
UNIT-8 ORGANIC COMPOUNDS CONTAINING NITROGEN

CONTENTS:

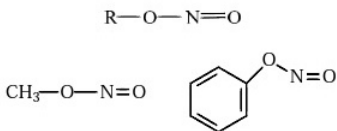
- 8.1 Objectives
- 8.2 Introduction
- 8.3 Structure of nitro-compounds
- 8.4 Nomenclature of nitro compounds
- 8.5 Nitroarenes
- 8.6 Preparation of nitroarenes
- 8.7 Physical properties of nitroalkanes
- 8.8 Chemical reactions of nitroalkanes
- 8.9 Mechanism of nucleophilic substitution in nitroarenes
- 8.10 Reduction of nitroarenes in different conditions
- 8.11 Picric acid (2, 4, 6- trinitrophenol)
- 8.12 Physical properties of picric acid
- 8.13 Chemical properties of picric acid
- 8.14 Summary
- 8.15 Terminal questions
- 8.16 Answers (MCQ)
- 8.17 References

8.3 STRUCTURE OF NITRO COMPOUNDS

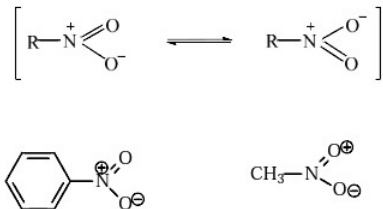
The nitro group is an ambident group and is capable of getting attached to carbon chain through nitrogen as well as through oxygen ($-O-N=O$) atom.



The compound in which the $-\text{NO}_2$ group is linked to the alkyl or aryl group through oxygen atom are called nitrites. Nitrites are isomeric with nitro compounds. These compounds are also known as alkyl esters of nitrous acid. The general formula of an alkyl nitrite is as:



The nitrogen is trigonal planar with a bond angles of 120° , there are two resonance forms so implying that the two oxygen's are equivalent.



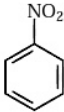
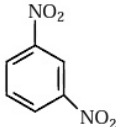
8.4 NOMENCLATURE OF NITRO COMPOUNDS

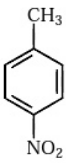
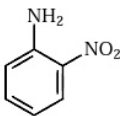
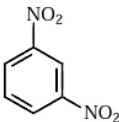
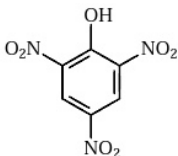
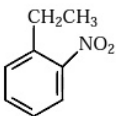
In IUPAC system, nitro compounds are named by prefixing "nitro" before the name of hydrocarbon in which the nitro group is substituted. Arabic numerals are used to indicate the position of nitro group and other substitutes if any.

Aliphatic nitro compounds:

COMPOUNDS	IUPAC NAME
\downarrow CH_3NO_2	\downarrow nitromethane
$\text{CH}_3\text{CH}_2\text{NO}_2$	nitroethane
$\text{CH}_3\text{CH}_2\text{CH}_2\text{NO}_2$	1- nitropropane
$\begin{array}{c} \text{NO}_2 \\ \\ \text{CH}_3-\text{CH}-\text{CH}_3 \end{array}$	2- nitropropane
$\begin{array}{c} \text{NO}_2 \\ \\ \text{CH}_3-\text{C}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	2- methyl - 2- nitropropane

Aromatic nitro compounds

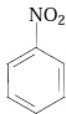
COMPOUNDS	IUPAC NAME
\downarrow 	\downarrow nitrobenzene
	m- nitrobenzene

COMPOUNDS	IUPAC NAME
	p- nitrotoluene
	o- nitroaniline
	m - dinitrobenzene
	2, 4, 6 - trinitrophenol
	2 - nitroethylbenzene

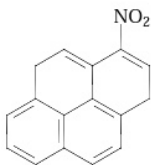
8.5 NITROARENES

Nitroarenes are organic compounds consist at least one $-\text{NO}_2$ group attached to an aromatic ring *e.g.* nitrobenzene, *o*-nitrotoluene, *p*-nitrotoluene, 4-nitrophenol, 2,6-dinitrotoluene, 2,4,6-trinitrotoluene, 1,3,5-trinitrobenzene etc. These compounds are mainly included:

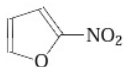
1. One or two nitrated fused ring ($\text{NO}_2\text{-Ar}$) compounds (e.g. nitrobenzene)
2. Nitrated polycyclic aromatic hydrocarbons ($\text{NO}_2\text{-PAH}$) (e.g. 1-nitropyrene)
3. Nitrated heterocyclic compounds (e.g. nitrofurans, nitropyridine etc.)



