unshared pair of e- s in the fourth orbital of nitrogen, the bond angle in 1° and 2° amines decreases from the tetraheral angle of 109.28' to 107°. However, the bond angle of 3° amines increased to 108° due to steric hindrance.
- Like NH_3 an amine is too **pyramidal** in shape (3bp + lp).

Classification of Amines

On the basis of number of H-atoms replaced by alkyl or aryl groups in NH_3-

1. Primary (RNH_2)
2. Secondary (R_2NH)
3. Tertiary $(R_3\ N)$

- All three kinds of amine are derived from ammonia by substituting alkyl or aryl groups for hydrogen atoms.

  $NH_3 \longrightarrow R-NH_2 \longrightarrow R_2NH \longrightarrow R_3\ N$
- Amines are named **aminoalkanes or alkanamines** in case of **primary amines**.

  Example: $CH_3CH_2CH_2NH_2$ (propanamine)

  $CH_2-CH-CH_3$ propan-1,2-diamine

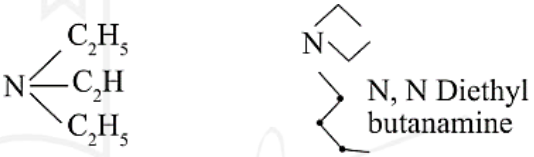
  NH_2 NH_2

  $NH_2–CH_2–CH=CH_2$ Prop, 2-enamine
- **Secondary amines** are named **n-alkyl alkanamine**.

  Example: $C_2H_5NHCH_2CH_2CH_3$

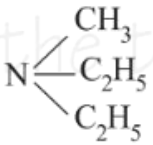
  n-ethyl propanamine
- **Tertiary amines** are called as **N, N-dialkyl alkanamine**.

  Example:

  N, N-diethyl ethanamine
- Tertiary amines are also named as N-alkyl N'-alkyl alkanamine.

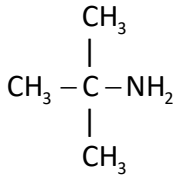
  Example:

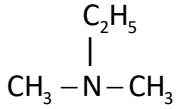
  

  N-ethyl N'-methyl ethanamine
- Amines demonstrate functional, chain, position, and metameric isomerism.Primary, secondary, and tertiary amines are isomers from a functional standpoint.
- $C_4H_{11}N$ has four primary, three secondary, and one tertiary amines, for a total of eight amines.

  Examples:

  1. $CH_3CH_2CH_2CH_2NH_2$
  2. $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2NH_2$
  3. $CH_3CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-NH_2$

4. 

5. $C_2H_5 - NH - C_2H_5$
6. $CH_3 - NH - CH_2CH_2CH_3$
7. $CH_3 - NH - CH(CH_3)_2$
8. 

Here $(1,2,3,4)$ w.r.t $(5,6,7)$ and (8) are functional isomers.

Here 1 is chain isomer w.r.t to 2 and 4. 1 and 3 are position isomers 5, 6 or 7 are metamers.

Methods of Preparation for all Types of Amines

- **By Hoffmann method**

Alkyl halide is treated with alcoholic ammonia.

$$RX + NH_3 \xrightarrow{\Delta} RNH_2 + HX$$

$$RNH_2 + RX \xrightarrow{\Delta} R_2NH + HX$$

$$R_2NH + RX \longrightarrow R_3N + HX$$

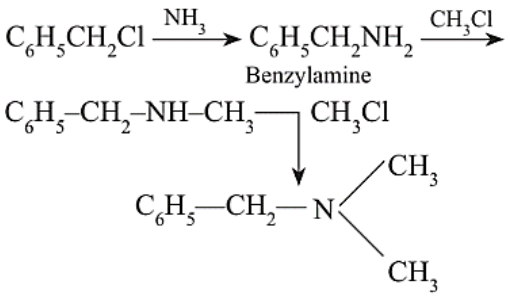
$$R_3N + RX \longrightarrow R_4N^+ X^-$$

quaternary ammonium salt

$$R - \overset{+}{N}H_3\overline{X} + NaOH \longrightarrow R - NH_2 + NaX + H_2O$$

Example:

$$C_2H_5Cl \xrightarrow{NH_3} C_2H_5NH_2 \xrightarrow[-HCl]{C_2H_5Cl} \underset{s^\circ}{(C_2H_5)_2NH} \xrightarrow[-HCl]{C_2H_5Cl} \underset{t^\circ}{(C_2H_5)_3N}$$



N, N- Dimethyl phenyl methanamine or benzylamine

Here **reactivity order of halides with amines is $R - I > R - Br > R - Cl$.**

When NH_3 is in excess, R-NH_2 is the most abundant product, whereas when R-X is in excess, quaternary ammonium salt is the most abundant product.

This is referred to as **alkyl halide ammonolysis**. The reaction is a **nucleophilic substitution.**

- **By ammonolysis of alcohols**: Vapours of alcohol and ammonia are passed over heated alumina or thoria at $350^\circ C$.

$$ROH + NH_3 \xrightarrow[350^\circ C]{Al_2O_3} RNH_2 + H_2O$$

$$RNH_2 + ROH \longrightarrow R_2NH + H_2O$$

$$R_2NH + ROH \longrightarrow R_3N + H_2O$$

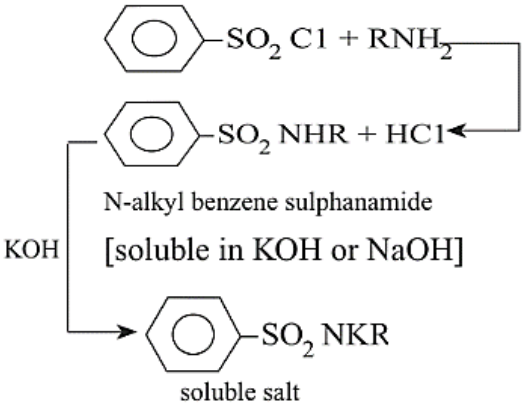
- **Separation of primary, secondary, and tertiary amine and quaternary ammonium salt:**

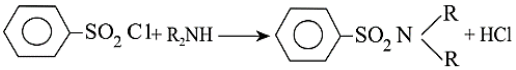
The mixture is initially treated with aqueous KOH, where the quaternary halide transforms into solid quaternary ammonium hydroxide.

