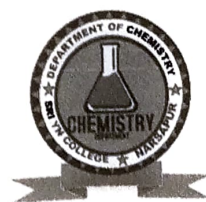




STUDENT STUDY PROJECT

2018-2019



Title of the project: **NITROALKANES**

Submitted by:

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NITROALKANES

INTRODUCTION:

Due to different tautomeric forms of nitrous acid ($\text{H} - \text{O} - \text{N} = \text{O}$ $\text{H} - \text{N} = \text{O}$) two kinds of Alkyl derivatives are formed, e.g. $\text{R} - \text{O} - \text{NO}$ (alkyl nitrites) and $\text{R} - \text{NO}_2$ (nitro alkanes). They are functional isomers.

Alkyl nitrites may be considered as esters of nitrous acid with alcohols.

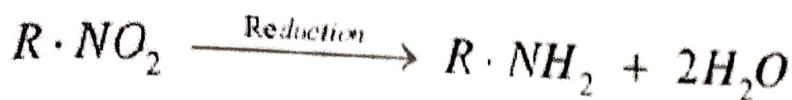
While nitro alkanes may be considered as nitro derivatives of alkanes.

The reaction which most clearly indicates their respective structures is reduction.

When alkyl nitrites are reduced, an alcohol and ammonia or hydroxylamine is formed. This Shows that the alkyl group in nitrites is attached to an oxygen atom

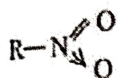


On the other hand, when nitroalkanes are reduced, a primary amine is formed. This shows that the alkyl group is attached to the nitrogen atom, since the structure of a primary amine is $\text{R} - \text{NH}_2$

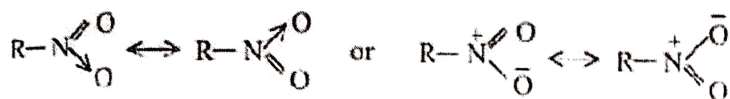


STRUCTURE :

The structure of the nitro-compounds is depicted as follows:



The dipole moments, however, indicate that they are resonance hybrids as follows:



From the Molecular Orbital point of view, the nitro-group is conjugated and delocalization of bonds increases its stability (the two oxygen atoms are equivalent just like the two oxygen atoms of the carboxylate ion ($--COO^-$)).

NOMENCLATURE OF NITROALKANES :

The name of any nitro compound is derived by adding the prefix nitro to the name of corresponding alkane or the arene. Aliphatic nitro compounds are called nitroalkanes or nitroparaffins, aromatic nitro compounds are called nitroarenes.

The positions of nitro group and other substituents, if any, on the parent nitroalkane or the nitro arene are indicated

by arabic numbers, i.e., 1,2,3,...etc. with the carbon atom bearing the nitro group getting the lowest possible number.

Examples:-

- CH_3NO_2 -Nitromethane
- $\text{CH}_3\text{CH}_2\text{NO}_2$ -Nitroethane
- $\text{CH}_3\text{CH}_2\text{NO}_2$ -1-Nitropropane
- $\text{CH}_3\text{CH}(\text{NO}_2)\text{CH}_3$ - 2-Nitropropane

CLASSIFICATION OF NITROALKANES :

There are three types of nitroalkanes. They are,

- 1.Primary nitroalkanes
- 2.secondary nitroalkanes
- 3.Tertiary nitroalkanes

1.Primary Nitroalkanes: The nitro group is attached to a primary carbon atom.

Example: RCH_2NO_2

2.Secondary Nitroalkanes: The nitro group is attached to a secondary carbon atom.

Example: R_2CHNO_2

3.Tertiary Nitroalkanes: The nitro group is attached to a tertiary carbon atom

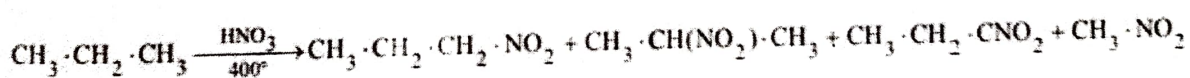
Example: R3CNO2

Preparation of Nitroalkanes:

1. By direct nitration of alkanes : Two techniques are used:

(a) Liquid-phase nitration : The hydrocarbon is heated with concentrated nitric acid under pressure at 140° . This is a slow reaction and a large amount of polynitro-compounds is also produced. Unlike for the aromatic hydrocarbons, the nitrating mixture (mixture of Nitric and sulphuric acid) is not suitable for nitrating alkanes.