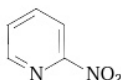
nitrobenzene



1 - nitropyrene

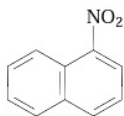


nitrofurans

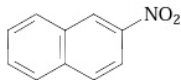


nitropyridine

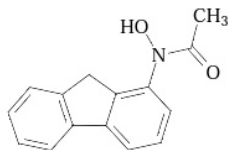
Nitroarenes are mainly exhausted in the atmosphere from combustion sources by the incomplete combustion of fossil fuels. Nitroarenes have been detected in particulate matter from diesel engine emissions, gasoline engine emissions, kerosene heaters, gas burners, motor oils, coal fly ash, extracts of coke-oven emissions, carbon black, cigarette smoke and grilled chicken. Nitroarenes have also been found in the indoor environment in particulate emissions from kerosene heaters, home heaters, gas burners and wood burning stoves used for cooking. Recent studies showed that several nitrated polycyclic aromatic hydrocarbons causes cancer. 1-nitronaphthalene, 2-nitronaphthalene, *N*-hydroxy-2-acetyl amino fluorene, 2-nitro fluorene, 1-nitropyrene, 1,8-dinitropyrene; nitroarenes have been reported as carcinogens.



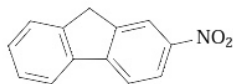
1 - nitronaphthalene



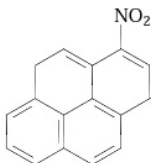
2 - nitronaphthalene



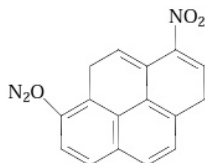
N - hydroxy- 2- acetyl amino fluorene



2 - nitrofluorene



1 - nitropyrene



1, 8 - dinitropyrene

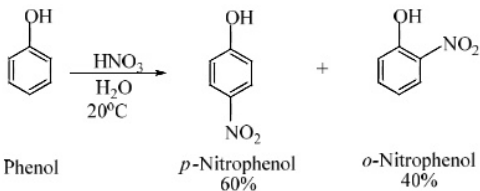
8.6 PREPARATION OF NITROARENES

Nitroarenes can be prepared by the following general methods:

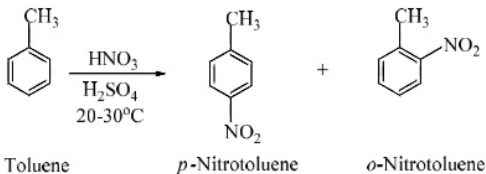
1. By the nitration of aromatics: The aromatic nitro compounds can be prepared by the direct nitration of aromatics. The formation of nitroarene depends upon the temperature, nature of the nitrated aromatic compound and nature of reagent used. For example, nitrobenzene is prepared by the direct nitration of benzene using concentrated HNO_3 and H_2SO_4 at about $30-40^\circ\text{C}$.



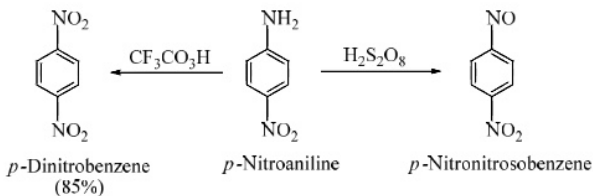
The nitrophenol is prepared by the nitration of phenol in presence of HNO_3 and H_2O at 20°C .



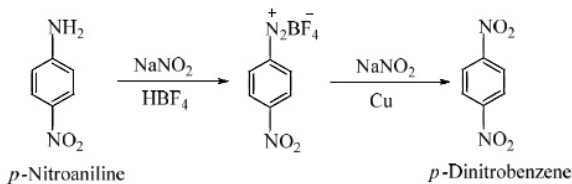
Nitrotoluene can be prepared by the nitration of toluene with concentrated HNO_3 and H_2SO_4 at about $20-30^\circ\text{C}$.