The mixture of primary, secondary, and tertiary amines is then distilled, leaving in the vessel salt residue.

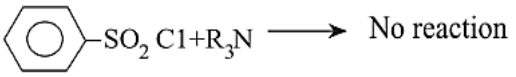
Using any of the following techniques, the mixture of primary, secondary, and tertiary amines can be separated:

- **By fractional distillation**: By subjecting the mixture to fractional distillation, all three amines are separated. The technique is only applicable when the boiling points of the three amines differ significantly.
- **By Hinsberg method**: Here, amines are treated with the Hinsberg reagent (benzene sulfonyl chloride).
  - Here, only **primary and secondary amines react with the reagent**, while tertiary amines do not.
  - Unreacted tertiary amine is extracted by distilling the mixture.
  - When the remaining mixture is treated with aqueous KOH, the primary amine derivative becomes soluble while the secondary amine derivative remains insoluble.



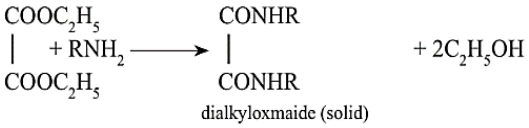


N, N-dialkyl benzene sulphonamide
(insoluble in KOH)

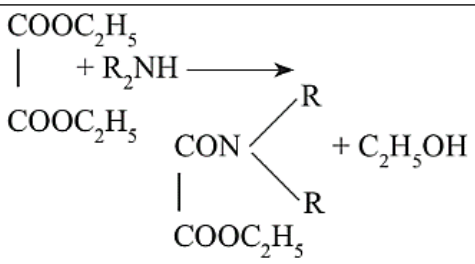


- Filtration then separates the solid residue of 2° amine from the soluble salt of 1°, which, upon hydrolysis, yields 2° and 1° Amines separately.
- p-Toluene sulphonyl chloride is now preferred to benzene sulphonylchloride because the formed substituted sulphonamide are stable compounds that can be readily purified via crystallisation.

- **By Hoffmann method**
  - Here, diethyl oxalate is heated with the amine mixture.
  - **Primary amines** produce a **solid product,** while **secondary amines** produce **an oily product** and **tertiary amines** do **not react.**
  - The mixture is distilled, with unreacted tertiary amines distilling out first, followed by the oily secondary amine product. The primary amine derivative is left in the vessel.
  - Hydrolysis of derivatives of primary and secondary amines produces respective amines.



dialkyloxmaide (solid)



dialkyl oxamic ester
(oily liquid)

Methods of Preparation of Primary Amines

- **By reduction of cyanides**

$$RCN + 4H \xrightarrow[\text{or Raney Ni/H}_2]{\text{LiAlH}_4,\ \text{Na + alcohol}} RCH_2NH_2$$

Example:

$$CH_3CN + 4H \xrightarrow[\text{Na + alcohol}]{\text{LiAlH}_4} CH_3CH_2NH_2$$

$$C_6H_5 - CH_2 - CN \xrightarrow[\text{Na + alcohol}]{\text{LiAlH}_4} \underset{\text{2-Phenyl ethanamine}}{C_6H_5 - CH_2 - CH_2NH_2}$$

- **By reduction of nitro alkanes**

$$RCH_2NO_2 + 6H \xrightarrow[\text{LiAlH}_4]{\text{Sn/HCl}} RCH_2NH_2 + 2H_2O$$

Example:

$$CH_3CH_2NO_2 + 6H \xrightarrow[\text{LiAlH}_4]{\text{Sn/HCl}} CH_3CH_2NH_2 + 2H_2O$$

- **By reduction of amides**

$$RCONH_2 + 4H \xrightarrow[C_2H_5OH/Na]{\text{LiAlH}_4} RCH_2NH_2 + H_2O$$

Example:

$$CH_3CONH_2 + 4H \xrightarrow[C_2H_5OH/Na]{\text{LiAlH}_4} CH_3CH_2NH_2 + H_2O$$

- **By reduction of oximes**

$$RCH = NOH + 4H \xrightarrow[Na/C_2H_5OH]{\text{LiAlH}_4} RCH_2NH_2 + H_2O$$

Example:

$$CH_3CH = NOH + 4H \xrightarrow[Na/C_2H_5OH]{\text{LiAlH}_4} CH_3CH_2NH_2 + H_2O$$

- **From alkyl halides and alcohols**

$$\underset{\text{excess}}{RX + NH_3} \longrightarrow RNH_2 + HX$$

$$\underset{\text{excess}}{ROH + NH_3} \xrightarrow[350°C]{Al_2O_3} RNH_2 + H_2O$$

Example:

$$\underset{\text{excess}}{C_2H_5Cl + NH_3} \longrightarrow C_2H_5NH_2 + HCl$$

$$\underset{\text{excess}}{C_2H_5OH + NH_3} \xrightarrow[350°C]{Al_2O_3} C_2H_5NH_2 + H_2O$$

