NITRO SOMPOUNDS

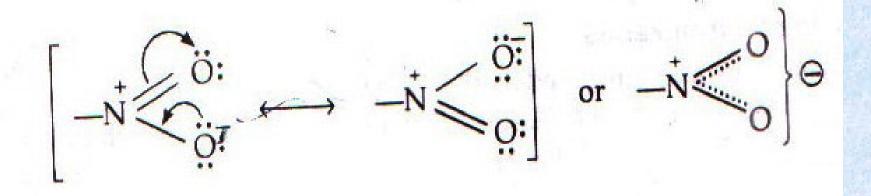
Introduction

Nitro compounds are an important class of organic compounds which may be regarded as derived from hydrocarbons by the replacement of one or more hydrogen atoms by nitro (NO_2) groups. Nitro arenes (i.e. nitro compounds in which $-NO_2$ group is directly attached to benzene ring) have been used as synthetic reagents since long.

Structure of Nitro group

Nitro group is quite often represented as containing a double bond between nitrogen and one oxygen and a co-ordinate or dative bond between nitrogen and other oxygen i.e. -N

But actually nitro group is stabilized by resonance and is a hybrid of two equal contributing structures:



Nomenclature of nitro compounds

Nitro compounds are named by writing the word nitro before the name of the parent compound.

PREPARATION OF NITRO COMPOUNDS

Nitro alkanes are usually prepared by the following methods:

1: VAPOUR PHASE NITRATION OF ALKANES: This reaction involves the substitution of a hydrogen atom of the alkane by a nitro *group*. It is carried out in the *vapour state* by heating the alkane with nitric acid at about 700k.

$$R-H+HNO_3$$
 RNO₂+H₂O

LIMITATIONS OF THE PROCESS: During the nitration of higher alkanes all possible isomeric nitro products are formed. More over rupture of carbon carbon bonds also take place leading to the formation of nitro alkanescontaining lesser number of carbon atoms.

2:ACTION OF SILVER NITRITE ON ALKYL HALIDES: Thisn is the metod generally employed for the laboratory preparion of nitro alkanes. When heated with silver nitrate alkyl halides undergo *nucleophilic substitution* to form nitro alkanes along with small quantities of alkyl nitrites.

$$R-X + AgNO_2 \longrightarrow R-NO_2 + R-O-N=O + AgBr$$
Alkyl halide

Nitroalkane
(Major product)

(Minor product)

MECHANISM

3: **OXIDATION OF AMINES:** When an amine in which the amino group is attached to a tertiary carbon atom is oxidised potassium permanganate, a tertiary nitro alkane is optained.

$$\begin{array}{c} R \\ R \\ -C \\ -NH_2 \\ R \end{array} + 3O \xrightarrow{KMnO_4} \begin{array}{c} R \\ R \\ -C \\ -NO_2 \\ R \end{array} + H_2O \\ R \\ Amine \end{array}$$

$$\begin{array}{c} R \\ -C \\ -NO_2 \\ R \end{array} + H_2O \\ -R \\ Tert. \ nitroalkane \end{array}$$

PREPARATION OF NITROARENES

Nitroarenes are almost invariably prepared by direct nitration of arenes . The nitrating agents generally used are

- 1: Concentrated or fuming nitric acid.
- 2: Mixture of concentrated or fuming nitric acid and concentrated sulphuric acid.

3: Mixture of concentrated nitric acid and acetic and anhydride or boron trifluoride.

4: Acetyl nitrate

5: Nitogen peroxide in the presence of anhydrous aluminium chloride.

Choice of nitrating agent to be used for nitation of a given compound depends upon following two factors:

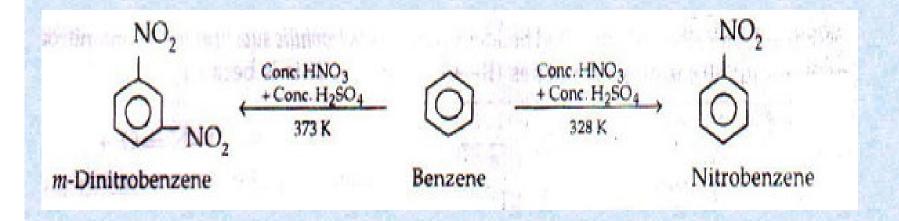
1: Nature of compound to be nitrated.