2. By the oxidation of amino group to nitro group: *p*-dinitrobenzene can be prepared by the oxidation of amino group into nitro group with per-acids such as persulphuric acid ($\text{H}_2\text{S}_2\text{O}_8$) and peroxy trifluoroacetic acid ($\text{CF}_3\text{CO}_3\text{H}$).



3. By the replacement of amino group by nitro group: The $-\text{NH}_2$ group in aromatic group can be replaced by treating the compound with $\text{NaNO}_2/\text{HBF}_4$ as follow



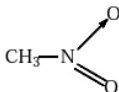
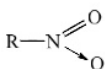
8.7 PHYSICAL PROPERTIES OF NITROALKANES

The nitroalkanes possess following physical properties

1. Most nitro compounds are yellow crystalline solids; few are pale yellow liquids (e.g. nitrobenzene) with strong characteristic odor, whereas nitro-alkanes are colorless oily liquids with pleasant smell.
2. Nitro compounds are insoluble in water but soluble in organic solvents.
3. The density of nitro compounds is greater than 1, therefore they are heavier than water.
4. Nitro compounds have high boiling points than their corresponding hydrocarbons due to high polarity. Their melting and boiling points increase with the number of nitro groups present. For example, the boiling point of nitrobenzene is 211°C whereas the boiling point of *m*-dinitrobenzene is 303°C .

- Aromatic nitro compounds are used as a solvent in many inorganic reactions.
- Aromatic nitro compounds such as 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitrobenzene (TNB), Research and development explosive (RDX) are highly toxic and used as explosives.

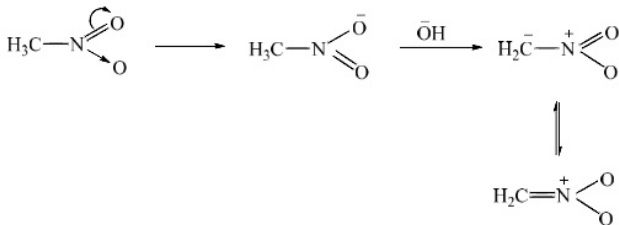
8.8 CHEMICAL PROPERTIES OF NITROALKANES



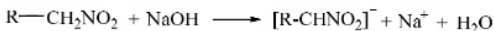
Nitroalkanes are nitro derivatives of alkanes obtained by the replacement of a hydrogen atom by a nitro group. They are isomeric with alkyl nitriles. Nitroalkanes are named by prefixing 'nitro' to the name of the parent hydrocarbon *e.g.*, $\text{C}_2\text{H}_5\text{NO}_2$ (nitroethane), $\text{C}_3\text{H}_7\text{NO}_2$ (nitropropane) etc.

Nitroalkanes may be primary, secondary or tertiary according to the nitro group attached to a primary, secondary and tertiary carbon. They are colorless liquids having pleasant odor. Nitromethane is sparingly soluble in water while higher nitroalkanes are insoluble in water but soluble in organic solvents. They have high boiling points. They are highly polar organic compounds.

1. Acidic character: The nitroalkanes containing α -hydrogen atoms exhibit acidic character due to the electron-withdrawing nature of the nitro group.

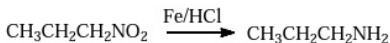
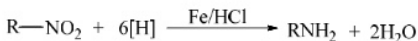


Nitroalkanes containing α -hydrogen react with a strong alkali to form salts.



2. Reduction: Nitro compounds can be reduced to primary amines under a variety of conditions. Various reduction stages of the nitro group are given below: The final product depends upon the pH of the reaction medium and nature of the reducing agent.

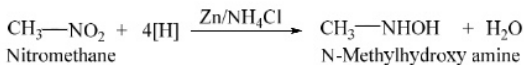
(i) Reduction in acidic medium: Nitroalkanes can be reduced to the corresponding primary amines by a combination of active metals (Zn, Fe or Sn) and concentrated hydrochloric acid (HCl).