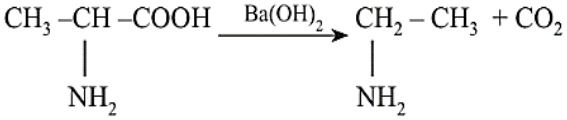
- **From Grignard reagent**

$$RMgX + NH_2Cl \longrightarrow RNH_2 + XMgCl$$

Example:

$$C_2H_5MgCl + NH_2Cl \longrightarrow C_2H_5NH_2 + MgCl_2$$

- **By decarboxylation of α-amino acids**



- **By hydrolysis of isocyanides and isocyantes**

$$RNC + 2H_2O \xrightarrow{H^+} RNH_2 + HCOOH$$

$$RNCO + 2KOH \xrightarrow{H} RNH_2 + K_2CO_3$$

Example:

$$C_2H_5NC + 2H_2O \xrightarrow{H^+} C_2H_5NH_2 + HCOOH$$

$$C_2H_5NCO + 2KOH \xrightarrow{H} C_2H_5NH_2 + K_2CO_3$$

- **From acids**

$$RCOOH + NH_3 \longrightarrow RCOONH_4 \xrightarrow{\Delta}$$

$$RCONH_2 \xrightarrow{Br_2/KOH} RNH_2$$

Examples:

$$CH_3COOH + NH_3 \longrightarrow CH_3COONH_4 \xrightarrow{\Delta}$$

$$CH_3CONH_2 \xrightarrow{Br_2/KOH} CH_3NH_2$$

- **By Schmidt reaction**

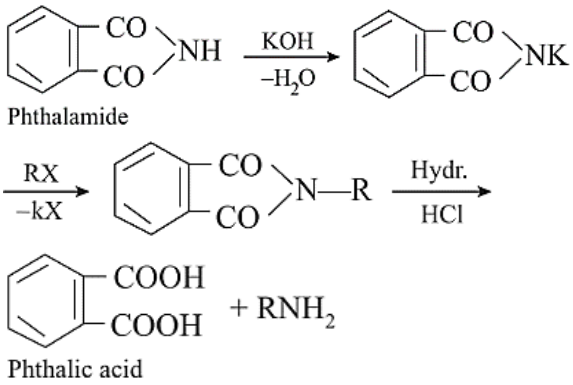
$$\underset{\text{hydrazoic acid}}{RCOOH + N_3H} \xrightarrow[H_2SO_4]{\text{conc.}} RNH_2 + N_2 + CO_2$$

Example:

$$CH_3COOH + N_3H \xrightarrow{\text{conc. } H_2SO_4} CH_3NH_2 + N_2 + CO_2$$

  - The intermediates of this reaction are **alkyl isocyanate** and **acyl azide**, which produce primary amines using the **Curtius degradation method.**

- **By Gabriel phthalamide synthesis**

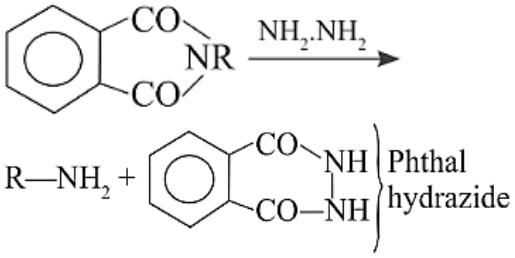


Phthalamide

Phthalic acid

$R \rightarrow CH_3$, C_2H_5 etc.

  - This method is incapable of producing $C_6H_5NH_2$ because C_6H_5 does not undergo nucleophilic substitution under moderate conditions.
  - The hydrazinolysis of N-alkyl phthalimides is a faster and more efficient process.



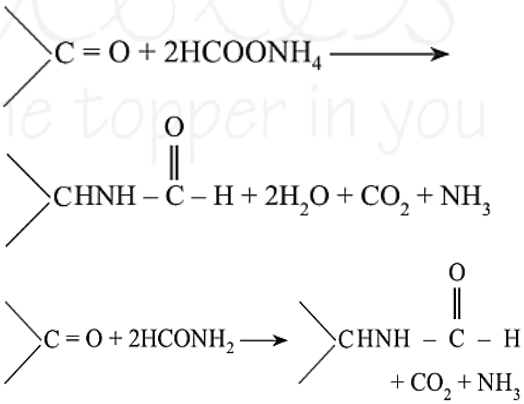
- **By the reaction of Azide with $NaBH_4$**

$$\underset{\text{sodium azide}}{R - X + NaN_3} \longrightarrow \underset{\text{alkyl azide}}{RN_3} \xrightarrow[H_2O]{NaBH_4} RNH_2$$

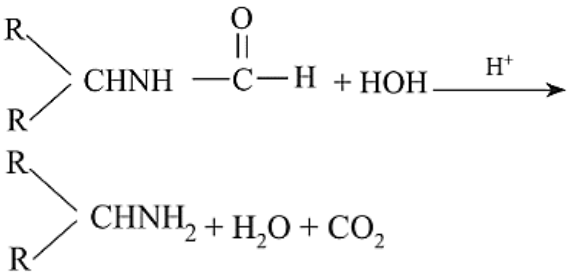
Example:

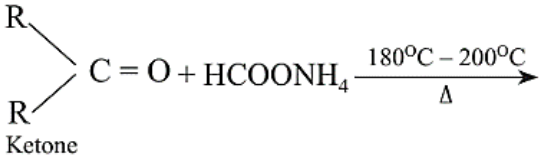
$$\underset{\text{sodium azide}}{C_2H_5Cl + NaN_3} \longrightarrow \underset{\text{ethyl azide}}{C_2H_5N_3} \xrightarrow[H_2O]{NaBH_4} C_2H_5NH_2$$

- **By Leuckart reaction**
  - Aldehydes or ketones react with ammonium formate or formamide to form primary amine formyl derivatives.

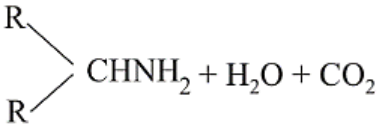


- These **formyl derivatives** are **hydrolyzed** by acids into **primary amines**.