(b) Vapour-phase nitration: The hydrocarbon is heated with nitric acid (or with oxides of nitrogen) at $150 - 475^{\circ}\text{C}$; (the temperature varies for different hydrocarbon). Here, the nitro derivatives of the smaller hydrocarbon, in addition to the nitro derivative of the starting one, are also formed. For example, propane on vapour phase nitration gives 1-Nitropropane, 2-nitropropane, nitroethane and nitromethane.

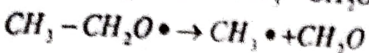
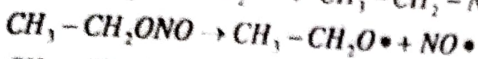
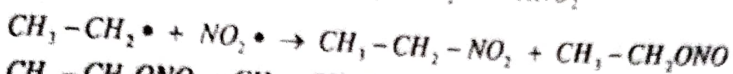


Out of the two nitration techniques, Vapour-phase nitration is more satisfactory than liquid-phase nitration.

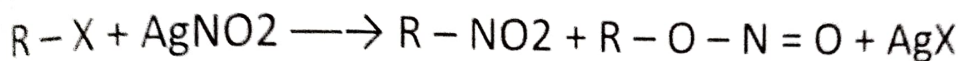
General rules of vapour phase nitration of alkanes (and cycloalkanes), as given by Hass and Shechter (1947):

- i. Polynitro compounds are formed only from alkanes of fairly high molecular weight. Smaller alkanes give mainly mono-nitro alkanes.
- ii. The ease of replacement of the hydrogen atom by nitro group is: Tertiary hydrogen > secondary hydrogen > primary hydrogen. At higher temperature, however, the ease of replacement is almost equal.
- iii. An alkyl group present in the alkane can also be replaced by a nitro-group, i.e, chain fission takes place. For example, isopentane yields nine nitroparaffins. The fission reaction increases as the temperature rises.
- iv. Oxidation always accompanies nitration, resulting in the formation of nitro-compounds and a mixture of acids, aldehydes, ketones, alcohols, nitrites, nitroso-compounds, nitro-Olefins, polymers, carbon monoxide and carbon dioxide. Catalysts such as copper, iron, Platinum oxide, etc., accelerate oxidation rather than nitration.

mechanism: proceeds by a free radical mechanism

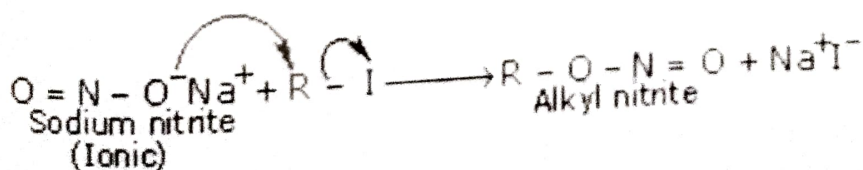
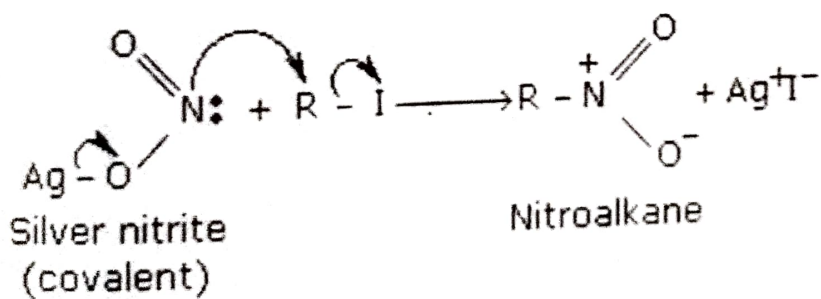


2. From alkyl halides: By heating an alkyl halide with silver nitrite in aqueous ethanolic solution.



Explanation: This reaction is an example of a nucleophilic substitution reaction.