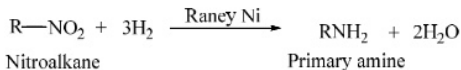
(ii) Reduction in neutral medium: Reduction with zinc dust and ammonium chloride solution in neutral medium, nitroalkanes are converted into corresponding *N*-alkyl hydroxyl amines.



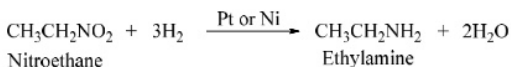
Nitromethane on reduction with zinc dust and ammonium chloride solution in neutral medium converted into *N*-methylhydroxy amine.



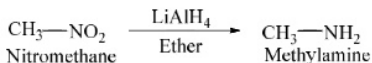
(iii) Catalytic reduction: The nitro group of an aliphatic and aromatic nitro compound is easily reduced to corresponding primary amines with hydrogen using raney Ni, Pt or Pd catalyst.



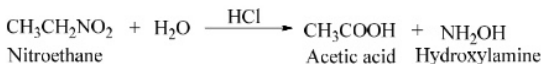
The nitroethane is reduced to ethylamine with Pt or Ni catalyst.



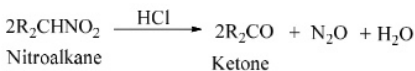
(iv) Reduction with metal hydrides: Nitroalkanes are easily reduced to corresponding primary amines with LiAlH_4 .



3. Hydrolysis: When primary nitroalkanes are heated with boiling HCl or H_2SO_4 undergo hydrolysis to form carboxylic acid and corresponding salt of hydroxyl amine. This reaction is used for the manufacturing of hydroxylamine.

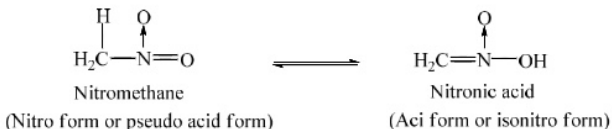


Secondary nitroalkanes hydrolyze with boiling HCl to give ketones and nitrous oxide.



Tertiary nitroalkanes, however do not generally undergo hydrolysis with hydrochloric acid.

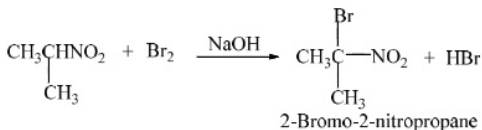
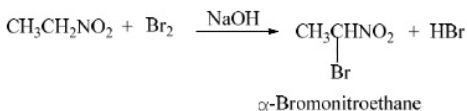
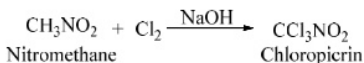
4. Tautomerism: Nitroalkanes containing α -hydrogen atoms, *i.e.*, primary and secondary nitroalkanes, show tautomerism. For example, nitromethane exists in two tautomeric forms, nitro form and isonitro form.



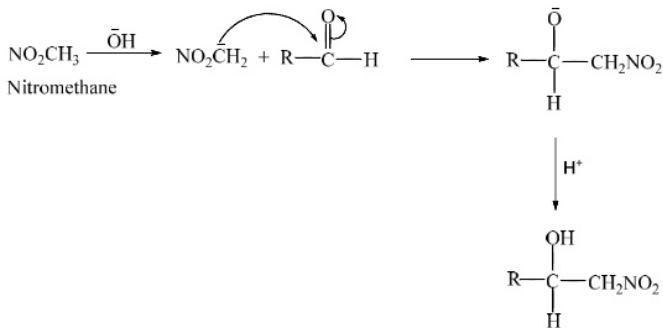
The nitro form is often called *pseudo acid form* whereas the aci-form is called *nitronic acid*. Similarly, nitroethane, 1-nitropropane, 2-nitropropane, show tautomerism whereas

aromatic nitro compounds like nitrobenzene, *m*-dinitrobenzene etc., and tertiary nitro compounds do not show tautomerism due to the absence of α -hydrogen atom on α -carbon atom.

5. Halogenation: Primary and secondary nitroalkanes on treatment with halogen (chlorine or bromine) in presence of alkali form halonitroalkanes. During this reaction, all three hydrogen atoms of nitroalkanes are replaced by the halogen atoms.

