15.1 ALIPHATIC NITRO COMPOUNDS

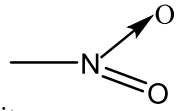
Learning outcomes
After the lesson, the students should be able to:

- Describe briefly the nomenclature and isomerism of nitro compounds.
- Show the preparation from haloalkane and alkane.
- State physical properties of nitro compounds.
- Explain the chemical properties of nitro compounds, i.e., reduction.

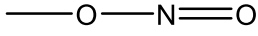
Introduction

What happens when a Haloalkane (alkyl halide) is treated separately with silver nitrite and potassium nitrite?

Organic compounds having $-NO_2$ functional group are called nitro compounds. Based on the hydrocarbon part, they can be classified as aromatic or aliphatic nitro compounds. The nitro group has the following structure, which should not be confused with the nitrite group.



nitro group



nitrite group

1. Why is nitro group is called an ambident group? *2*

Classification

Based on carbon atoms to which nitro group is bonded, the aliphatic nitro compounds can be further classified into:

1. **Primary Nitroalkane**

Here the $-NO_2$ group is bonded to primary carbon.

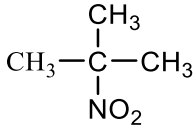
e.g., CH_3-NO_2 Nitromethane, CH_3-CH_2-NO_2 Nitroethane etc.

2. **Secondary Nitroalkane**

The nitrogen atom of the nitro group in this case is bonded with secondary carbon atom. e.g., $CH_3CH(NO_2)CH_3$ 2-nitropropane

3. **Tertiary Nitroalkane**

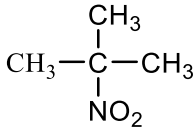
In this case, the nitro group is attached with tertiary carbon atom.



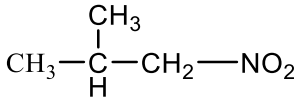
2-methyl-2-nitropropane

Nomenclature (Upto Nitrobutanes)

CH_3NO_2	Nitromethane
$CH_3CH_2NO_2$	Nitroethane
$CH_3CH_2CH_2NO_2$	1-nitropropane
CH_3-$CH(NO_2)$-CH_3	2-nitropropane
$CH_3CH_2CH_2CH_2NO_2$	1-nitrobutane
$CH_3CH_2CH\,(NO_2)CH_3$	2-nitrobutane



2-methyl-2-nitropropane



2-methyl-2-nitropropane

Isomerism

1. Chain Isomerism

Nitroalkanes with more than 3 carbon atoms exhibit this kind of isomerism. e.g., 1-nitrobutane and 2-methyl-1-nitropropane.

2. Positional Isomerism

Aliphatic nitro compounds with 3 or more carbons can exhibit such isomerism. e.g., 1-nitropropane and 2-nitropropane.

3. Functional isomers

Nitroalkanes exhibit isomerism with alkyl nitrites. E.g., Nitromethane and methyl nitrite.

2. *Why nitro group is called an ambident group?* *1*

1. The number of possible isomeric nitro compounds with molecular formula $C_4H_9O_2N$ is

   a. 2 *b. 3* *c. 4* *d. 5*

General methods of preparation

1. **From Alkanes** *(with fuming conc. Nitric acid at 400^0C)* (studied in class 11)

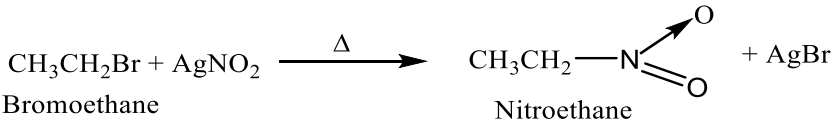
When Alkane is heated with fuming nitric acid at 400^0C (vapour phase nitration), a mixture of all possible Nitroalkanes are formed by carbon chain fission reaction of alkanes.

$$\underset{\text{Methane}}{CH_4} \xrightarrow{HNO_3,\ 400^oC} \underset{\text{Nitromethane}}{CH_3NO_2}$$

$$CH_3CH_2CH_3 \xrightarrow{HNO_3,\ 400^oC} \underset{\text{1-nitropropane}}{CH_3CH_2CH_2NO_2} + \underset{\text{2-nitropropane}}{CH_3CH(NO_2)CH_3} + \underset{\text{Nitroethane}}{CH_3CH_2NO_2} + \underset{\text{Nitromethane}}{CH_3NO_2}$$

2. **From Alkyl halides** (with Silver nitrite)(studied in haloalkanes)

When primary Alkyl halides (especially bromides and iodides is heated with aqueous or (alcoholic) ethanolic solution of Silver nitrite, Nitroalkane is obtained along with very little Alkyl nitrite. e.g.



Bromoethane — Nitroethane

But Potassium nitrite and Sodium nitrites gives *alkyl nitrite*.

