

Nitro Compounds

Nitro compounds are characterized by the presence of nitro group (-NO₂) in their molecules. They may be aliphatic or aromatic compounds according to whether the nitro group is attached to alkyl or aryl groups.

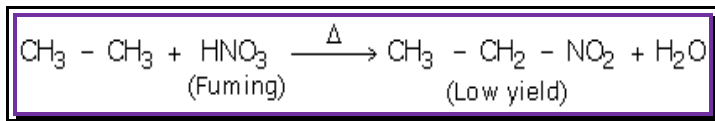
1. Aliphatic nitro compounds R - NO₂
2. Aromatic nitro compound Ar - NO₂

The aliphatic nitro compounds may be further classified into primary, secondary or tertiary nitro compounds according as the nitro group is attached to primary, secondary or tertiary carbon atom respectively.

❖ Preparation of aliphatic nitro compounds

A. Vapour phase nitration of alkanes:

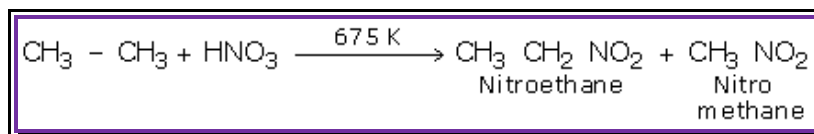
Hydrocarbons when heated with forming nitric acid at 693 - 793 K, are converted to nitro alkenes. Nitration of methane end lower members can be carried out by this nitration technique.



This direct nitration of alkanes is relatively more difficult in comparison to the nitration of arenes. Hence this method has no significance as a laboratory method but may be of commercial importance in the bulk production of small nitro alkanes

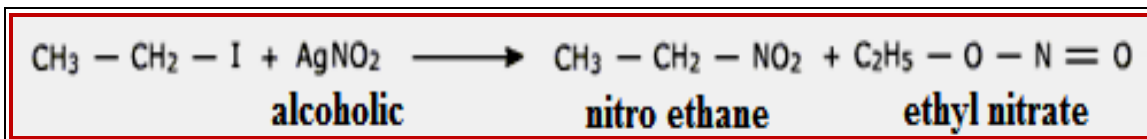
Since the process occurs at high temperature therefore, C - C bond of alkanes also undergo cleavage at this temperature and a mixture of nitro alkanes are formed.

For e.g.,



B. Treatment of alkyl halides with alcoholic silver nitrate:

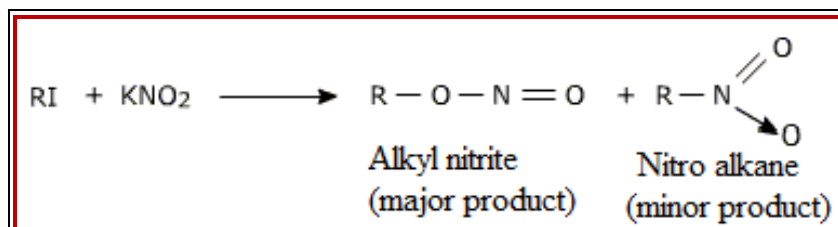
Alkanes (iodo) on treatment with alcoholic AgNO_2 give 80% of nitroalkanes and 20% alkyl nitrites.



This method is primarily used to prepare primary nitro compounds. Secondary and tertiary halides give major proportion of alkenes due to β -elimination reaction.

Hence 2° and 3° nitro alkenes are not prepared by this method.

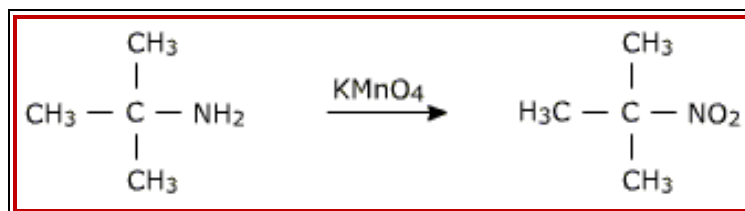
When alkyl bromides or iodides are treated with potassium nitrites, the major product is alkyl nitrite with nitro alkanes as the minor product.



Even NaNO_2 or KNO_2 give a fairly good yield (60%) of nitro compound if the reaction is carried out in solvents like dimethyl formamide (DMF) or dimethyl sulfoxide (DMSO).

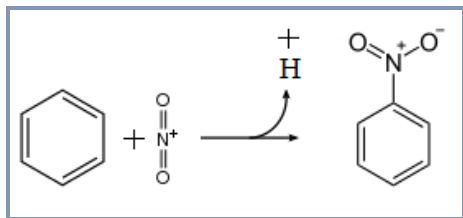
C. Oxidation of t-alkyl amines with KMnO_4 :

In this reaction, the amine must be primary and $-\text{NH}_2$ group should be attached to a tertiary carbon.

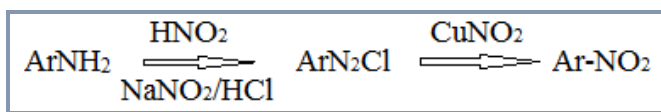


❖ Preparation of Aromatic nitro compounds:

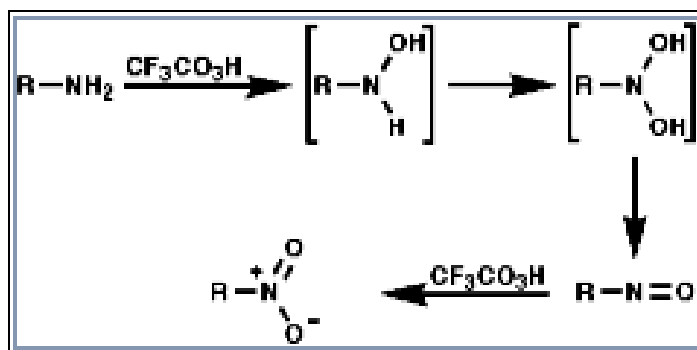
- A. Aromatic nitro compounds are typically synthesized by nitration. Nitration is achieved using a mixture of nitric acid and sulfuric acid, which produce the nitronium ion (NO_2^+), which act as an electrophile



- B. Displacement of the diazonium group by CuNO_2 leads to nitroarenes (the **Sandmeyer reaction**):



- C. Nitro compounds can be produced by oxidation of amine by peracids



As the nitro group is strongly electron withdrawing and shows affinity with the $\text{C}=\text{O}$ group. An anion is easily formed with base and stabilised by resonance as nitronate anion.

Nitro methane, MeNO_2 , have a pK_a of 10.2. So in order to remove the proton of nitro alkane an appropriate base is required.

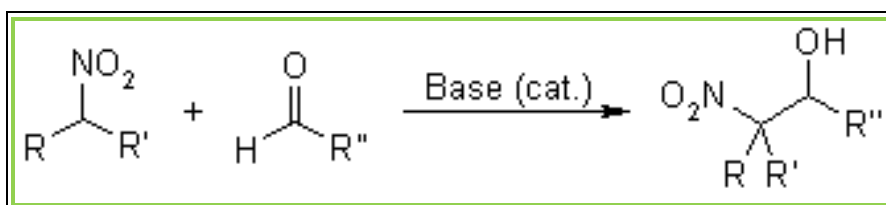
As the nitronate ion is delocalized, it is a soft nucleophile and reacts as stabilized, soft, carbanion.