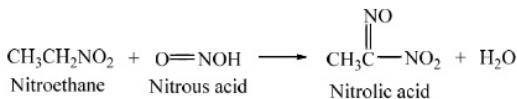


6. Reaction with aldehydes: Nitroalkanes having α -hydrogen can undergo nucleophilic addition reaction with aldehydes similar to aldol type addition reaction.

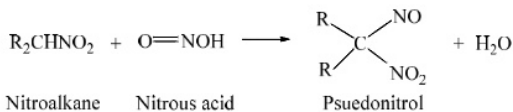


7. Action with nitrous acid: Nitroalkanes on reaction with nitrous acid give different products depending upon the type of nitro compound.

Primary nitroalkanes on reaction with nitrous acid give nitrolic acids which dissolve in alkalies to form a red solution.



Whereas, secondary nitroalkanes on reaction with nitrous acid give blue colored pseudo-nitroles which do not dissolve in alkali.



Tertiary nitroalkanes do not react with nitrous acid since they do not have α -hydrogen atom.

Uses of nitro compounds: Nitroalkanes *e.g.* nitromethane, nitroethane etc. and nitrobenzene are extensively used as solvent in industry.

1. Nitroarenes are important intermediates in the manufacture of polymers detergents, dyes and pharmaceuticals.

2. Nitroarenes are also used for the preparation of explosives such as 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitrobenzene (TNB), research and development explosive (RDX).

3. Chloropicrin is used as an insecticide.

8.9 MECHANISM OF NUCLEOPHILIC SUBSTITUTION IN NITROARENES

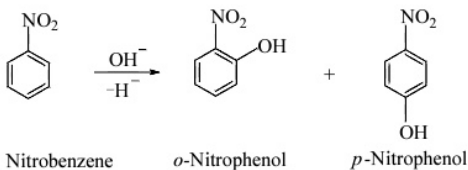
Nucleophilic aromatic substitution occurs with a variety of strong nucleophiles, including -OH , -OR , -NH_2 , -SR , and neutral nucleophiles such as NH_3 and RNH_2 . The mechanism of nucleophilic aromatic substitution is an addition-elimination type; therefore the mechanism of these reactions has two important steps:

1. Addition of the nucleophile to form a resonance-stabilized carbanion

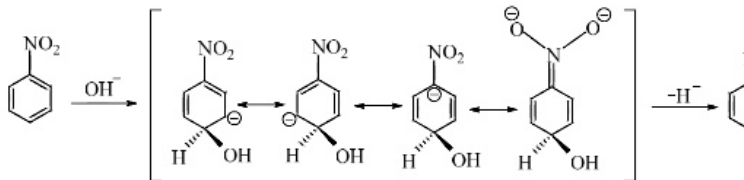
2. Elimination of hydrogen or halogen leaving group.

For example: 1. Nucleophilic aromatic substitution in nitrobenzene

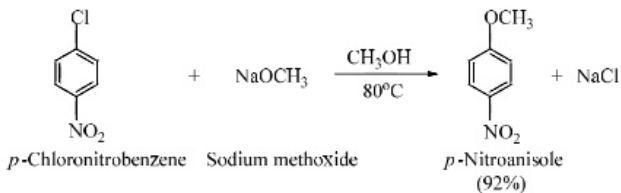
Nitrobenzene reacts with -OH nucleophile to form the *o*-nitrophenol and *p*-nitrophenol.



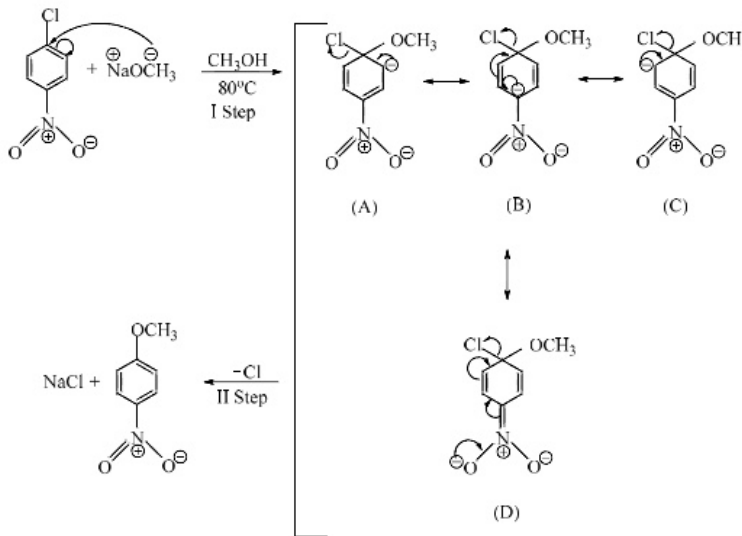
Mechanism: The mechanism for the formation of *p*-nitrophenol from nitrobenzene is as follows:



2. Addition elimination mechanism of nitrochlorobenzene: The nitro substituted aryl halides undergo reaction with nucleophiles such as ammonia and hydroxide, where the chlorine is eliminated/substituted *e.g.* *p*-chloronitrobenzene reacts with sodium methoxide at 85 °C to form the *p*-nitroanisole.



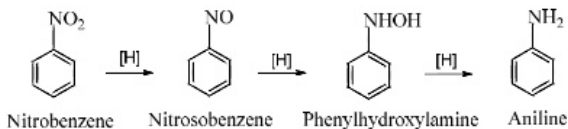
The mechanism of the formation of *p*- nitroanisole from *p*-chloronitrobenzene is as follows:



8.10 REDUCTION OF NITROARENES IN DIFFERENT CONDITIONS

The nitroarenes give different products while reduced in different reaction conditions such as nature of reducing agents and the pH of the reaction medium as follow

(i) Reduction of nitroarenes in acidic medium: Nitroarenes can be easily reduced to corresponding primary aryl amines by tin metal and hydrochloric acid. For example, the reduction of nitrobenzene with tin metal and hydrochloric acid gives aniline.

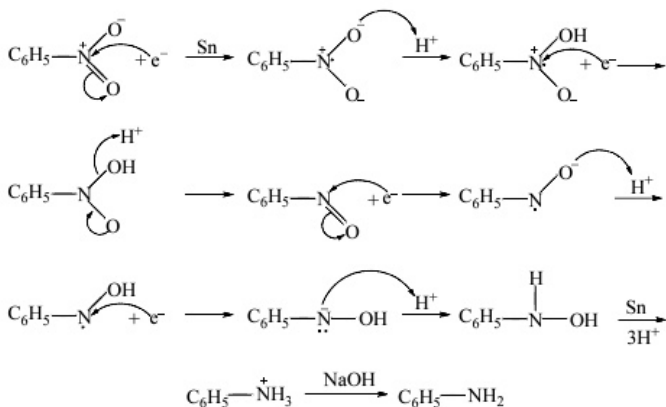


Mechanism:

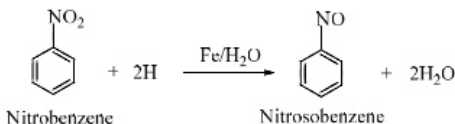
1. The reduction of nitrobenzene to aniline is an example of oxidation reduction reaction in which the Sn^0 is oxidized to stannic ion Sn^{4+} by the donation of four electrons to substrate to form an intermediate.

2. This intermediate radical is then ion protonated, the protons are provided by the acid.

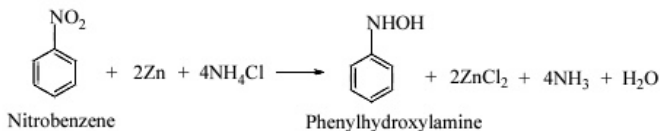
3. The oxygen atom from the nitro group is removed as water molecule. The scheme of this reaction mechanism is as:



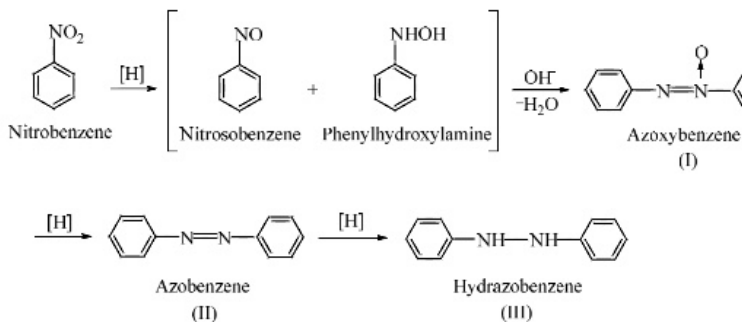
(ii) Reduction of nitroarenes in neutral medium: With iron and steam a nitro compound gets reduced to nitroso compounds.



The reduction of nitrobenzene with zinc metal and ammonium chloride or calcium chloride gives only *N*-phenylhydroxylamine. The hydroxylamines are reducing agents and can reduce *Tollen's reagent*.



(iii) Reduction of nitroarenes in alkaline medium: Whilst acidic and neutral reduction result in the formation of mono-nuclear compounds, reaction in alkaline medium yields a variety of binuclear compounds due to the interaction of nitroso- and hydroxylamine derivatives formed during the reduction. The reduction of nitrobenzene yields different products depending upon the nature of reducing agent used. The scheme of alkaline reduction is given below:

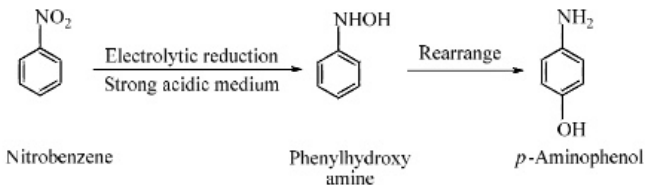
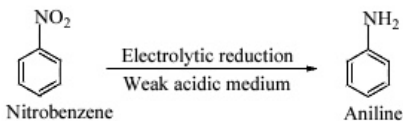


(i) The product-I, azoxybenzene is formed by the reduction of nitrobenzene with alkaline sodium arsenite ($\text{Na}_3\text{AsO}_3/\text{NaOH}$).

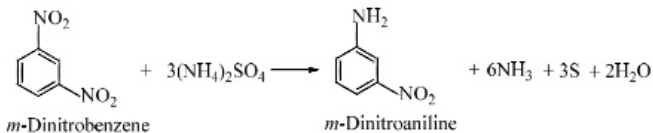
(ii) The product-II, azobenzene is formed, when nitrobenzene is reduced with zinc dust and methanolic caustic soda solution, or by alkaline stannite.

(iii) The product-III, hydrazobenzene is obtained by reduction of nitrobenzene with zinc dust and aqueous sodium hydroxide (Zn/NaOH).

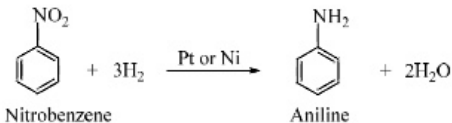
(iv) **Electrolytic reduction:** Electrolytic reduction of nitrobenzene in weakly acidic medium gives aniline but in strongly acidic medium, it gives *p*-aminophenol obviously through the acid catalyzed rearrangement of initially formed phenyl hydroxyl amine.



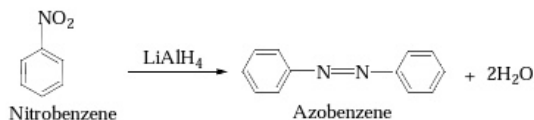
(v) **Selective reduction:** If two or more nitro groups are present in the benzene ring, it is possible to reduce one of them without affecting the others. Such reductions are called selective reductions. For example, reduction of *m*-dinitrobenzene with sodium or ammonium sulphide gives *m*-nitroaniline. This reduction of nitro compounds with sulphides and polysulphides is called **Zinin reduction**.



(vi) **Catalytic reduction:** Nitrobenzene is reduced to aniline with hydrogen using Pt or Ni catalyst.

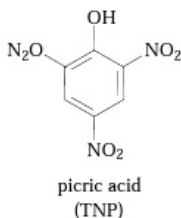


(vii) **Reduction with metal hydride:** Aromatic nitro compounds on reduction with LiAlH_4 give azo compounds.