Nitrite ion ($\text{O}^- - \text{N} = \text{O}$) is an ambident nucleophile, since, it has two sites through which it can attack the alkyl halide and attach through nitrogen to give nitro alkanes whereas through oxygen gives nitrites. i.e.,



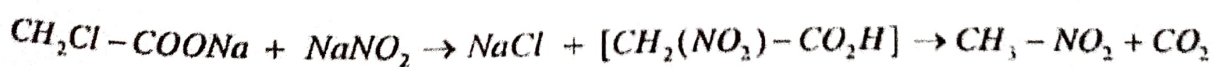
Alkali metal nitrites are ionic compounds, therefore, NaNO_2 , or KNO_2 attacks chiefly through negative charge on the oxygen to form alkyl nitrites. In contrast, silver nitrite is covalent compound and, hence, the more nucleophilic nitrogen through its lone pair of electrons attacks and as a result, nitro compounds are formed as major products.

This method is only useful for the preparation of primary nitroalkanes. With the secondary halides the yield is very low, and with tertiary halides even lower.

This method has been modified by Kornblum et al for the synthesis of primary and secondary Nitro-compounds. Here, the alkyl halide is reacted with sodium nitrite in the presence of dimethyl formamide as solvent, and urea which increases the solubility of sodium nitrite. Here, Nitro alkanes are obtained (55 – 62 %) together with alkyl nitrites (25 – 33 %).

Alkyl bromides and iodides are most satisfactory; the chlorides react too slowly to be useful.

3. From halogeno-acetic acid: Nitromethane is prepared by boiling an aqueous solution of Sodium nitrite with sodium salt of halogeno acetic acid. E.g.,



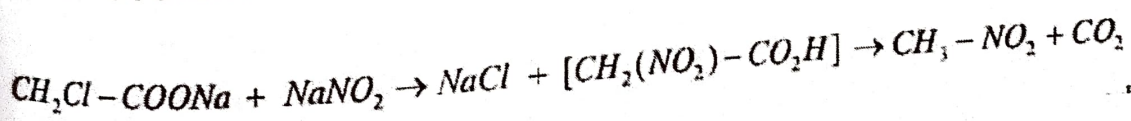
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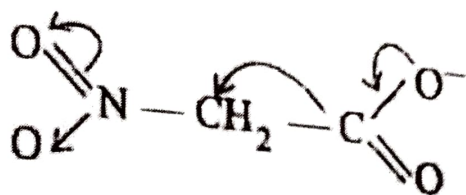
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Initially, an unstable intermediate nitro acetic acid is formed, which readily decarboxylates to give nitromethane. The loss of carbon dioxide is facilitated by the electron withdrawing nitro group.



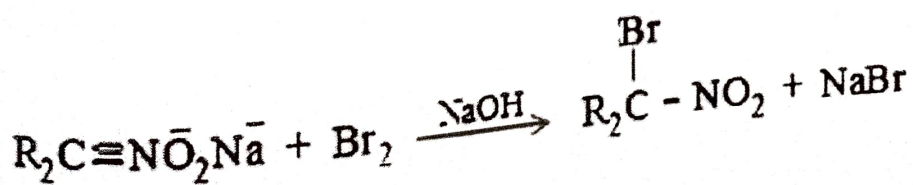
This method, however, cannot be used for preparing higher nitroalkanes.

4. From α -nitro alkenes: By the hydrolysis of α -nitroalkenes with water, acid or alkali, e.g., 2-Methyl-1-nitroprop-1-ene gives acetone and nitromethane in almost quantitative yield.