2: No of nitro groups to be introduced.

In the nitration of aromatic compouds containing electron releasing or activating groups

Such as $-NH_2$, -- OH, -- CH_3 , the reation takes place readily at room temperature by emplyoing conc. HNO_3 .

For nitrating compounds containing electron attracting or deactivating group such as – COOH or when it is desired to introduce more than one nitro group a suitably strong nitrating mixture has to employed and the reaction is carried out at higher temperature. Nitro benzene and m-dinitrobenzene can be obtained from benzene under the conditions shown below:



MECHANISM OF NITRATION

Nitration of aromatic compounds involves a nitronium ion as the attacking electrophile . The mechanism may be summmed up as follows:

1: generation of electrophile :

$$HONO_2 + 2H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2HSO_4^-$$

Nitronium ion

2: Formation of carbocation

: Proton transfer from the carbocation to yield the final product

$$H \longrightarrow NO_2 \longrightarrow OO_2 \longrightarrow H_2SO_4$$

COMPARISON OF NITRATION OF ARENES AND NITRATION OF ALKANES

It may be noted that nitration of arenes takes place at relatively low temperature where as nitration of alkanes requires a very high temperature. This may be due to the fact that the nitration of arenes involves the initial formation of electrophilic reagent while the nitration of alkanes is supposed to involve the initial formation of free radical. The formation of free radical takes through homolysis requires stronger condition than the formation of electrophile that takes place through heterolysis. As such nitration of arenes takes place more easily than nitration of alkanes

PHYSICAL PROPERTIES OF NITRO COMPOUNDS

Nitro alkanes have pleasant smell and are sparingly soluble in water. Aromatic nitro compounds except benzene are yellow crystalline solids. Nitro compounds are heavier than water.

Due to the presence of highly polar nitro group, nitro compounds have strong dipole-dipole interaction. hence they posses high boiling points, much higher than hydrocarbons of comparable molecular masses.

CHEMICAL REACTIONS OF NITRO ALKANES

1: **ACIDIC NATURE**: Nitro alkanes containing alpha hydrogen atoms exhibit acidic character

 $RCH_2NO_2 + NaOH \longrightarrow [RCHNO_2]^-Na^+ + H_2O$

2 REDUCTION OF NITRO ALKANES:

$$R - NO_2 \longrightarrow R - NO \longrightarrow R - NHOH \longrightarrow R - NH_2$$
Nitro Nitroso Substituted Primary compound compound hydroxylamine amine

The product obtained depend upon the nature of the reducing agent and Ph OF THE REACTION MEDIUM.

ACIDIC MEDIUM: primary amines are formed.

$$R$$
— NO_2 + $6H$ $\xrightarrow{Fe/HCl}$ R — NH_2 + $2H_2O$ $Primary amine$

CATALYTIC REDUCTION:

$$R-NO_2 \xrightarrow{\text{Li Al H}_4} R-NH_2 + H_2O$$

NEUTRAL MEDIUM:hudroxyl amine derivative is obtained.

$$R-NO_2 + 4H \xrightarrow{Zn/NH_4Cl} R-NHOH + H_2O$$

Nitroalkane Alkyl hydroxylamine

3 HYDROLYSIS: When boiled with conc. HCL or H₂SO₄, primary nitro alkanes undergo hydrolysis to form carboxylic acids and the corresponding salt of hydroxylamine.

$$RCH_2NO_2 + H_2O + HCl \xrightarrow{Heat} RCOOH + NH_2OH.HCl$$

Nitroalkane (1°)

4 NEF REACTION: When sodium salts of primary and secondary nitro alkanes are hydrolysed with dil sulphuric acid aldehydes and ketones respectively are obtained. The reaction proceeds through aci nitro form of nitro alkanes.