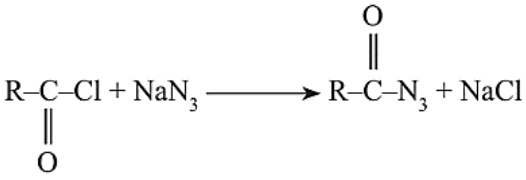


Ketone



primary amine

- **By Curtivs rearrangement**



Acidazide

Methods of Preparation for Secondary Amines

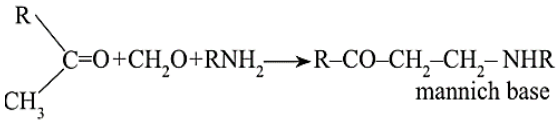
- **Platinum catalysed reduction of Iso Cyanides**

$$RN \equiv C + 4[H] \xrightarrow{Pt} \underset{\text{secondary amine}}{RNHCH_3}$$

Example:

$$C_2H_5N \equiv C + 4[H] \xrightarrow{Pt} \underset{\text{N-methyl ethanamine}}{C_2H_5NHCH_3}$$

- **Mannich reaction**



mannich base

$$R - CONHR + 4[H] \xrightarrow{LiAlH_4} RCH_2NHR + H_2O$$

Example:

$$CH_3 - CONHCH_3 + 4[H] \xrightarrow{LiAlH_4} \underset{\text{N-methyl ethanamine}}{CH_3CH_2NHCH_3 + H_2O}$$

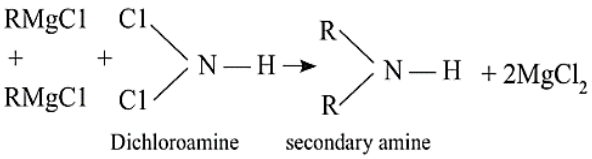
- **Hydrolysis of Dialkyl cyanamide**

$$R_2N - CN + 2H_2O \xrightarrow{H^+} R_2NH + CO_2 + NH_3$$

Example:

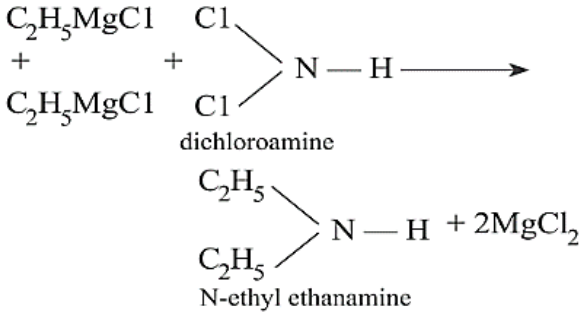
$$(CH_3)_2N - CN + 2H_2O \xrightarrow{H^+} \underset{\text{N-methyl methanamine}}{(CH_3)_2NH + CO_2 + NH_3}$$

- **Using Grignard reagent**



Dichloroamine secondary amine

Example:



N-ethyl ethanamine

Methods of Preparation for Tertiary Amines

- **Reduction of N, N-disubstituted amides**

$$RCONR_2 \xrightarrow[4[H]]{LiAlH_4} RCH_2NR_2 + H_2O$$

Example:

$$CH_3CON(CH_3)_2 \xrightarrow[4[H]]{LiAlH_4} \underset{\text{N, N-dimethyl ethanamine}}{CH_3CH_2N(CH_3)_2 + H_2O}$$

- **By decomposition of Tetra-ammonium hydroxides**

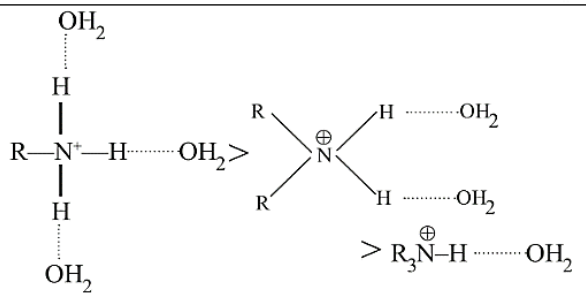
$$(R)_4NOH \xrightarrow{\Delta} (R)_3N + Alkene + H_2O$$

Example:

$$(C_2H_5)_4NOH \xrightarrow{\Delta} \underset{\text{N, N-diethyl ethanamine}}{(C_2H_5)_3N + C_2H_4 + H_2O}$$

Physical Properties of Amines

- Methyl amine and ethyl amine are the only gases in the amine family; the remaining members are either solids or liquids.
- Due to hydrogen bonding, these are very soluble in water.
- **Solubility ∝ 1/Molecular weight**
- The decreasing order of solubility of amines is indicated below:
  $CH_3NH_2 > C_2H_5NH_2 > C_3H_7NH_2 > \ldots\ldots$
  $R - NH_2 > R_2NH > R_3N$
- These are combustible and basic in nature.
- Because amines have weaker hydrogen bonds than alcohols, their boiling points are lower.
  Example:
  $C_3H_5OH > C_2H_5NH_2$



It is in decreasing order of H-bonding in water and solvation stability of ions.

Chemical Properties

Basic nature

As the nitrogen atom has a lone pair of electrons to donate, amines are basic. Consequently, they form salts with acids.

$$R\ddot{N}H_2 + HCl \longrightarrow RNH_3^+Cl^-$$

$$R-\ddot{N}H_2 + H_2O \longrightarrow R-\overset{+}{N}H_3 + \bar{O}H$$

Due to formation of $\bar{O}H$ aqueous solution of Amines is basic in nature

$$2R-NH_2 + H_2PtCl_6 \longrightarrow \underset{\text{chloroplatinate}}{\left(R^+NH_3\right)_2 PtCl_6^{-2}}$$

Amines' equivalent and molecular masses can be determined using chloroplatinates.

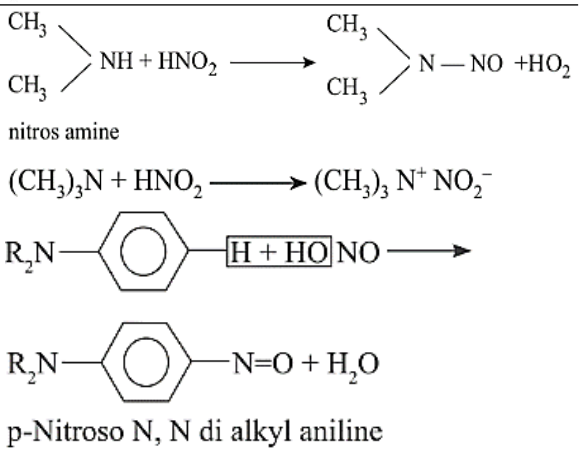
$$AgCl + 2R-NH_2 \longrightarrow$$
$$[R-NH_2 \longrightarrow Ag \longleftarrow NH_2R]^+Cl^-$$