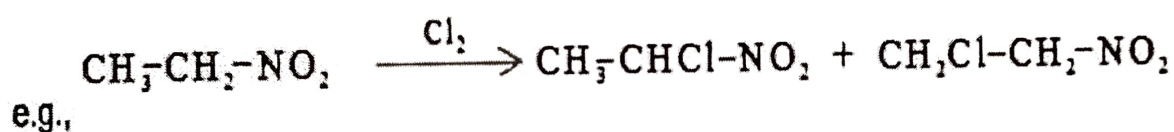
Chemical reactions of Nitro alkanes:

1. Halogenation: When primary and secondary nitroalkanes are reacted with halogen in the presence of base, α -halogenation takes place.



Primary nitro-alkanes can form the mono- as well as dibromo-derivatives, but the secondary nitroalkanes form only the monobromo derivative. Nitromethane can form the tribromo-derivative. The trichloro-derivative of nitro methane is called chloropicrin.

When liquid or gaseous nitro-compounds are treated with halogen in the absence of alkali, then all the α -, β -, γ -, halogeno-nitroalkanes are formed.



2.Reaction with Nitrous acid: Nitro-compounds react with nitrous acid, the product formed depending on the nature of the alkyl group.

Primary nitro-alkanes form nitrolic acids, which dissolve in sodium hydroxide to give red Solutions.



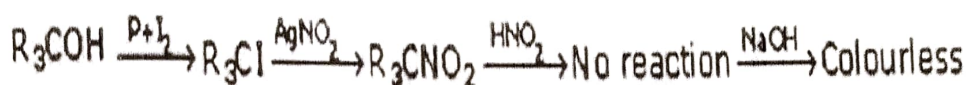
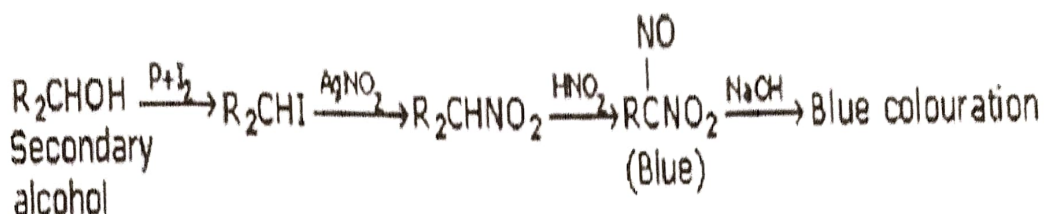
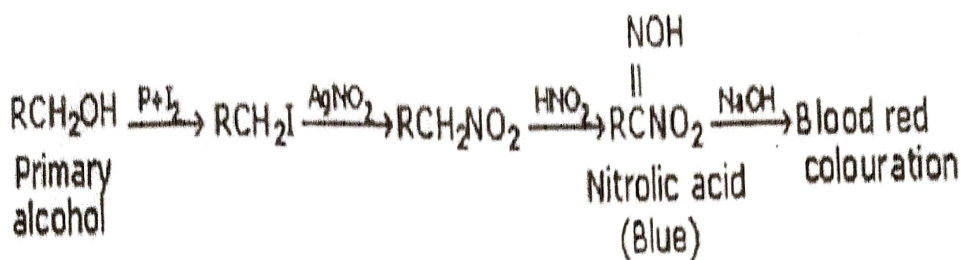
Secondary nitro-alkanes form pseudonitroles; which are blue in colour. (the blue colour is Probably due to the presence of the nitroso-group).



Tertiary nitro-alkanes do not react with nitrous acid since they have no α -hydrogen atom.

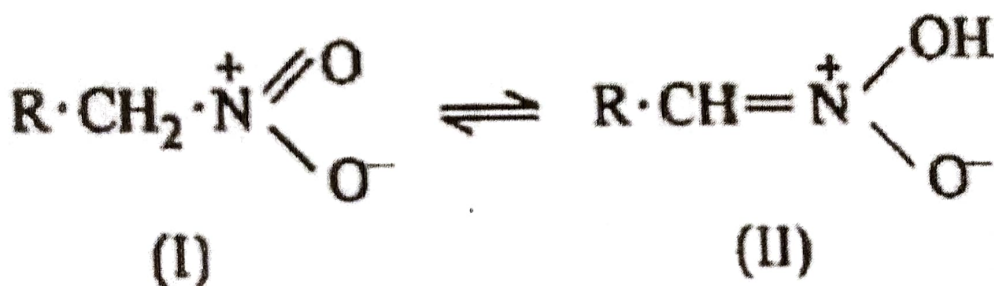
These reactions with nitrous acid are the basis of the 'red, white and blue' test for the differentiation between different monohydric alcohols (Victor Meyer Test). In this test,