❖ Reaction

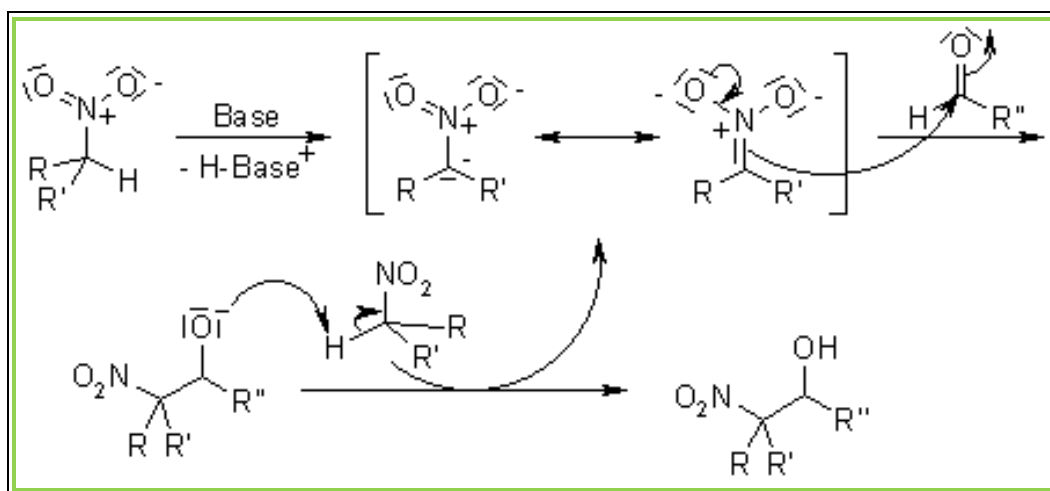
A. Alkylation:



B. Henry Reaction: This reaction is analogous to the Aldol reaction;

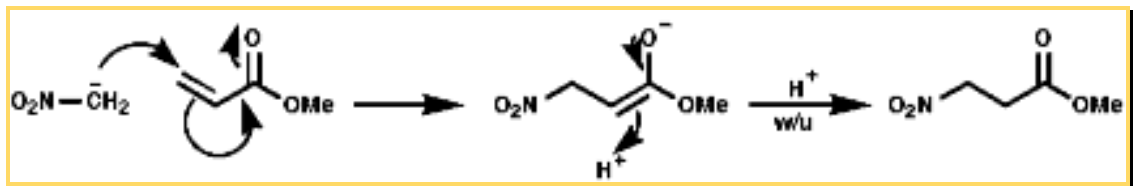


Mechanism:



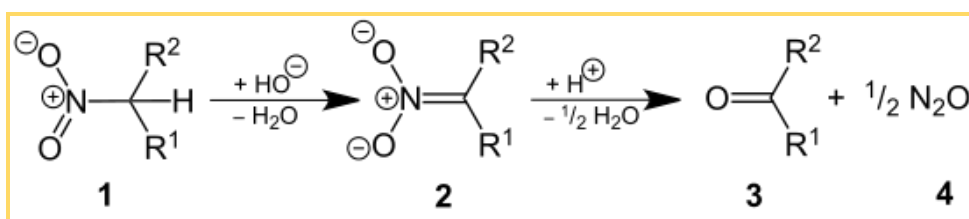
C. Michael Additions

The Michael addition is a conjugate addition of nitronate ion to the double bond of α,β -unsaturated carbonyl compound as double bonded C atom is the soft centre and the carbonyl carbon being the hard centre. It proceeds by the following mechanism;