Dialkylamine silver 1 (chloride)

Basic nature orders of amines

- $\left.\begin{array}{l}(CH_3)_2NH > CH_3-NH_2 > (CH_3)_3N\\ (C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2\end{array}\right]$ In aquous solution
- $R_3N > R_2NH > R-NH_2$
  In gas phase or in non-aquoues solvents
- $R-NH_2 > NH_3 > \varnothing-NH_2 > \varnothing_2NH > \varnothing_3N$
- $C_6H_5N(CH_3)_2 > C_6H_5-NHCH_3 > C_6H_5NH_2$
- **Reaction with nitrous acid (HNO_2)**
  A **primary amine** reacts with an **alcohol**, whereas a **secondary amine** reacts with a **nitroso amine**. The formation of **trialkyl ammonium nitrate** by a **tertiary amine**.

$$CH_3CH_2NH_2 + HNO_2 \longrightarrow \underset{\text{(N free)}}{C_2H_5OH} + N_2 + H_2O$$



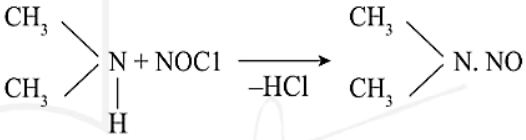
nitros amine

$$(CH_3)_3N + HNO_2 \longrightarrow (CH_3)_3N^+NO_2^-$$

p-Nitroso N, N di alkyl aniline

- **Reaction with NOCl**
  A primary amine reacts with NOCl to produce an alkyl halide, whereas a secondary amine produces an oily byproduct; a tertiary amine does not react with NOCl. This reaction is also known as **Nitrosation**.

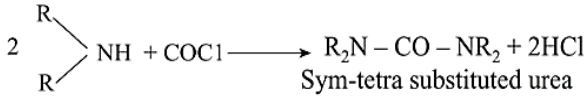
$$CH_3CH_2NH_2 + NOCl \longrightarrow CH_3CH_2Cl + N_2 + H_2O$$



nitroso amine
(oily product)

- **Libermann's nitroso test**: When nitroso amine and phenol are heated in the presence of sulphuric acid, a red product is produced, which transforms to blue and then green. This test detects both Aliphatic and Aromatic sec. amines. $N-$ Nitrosoamines are cancer producing agents i.e carcinogens.
- **Reaction with $COCl_2$** : This reaction is only produced by primary and secondary amines.

$$2R-NH_2 + COCl_2 \longrightarrow \underset{\text{Sym-disubstituted urea}}{R-NH-\overset{\overset{O}{\|}}{C}-NH-R} + 2HCl$$



Sym-tetra substituted urea

- **Acetylation or reaction with CH_3COCl**
  This reaction confirms the presence of NH_2 group.

$$CH_3COCl + RNH_2 \longrightarrow \underset{\text{N-alkyl ethanamide}}{CH_3CONHR} + HCl$$

- **Carbylamine reaction**
  - This test **detects primary amines**.
  - Here, the **foul-smelling isocyanide** compound is formed.
  - The intermediate of the reaction is **dichloro carbene**.

$$RNH_2 + CHCl_3 + 3KOH \xrightarrow{\text{alc. KOH}} RNC + 3KCl + 3H_2O$$

Carbylamine (Irocyanide)

Examples:

$$CH_3NH_2 + CHCl_3 + 3KOH \xrightarrow{\text{alc. KOH}} CH_3NC + 3KCl + 3H_2O$$

methyl isocyanide (M I C)

$$C_6H_5NH_2 + CHCl_3 + 3KOH \xrightarrow{\text{alc. KOH}} C_6H_5NC + 3KCl + 3H_2O$$

phenyl isocyanide

- **Oxidation**
  - It is a distinguishing test for amines because oxidation of a primary amine yields aldimine, which, upon hydrolysis, yields an aldehyde.
  - Reaction:

$$CH_3CH_2NH_2 \xrightarrow[KMnO_4]{[O]} \underset{\text{aldimine}}{CH_3CH{=}NH} \xrightarrow{H_2O} \underset{\text{acetaldehyde}}{CH_3CHO} + NH_3$$

The **oxidation** of a **secondary amine** yields **ketamine**, which upon **hydrolysis** yields **ketone**.

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH-NH_2 \xrightarrow{[O]} \underset{\text{ketamine}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C{=}NH} \xrightarrow{H_2O} \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CO + NH_3$$

On oxidation with H_2O_2 or Caro's acid, a **secondary amine** produces **dialkyl hydroxylamine**.

$$R_2NH \xrightarrow[\text{or } H_2SO_5]{H_2O_2} R_2N-OH$$

N-hydroxy dialkyl amines

The oxidation of a **secondary amine** by **$KMnO_4$** yields **tetralkyl hydrazine**.

$$R_2NH \xrightarrow{KMnO_4} R_2N-NR_2 + H_2O$$

A tertiary amine on oxidation by **Caro's-acid or Fenton's reagent** gives **tertiary amine oxide**.

$$R_3N + [O] \xrightarrow[O_3\ H_2SO_5]{H_2O_2} R_3NO \longrightarrow R_3\overset{\oplus}{N}-\overset{\ominus}{O}$$

- **Hoffmann mustard oil reaction**

It is a **primary amine test**. Here, primary amine produces alkyl isothiocyanate with a mustard oil-like odour.

$$RNH_2 + S{=}C{=}S \longrightarrow S{=}C\begin{matrix}\diagup SH\\\diagdown NHR\end{matrix}$$

Dithio alkyl Carbanic acid

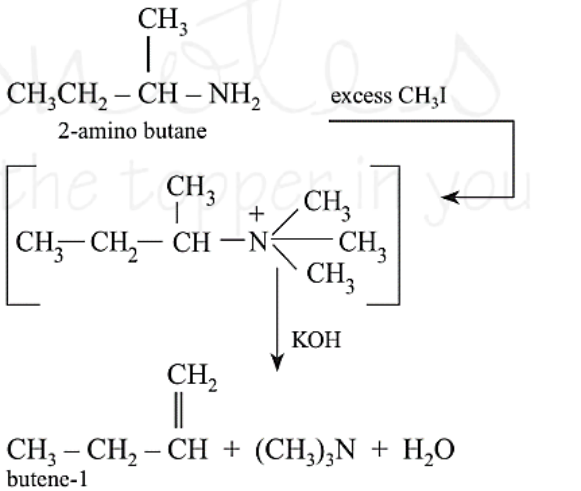
$$\xrightarrow{HgCl_2} RNCS + HgS + 2HCl$$

Alkyl Isothiocyanate

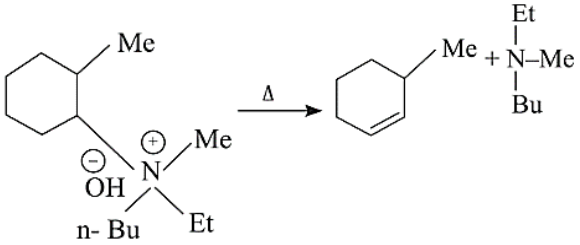
- **Hoffmann exhaustive methylation and degradation**

It involves the formation of alkene by following to the Hoffman rule, with the less stable alkene being the predominant product.

Example:

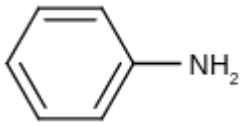


The preceding elimination complies to the Hoffmann rule. According to this rule, the β-hydrogen atom is eliminated from the carbon containing more hydrogen atoms, resulting in the formation of a less stable alkene.



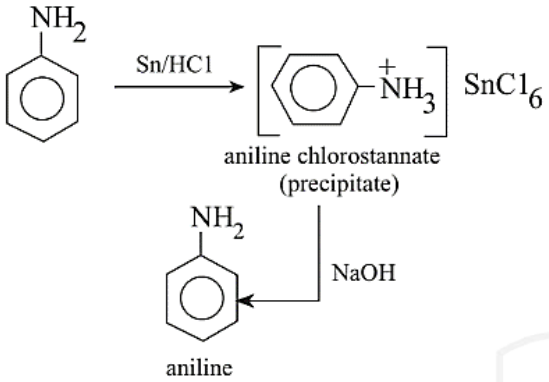
Aniline or Amino Benzene

- Also known as **benzenamine** or **phenylamine**.



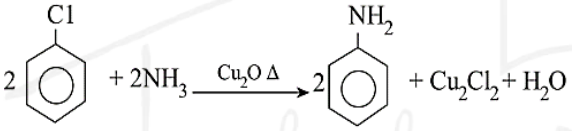
Methods of Preparation

- **By reduction of nitro benzene**

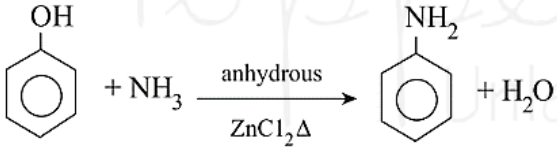


  - Fe + HCl is used in commercial preparation.

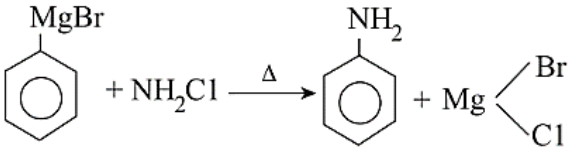
- **From chlorobenzene**



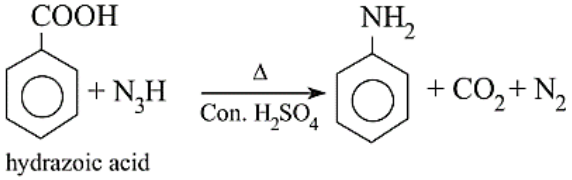
- **From phenol**



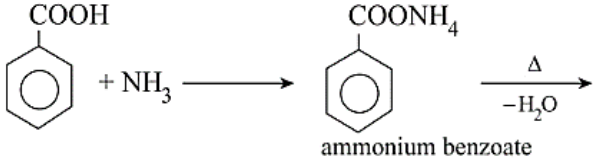
- **From phenyl magnesium bromide**

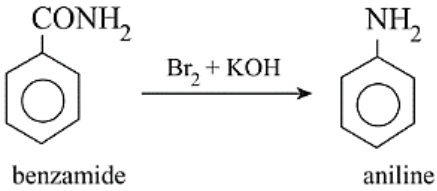


- **Schmidt reaction**



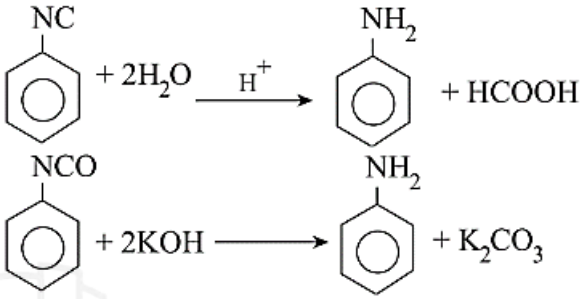
- **From benzoic acid**



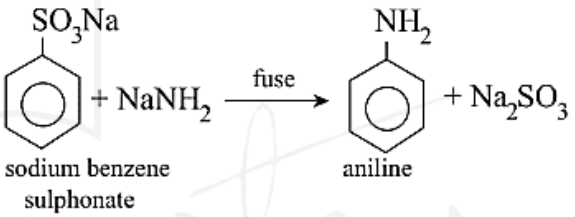


The **conversion** of **benzamide** into **aniline** is referred to as **Hoffmann bromamide reaction.**

- **By the Hydrolysis of Isocyanide and Isocyanate**



- **From benzene sulphonic acid**



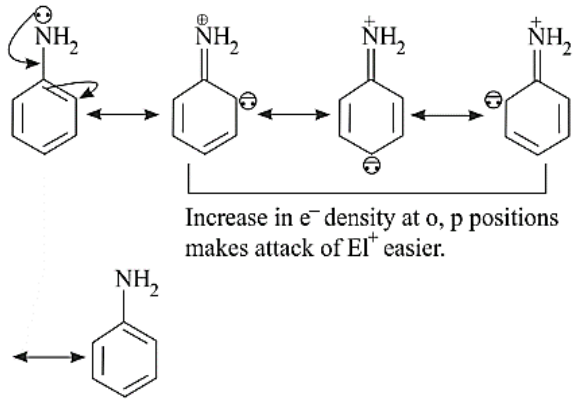
Physical Properties

- Pure aniline is a colourless, oily liquid, but when left exposed to light and air, it turns dark brown.
- It has a boiling point of 183°C.
- It is water-soluble but volatile in steam.
- It can be purified by distillation with vapour.

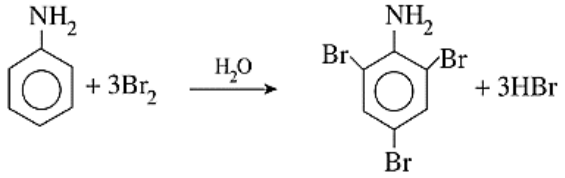
Chemical Properties

Electrophilic substitution

- The **-NH_2 group** in aniline is **highly ring-activating** because the **lone pair of electrons** on the nitrogen atom becomes **delocalized due to resonance**, thereby increasing the electron density at **ortho and para positions**. This also confirms that the delocalization of aniline's lone pair of electrons has decreased its basicity.

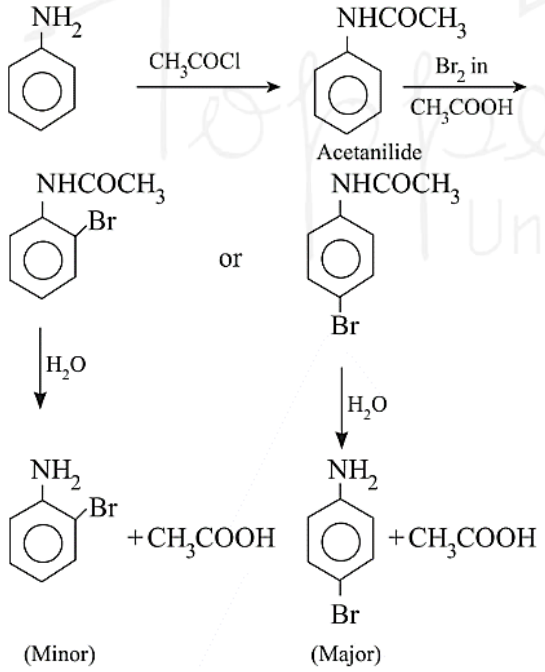


- **Halogenation**

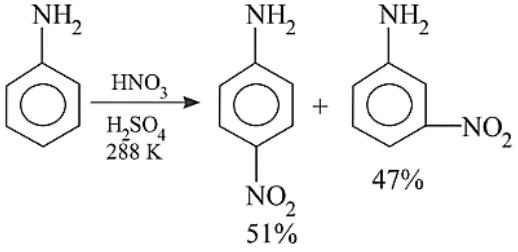


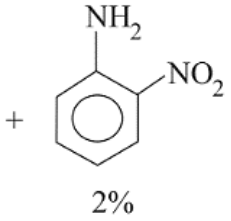
Facts to Remember:

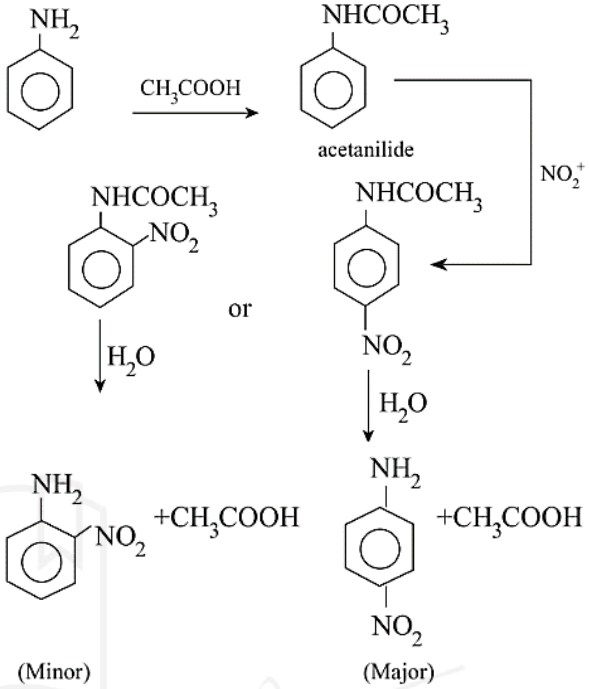
In order to convert aniline into ortho- and para-bromoanilines, it must first be converted into acetanilide, followed by bromination.