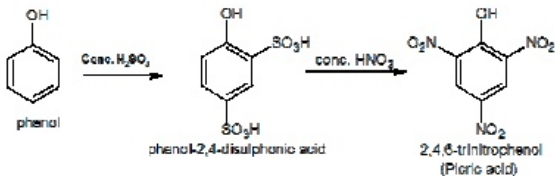
8.11 PICRIC ACID (2, 4, 6-TRINITROPHENOL)

Picric acid is the chemical compound formally called 2, 4, 6-trinitrophenol (TNP). It has a chemical formula $\text{C}_6\text{H}_3\text{N}_3\text{O}_7$. Its name comes from a Greek word *pikros* means "bitter", reflecting the bitter taste of picric acid.

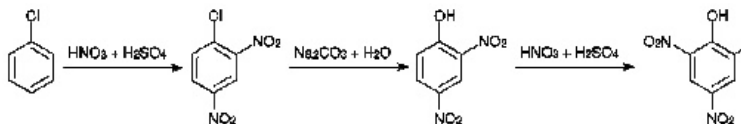


Preparation of picric acid: TNP can be synthesized by various methods as:

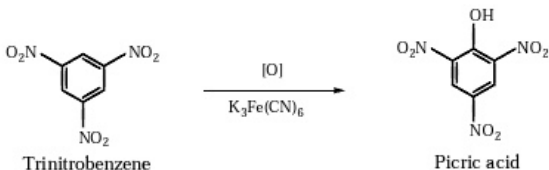
1. From phenol: Picric acid can be prepared from phenol by sulphonation followed by the nitration.



2. From chlorobenzene: Picric acid can be obtained by the reaction of nitric acid followed by hydrolysis and followed by nitration.



3. From trinitro benzene: Picric acid can be prepared by the oxidation of sym-trinitrobenzene with potassium ferricyanide.

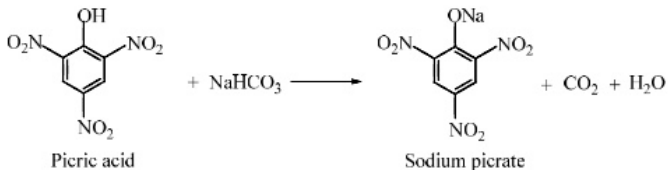


8.12 PHYSICAL PROPERTIES OF PICRIC ACID

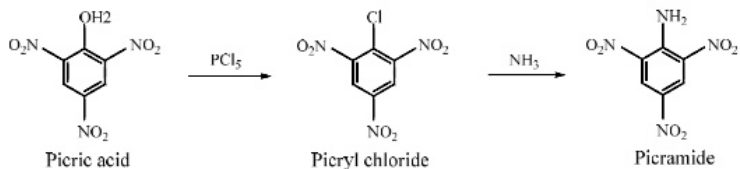
Picric acid is a yellow crystalline solid and one of the most acidic phenols. It is volatile, flammable, highly toxic and bitter in taste. Its melting point is 122°C . It is sparingly soluble in water, but soluble in hot water, alcohols and ethers. It is explosive when dry and forms picrates when exposed with metals. Picric acid is especially hazardous because it is volatile and slowly sublimates even at room temperature.

8.13 CHEMICAL PROPERTIES OF PICRIC ACID:

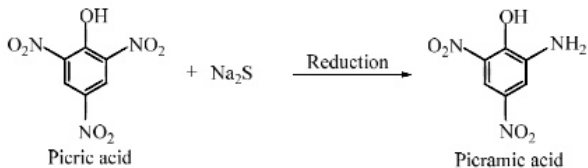
1. Picric acid is much stronger acidic than phenol due to $-\text{NO}_2$ functional group. Picric acid reacts with NaHCO_3 to liberate CO_2 .



2. Picric acid on reaction with phosphorus pentachloride forms picryl chloride.



3. On reduction with sodium sulphide (Na_2S) in presence of water, picric acid gives picramic acid.



Uses: Picric acid is used in electric batteries, leather industry, dyes, pigments, inks, paints, manufacture of colored glass, textile mordents, as a laboratory reagent, in matches and explosives.