$$2 \text{ R} - \text{CH} = \text{N} + 2 \text{H}_2 \text{SO}_4 \longrightarrow 2 \text{ R} - \text{C} = \text{O} + 2 \text{ NaHSO}_4 + \text{N}_2 \text{O} + \text{H}_2 \text{O}$$

$$\text{Aldehyde}$$
Sod. salt of primary nitroalkane (corresponding to aci form)

5 ACTION WITH NITROUS ACID:

PRIMARY NITRO ALKANES react with nitrous acid to form nitrolic acids which dissolve in NAOH to give a **RED SOLUTION**.

$$RCH_2NO_2$$
 + HONO \longrightarrow $R-C=NOH+H_2O$
Nitroalkane (1°) NO₂
Nitrolic acid
(Dissolves in NaOH to give red colour due to the formation of sodium salt)

SECONDARY NITRO ALKANES react with nitrous acid to form <u>pseudonitroles</u> which have blue colour but do not dissolve in NAOH.

$$R_2CHNO_2 + HONO \longrightarrow R_2C-N=O + H_2O$$

Nitroalkane (2°) NO_2
Pseudonitrole
(Blue colour, insoluble in NaOH)

TERTIARY NITRO ALKANES do not react with nitrous acid since they do not contain any alpha hydrogen atoms.

The above test can be used as a test for distinguishing between primary, secondary and tertiary nitro compounds.

6HALOGENATION: Primary and secondary nitro alkanes undergo halogenation at alpha

positio
$$CH_3$$
— CH_2 — NO_2 $\xrightarrow{Cl_2}$ CH_3 — $CHCl$ — NO_2 $\xrightarrow{Cl_2}$ CH_3 — CCl_2 — NO_2 $\xrightarrow{Nitroethane}$ 1-Chloronitroethane 1, 1-Dichloronitroethane

Tertiary alkanes do not undergo halogenation since they do not have alpha hydrogens. **7 CONDENSATION WITH ALDEHYDES:** Primary and secondary nitro alkanes undergo aldol type condensation with aldehydes in the presence of abase to form nitro alcohols.

8 MANNICH REACTION: This is a condensation reacion which involves HCHO, Ammonia or a primary or secondary amine (generally taken as hydrochloride) and a compound with atleast one active hydrogen.

CHEMICAL REACTIONS OF NITROARENES

REDUCTION IN ACIDIC MEDIUM: The nature of the final products depends upon the pH of the solution.

$$\begin{array}{c|c}
NO_2 & NH_2 \\
\hline
Or Sn/HCl & Or Sn/HCl
\end{array}$$
Nitrobenzene Aniline

MECHANISM: It involves a no. of steps in which addition of electrons and protons takes place and nitro benzene fre radical anion and nitrosobenzene free radical anions are formed as intermediates.

$$C_6H_5-\overset{\bullet}{N}=\overset{\bullet}{O} \xrightarrow{C_6H_5-\overset{\bullet}{N}} \overset{\bullet}{C_6H_5-\overset{\bullet}{N}} \overset{\bullet}{C_6H_5-\overset{\bullet}{N}} \overset{\bullet}{C_6H_5-\overset{\bullet}{N}} \overset{\bullet}{C_6H_5-\overset{\bullet}{N}} \overset{\bullet}{O} \xrightarrow{-OH^-} \overset{\bullet}{O} \overset{\bullet}{N} \overset{\bullet}{O} \overset{\bullet}{A} \overset{\bullet}{O} \overset{\bullet}{O$$

Catalytic reduction also leads to the formation of aniline Reduction in neutral medium: The reaction stops at hydroxylamine stage.