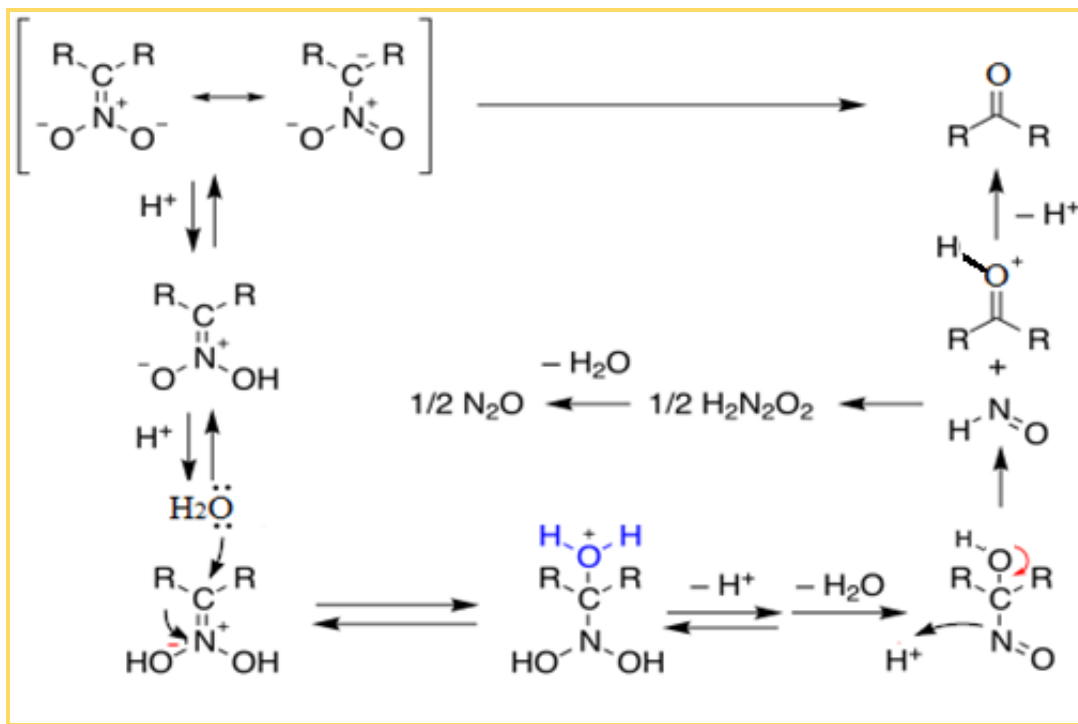


D. Nef reaction

The Nef reaction is an organic reaction describing the acid hydrolysis of a salt of a primary or secondary nitroalkane (**1**) to an aldehyde or a ketone (**3**) and nitrous oxide (**4**). The ambident behaviour can be seen in the Nef reaction.

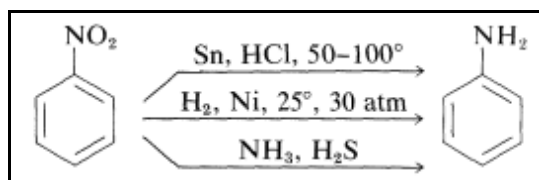


Mechanism:

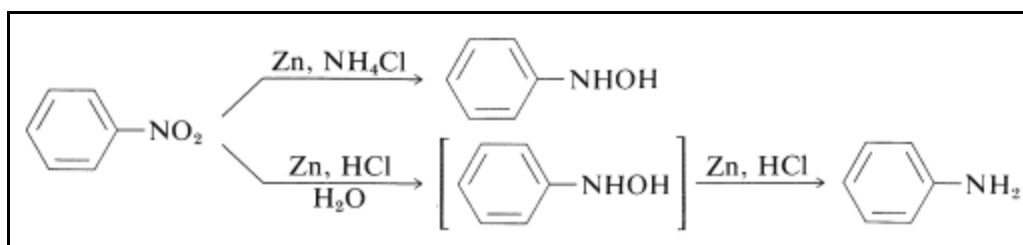


E. Reduction:

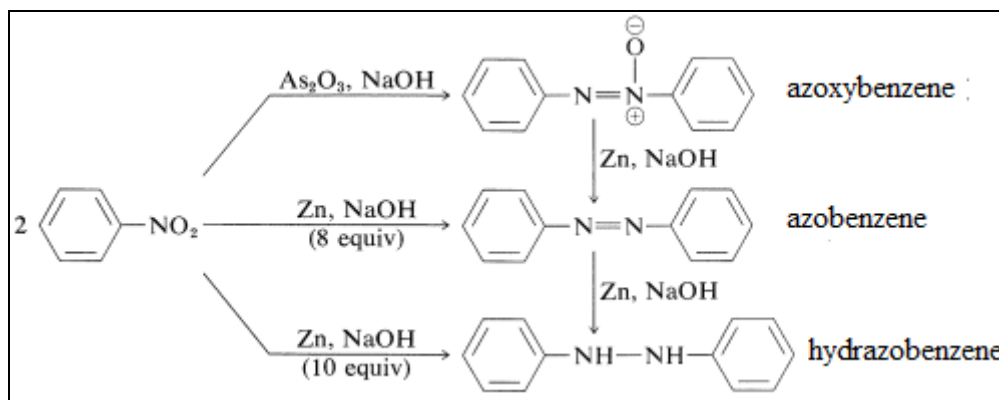
Reduction of nitro compounds occurs readily with a variety of reducing agents and such reductions afford a particularly useful synthesis of aromatic amines



Thus N-aryl-substituted azanols can be obtained directly from the corresponding nitro compounds with zinc and ammonium chloride solution. However, zinc and hydrochloric acid gives the amine.



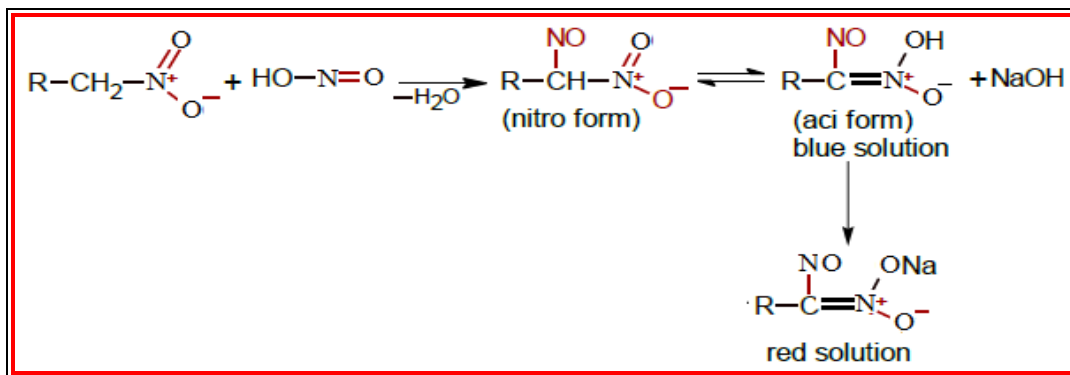
Reduction of aryl nitro compounds with less-powerful reducing agents, especially in alkaline media, gives what may appear to be a mysterious conglomerate of bimolecular reduction products. For example with nitrobenzene,



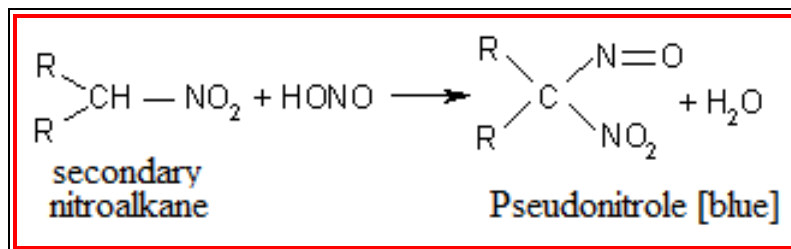
F. Reaction with nitrous acid:

Primary, secondary & tertiary nitroalkanes react in different way with nitrous acid.

a) **Primary nitroalkanes** react with nitrous acid to give blue solution of nitroso-nitroalkane (aci form) & dissolve in sodium hydroxide to give red solution.



b) Secondary nitroalkanes react with nitrous acid to give blue solution of nitroso-nitroalkane (pseudo aci form) & not dissolve in sodium hydroxide due to absence of α -hydrogen atom.



c) Tertiary nitroalkanes does not react with nitrous acid due to absence of α -hydrogen atom.