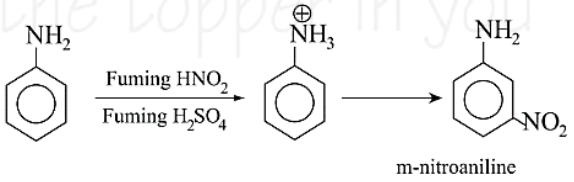
- **Nitration**



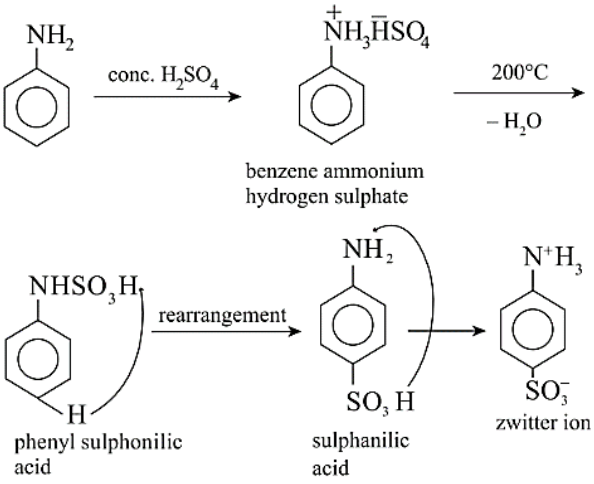




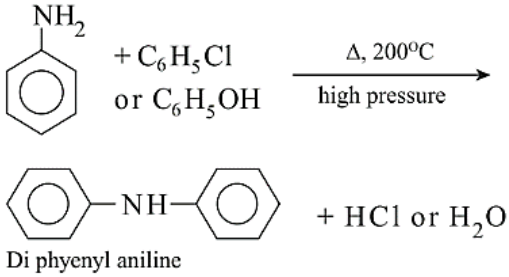
- As HNO_3 is a potent oxidising agent, it also oxidises the NH_2 group, so direct nitration cannot be performed.
- Therefore, the NH_2 group is protected by acetylation prior to nitration.



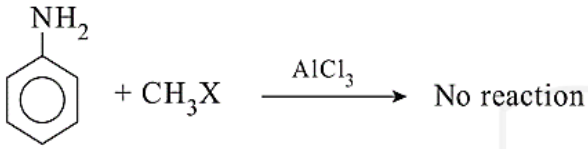
- **Sulphonation**



- **Arylation**: Aniline reacts with chlorobenzene or phenol to give diphenyl aniline.



- **Friedel crafts reaction**: Aniline does not undergo the Friedel-Crafts reaction because it is a Lewis base, and $AlCl_3$, being an electrophile, forms a salt with it, i.e, $C_6H_5NH_2^+.\ AlCl_3^-.(-NH_2AlCl_3^-$ is a strong deactivating group)

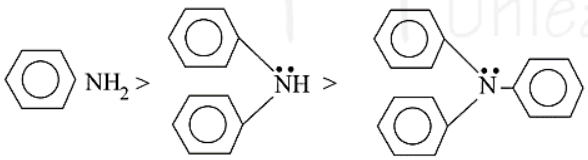


Reactions Due to NH_2 Group

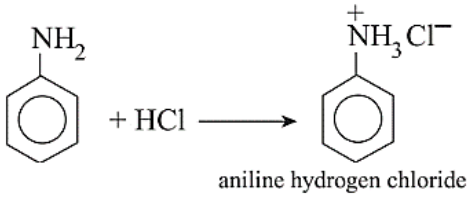
Basic nature

- Although its nitrogen atom has a lone pair of electrons, they are delocalized due to resonance, making aniline a weak base.
- Basic nature $\propto \frac{1}{\text{Resonance}}$

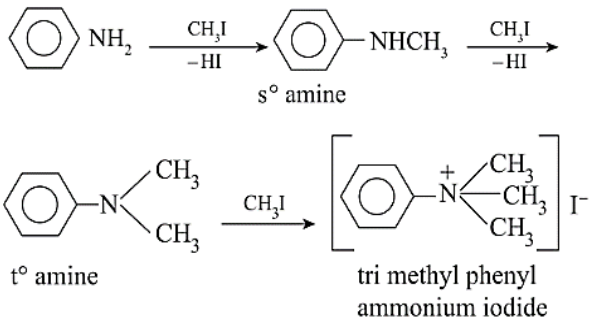
Example:



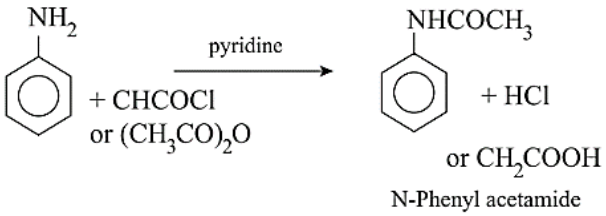
- **Salt formation**



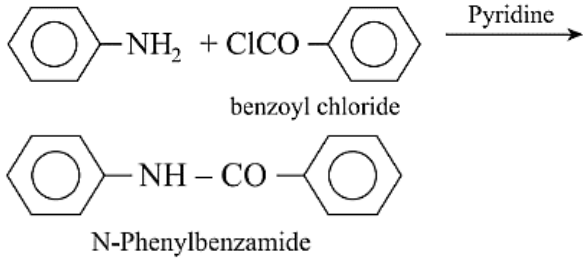
- **Alkylation**



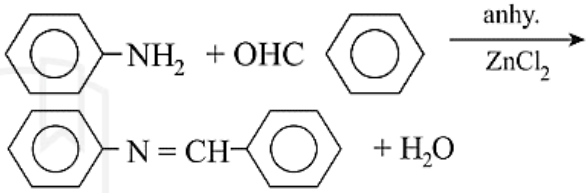
- **Acylation**



- **Benzylation (schotten bauman reaction)**

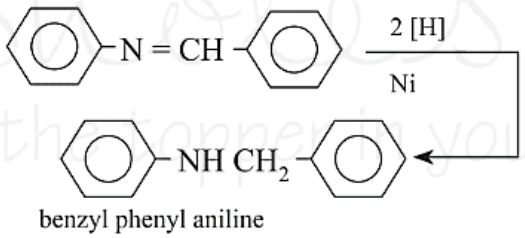


- **With benzaldehyde**

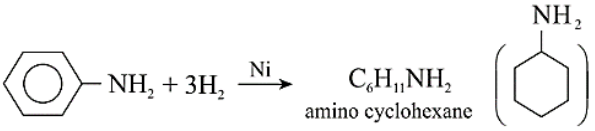


Benzal aniline or
Schiff's base or Anils or benzilidine

- **Schiff base** on **hydrogenation**, results in the formation of **benzylphenyl aniline**.



- **Reduction**



- **Carbylamine reaction**
  - This is a **primary amines** and **chloroform test**.
  - Here, **aromatic**, **foul-smelling isocyanites** are produced, and **dichlorocarbene** is the **intermediate product**.