3. *Give a reaction to prepare Nitroalkane from haloalkane.* 1

Physical properties

1. Generally, nitroalkanes are colourless liquids with pleasant odour, heavier than water.
2. They are soluble in organic solvents like Benzene, Ethanol etc. The lower members are sparingly soluble in water & higher members are insoluble.
3. Due to polar nature the boiling points of nitro compounds are higher than that of alkanes with comparable molecular mass.

Chemical properties

1. **Reduction:**
   a. *with Sn/HCl or Fe/HCl or Zn/HCl or H_2/Ni or Pt or $LiAlH_4$ produces primary amines*

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

Nitroalkane — Amino alkane

$CH_3CH_2NO_2 + 6\,[H] \xrightarrow{Fe/HCl} CH_3CH_2NH_2 + 2\,H_2O$

Nitroethane — Amino ethane

$CH_3CH_2CH_2NO_2 + 6\,[H] \xrightarrow{LiAlH_4} CH_3CH_2CH_2NH_2 + 2\,H_2O$

1-nitropropane — 1-aminopropane

$CH_3\underset{\displaystyle NO_2}{\underset{|}{C}}HCH_3 + 3\,H_2 \xrightarrow{Ni} CH_3\underset{\displaystyle NH_2}{\underset{|}{C}}HCH_3 + H_2O$

2-nitropropane — 2-aminopropane

4. *How does Nitroalkane react with Sn/HCl?* *1*

b. *In neutal medium($Zn/NH_4Cl(aq)$ produces N-alkylhydroxylamine*

$R-N(=O)=O + 4\,[H] \xrightarrow{Zn/NH_4Cl\ (aq)} R-N(H)-OH + H_2O$

Nitroalkane — N-alkylhydroxylamine

$CH_3-N(=O)=O + 4\,[H] \xrightarrow{Zn/NH_4Cl\ (aq)} CH_3-N(H)-OH + H_2O$

Nitromethane — N-methyl hydroxyl amine

5. *How does Nitroalkane react with Zn/NH_4Cl?* *1*
6. *How is* following *conversion carried out: Nitroethane to N-ethyl hydroxyl amine?* *1*

1. $-NO_2$ group is an example of
   a. Ambident group
   b. Reducing group
   d. Amphoteric group
   c. Auxochrome

2. Nitroethane and ethyl nitrite are
   a. Tautomers
   b. Optical isomers
   c. Metamers
   d. Functional isomers

3. Ethyl bromide reacts with alcoholic silver nitrite give
   a. Nitrolic acid
   b. Ethylnitrite
   c. Pseudonitrol
   d. Nitroethane

4. Primary nitroalkanes react with nitrous acid to form nitrolic acids which dissolve in aqueous NaOH giving
   a. Yellow colour
   b. Blue colour
   c. Intense green colour
   d. Blood red colour

5. You are provided with two organic compounds X and Y with molecular formula $C_3H_7NO_2$. The compounds X and Y probably are;
   a. Aminoethane and ethylnitrite
   b. Nitroethane ethylnitrate
   c. Nitroethane and ethylnitrolate
   d. Nitroethane and ethylnitrite

6. You are provided with an organic compound X with molecular formula C_2H_5Cl. The compound X reacts further with alc. $AgNO_2$ to produce a compound Y. The compounds X and Y probably are;
   a. Chloroethane and nitroethane
   b. Chloroethane and nitromethane
   c. Chloromethane and nitroethane
   d. Chloroethane and ethylnitrite

7. A 2 – carbon alkene is treated with HBr to produce P. The compound P further reacts with alc. $NaNO_2$ to produce a compound Q. Compounds P and Q probably are;
   a. Bromoethane and nitroethane
   b. Bromoethane and aminoethane
   c. Bromoethane and ethylnitrite
   d. Chloroethane and ethylnitrite

8. Ethanol is treated with $SOCl_2$ to obtain an organic compound A. The compound A reaction with alc. $AgNO_2$ gives B. Further, compound B yields compound C on heating with Sn/HCl. The compounds A, B and C respectively are;
   a. Chloroethane, nitroethane and ethanenitrile
   b. Chloroethane, aminoethane and nitroethane
   c. Chloroethane, nitroethane and ethanamide
   d. Chloroethane, nitroethane and aminoethane

9. Propene reacts with HBr in presence of peroxides to produce X. The compound X is treated with alc. $AgNO_2$ to give Y. The compound Y on heating with Zn/H_2O yields Z. The compounds X, Y and Z probably are;
   a. 1-bromopropane, 1-nitropropane and propylhydroxylamine
   b. 1-bromopropane, 1-nitropropane and 1-aminopropane
   c. 2-bromopropane, 2-nitropropane and 2-aminopropane
   d. 2-bromopropane, 2-nitropropane and propylhydroxylamine

10. Nitroethane undergoes reduction to produce ethylhydroxylamine. The reagents with which this reduction can be achieved is/are;
    a. Both Zn/H_2O and Ni or Pt
    b. Zn/H_2O
    c. Sn/HCl
    d. Both Sn/HCl and Ni or Pt

*****This is not a complete note. It is just to guide you. It is recommended to study the prescribed textbooks along with this material. *****