$$O_{2}$$

$$Z_{D/aq.NH_{4}Cl} \rightarrow O + H_{2}O$$

Alkaline medium:

$$NO_{2}$$

$$NO_{2}$$

$$NO_{2}$$

$$NO_{2}$$

$$NO_{3}/NaOH in CH_{3}OH$$

$$NO_{4}/NaOH in CH_{3}OH$$

$$NO_{5}/NaOH$$

$$NO_{5}/NaOH$$

$$NO_{6}/NaOH$$

$$NO_{6}/NaOH$$

$$NO_{6}/NaOH$$

$$NO_{6}/NaOH$$

$$NO_{7}/NaOH$$

$$NO_{8}/NaOH$$

$$NO_{8}/NaOH$$

$$NO_{9}/NaOH$$

$$NO_{9}/NaO$$

Reduction with liAlH4:

$$2 \bigcirc -NO_2 \xrightarrow{LiAlH_4} \bigcirc -N = N - \bigcirc$$
Azobenzene

Electrolytic reduction: In weakly acidic medium nitrobenzene gives aniline but in strongly acidic medium p-aminophenol is formed.

Selective reduction:In case of compounds containing more than one nitro group selective reduction is carried out with a mild reducing agent such as ammonium hydrosulphide.

This reduction is called zinin reduction.

$$NO_2$$

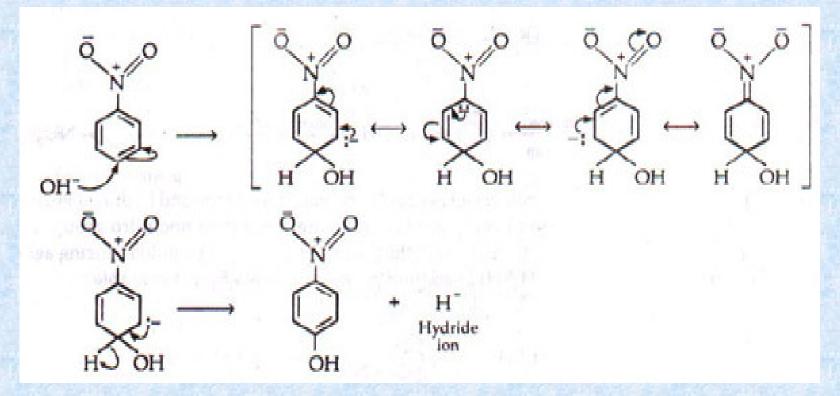
 NO_2
 $M-Dinitrobenzene$
 NO_2
 NO_2
 NO_2
 NH_2
 NH_2
 NH_2
 NH_2
 $M-Nitroaniline$

2Electrolytic substitution: Under strong conditions, nitro compounds may undergo electrophilic substitution at meta position.

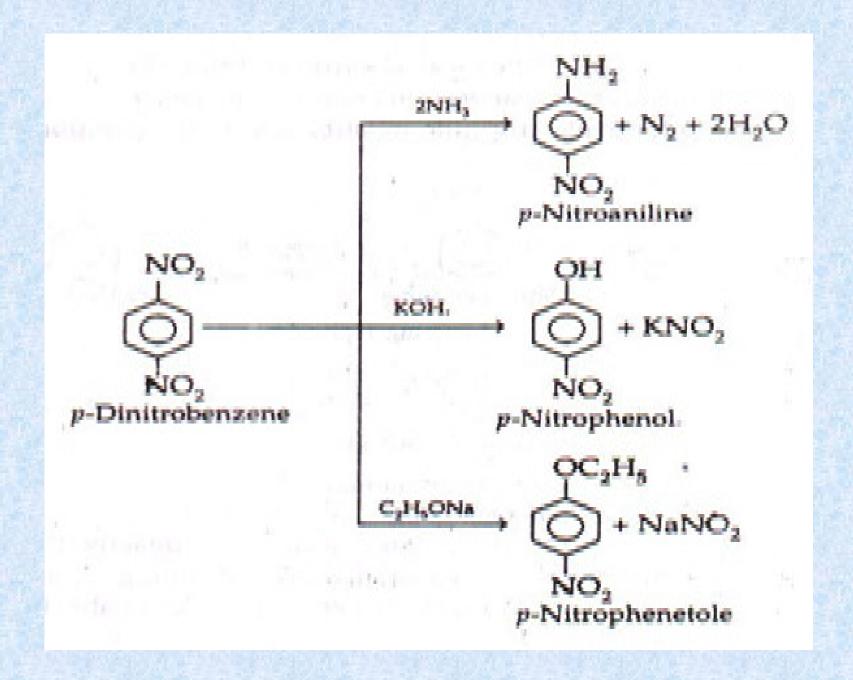
$$\begin{array}{c} NO_2 \\ \hline \\ m\text{-Chloronitrobenzene} \end{array} \begin{array}{c} NO_2 \\ \hline \\ Nitrobenzene \end{array} \begin{array}{c} Fuming HNO_3 \\ \hline \\ Fonc. H_2SO_4 \end{array} \begin{array}{c} NO_2 \\ \hline \\ m\text{-Dinitrobenzene} \end{array}$$

3Nucleophilic substitution:Nitro benzene on heating with sodium hydroxide gives small amounts of ortho and para nitro phenols.

Mechanism:



4 Replacement of the nitro group:In case of polynitro compounds one of the nitro groups can be replaced by nucleophilic groups.



Picric acid

PREPARATION

1 From phenol:

OH

$$H_2SO_3$$
 SO_3H
 $Phenol-2, 4-disulphonic acid$

OH

OH

OH

 OH
 OOH
 OOH

2 From chlorobenzene:

Physical properties

It is a crystalline solid sparingly soluble in water but readily soluble in alcohol and ether.

Chemical properties

1 Acidic character: Due to the presence of three nitro groups it is much stronger acid than phenols.

$$O_{2}N \xrightarrow{O_{2}} NO_{2} \xrightarrow{NaHCO_{3}} O_{2}N \xrightarrow{O_{2}N} NO_{2} + CO_{2} + H_{2}O$$

$$NO_{2}$$
Picric acid
Sodium picrate

Reaction with PCI₅

$$O_{2}N \xrightarrow{O_{2}N} O_{2} + PCl_{5} \longrightarrow O_{2}N \xrightarrow{Cl} NO_{2}$$

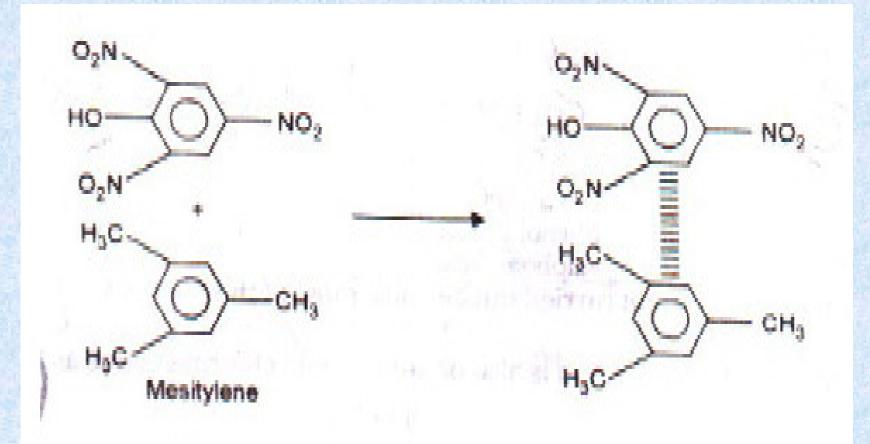
$$O_{2}N \xrightarrow{NO_{2}} O_{2}N \xrightarrow{NO_{2}$$

3 Reaction with Na₂S:

$$\begin{array}{c|c}
OH & OH \\
O_2N & O_2N & O_2N & O_2N \\
\hline
NO_2 & NO_2
\end{array}$$

$$\begin{array}{c}
NO_2 \\
Picramic acid
\end{array}$$

4 Formation with picrates: picric acid reacts with electron rich aromatic compounds such as naphthalene and mesitylenene to form addition products called charge transfer complexes.



USES:

PICRIC ACID IS USED AS:

- 1 An antisceptic and a dye for wooland silk.
- 2 In the manufacture of explosives.
- 3 As a laboratory reagent for the identification of poly nuclear hydrocarbons, amines, alkaloids etc.