- a) Treat alcohol with P + I₂ to get alkyl iodide.
 - b) Alkyl iodide is then converted to nitroalkane by treating with AgNO₂.
 - c) The nitroalkane is treated with HNO₂ (NaNO₂ + HCl).
 - d) Finally, the solution is made alkaline with aqueous NaOH (or KOH) solution.
- A blood red colouration indicates primary alcohol.
 - A blue colouration indicates secondary alcohol.
 - Colourless solution indicates tertiary alcohol.



3. Salt formation with bases: These nitro-compounds dissolve in aqueous sodium hydroxide to form salts.

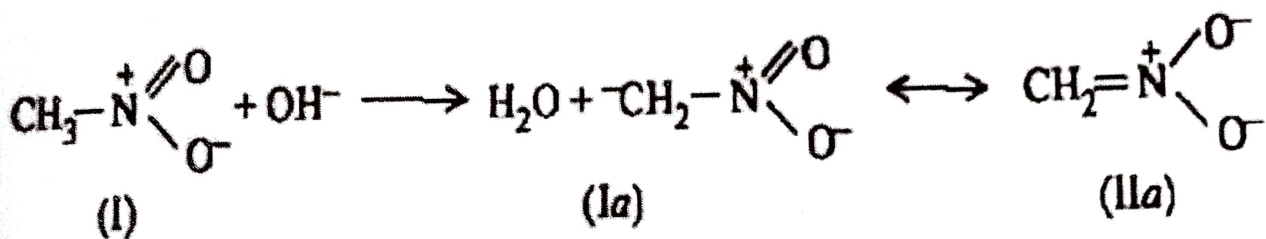
Explanation: Primary and secondary nitro-compounds, i.e., those containing α -hydrogen atoms, exhibit tautomerism.



The nitro-form (I) is also known the pseudo-acid form; (II) is known as the aci-form or nitronic acid.

This is called the nitro-acinitro system of tautomerism. The equilibrium is almost completely on the left, as the nitro-form is more stable due to resonance.

In the formation of salt, the hydroxide ion removes the α -hydrogen atom from the nitro form. The removal of the proton is made possible by the strong $-I$ effect of the nitro-group and the resulting anion is resonance stabilised.



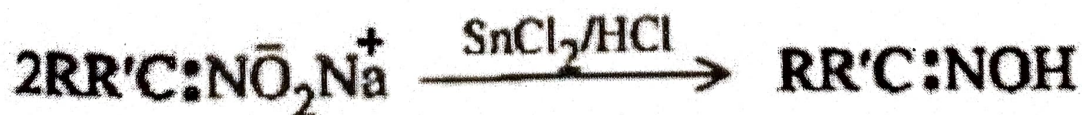
Reactions of sodium salt of nitro alkanes:

- a. When the sodium salt is acidified at low temperature, there is a slow formation of Yellow oily nitro-form.
- b. When the sodium salt solution is acidified with 50 % sulphuric acid at room temperature, an aldehyde (from a primary nitro-compound) and a ketone (from a secondary nitro-compound) is obtained.

E.g. (R' is either an alkyl group or a hydrogen atom):



- c. When treated with stannous chloride and hydrochloric acid, the sodium salt of the nitronic acid is reduced to the aldoxime or ketoxime :



These oximes can be readily converted into the parent carbonyl compound by steam Distillation or by direct hydrolysis with acid.

4. Mannich Reaction: Primary and secondary nitro-compounds undergo this reaction. This is the condensation between formaldehyde, ammonia or a primary or secondary amine (preferably as the hydrochloride), and a compound containing at least one active hydrogen atom.

In this reaction, the active hydrogen atom is replaced by an amino-methyl group or substituted amino-methyl group:

