

Study Material: 4

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Discipline- B.Sc (H)

Subject- Chemistry

Semester- IV

Course Code- CC10

Topic- Organic Chemistry, Nitrogen Compounds

ORGANIC COMPOUNDS OF NITROGENS:

:Aliphatic Nitro Compounds:

Nitro alkanes are named by prefixing ‘nitro’ to the name of the parent hydrocarbon e.g.

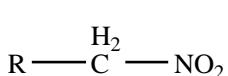


Nitroethane

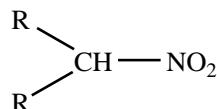


Nitropropane

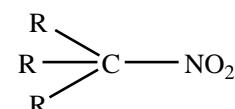
They may be primary, secondary or tertiary according to the fact whether nitro group is attached to a primary, secondary or tertiary carbon atom.



Primary nitro compound



Secondary nitro compound



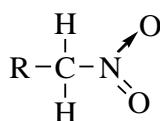
Tertiary nitro compound

- Isomerism:**

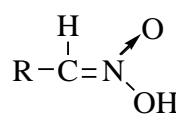
Chain Isomerism	Position Isomerism	Functional Isomerism
$\begin{array}{c} \text{H}_2 & \text{H}_2 \\ & \\ \text{H}_3\text{C} - \text{C} - \text{C} - \text{NO}_2 \\ & \\ & \text{H}_2 \end{array}$ 1-Nitrobutane	$\begin{array}{c} \text{H}_2 \\ \\ \text{H}_3\text{C} - \text{C} - \text{C} - \text{NO}_2 \\ \\ \text{H}_2 \end{array}$ 1-Nitropropane	$\begin{array}{c} \text{O} \\ \\ \text{H}_3\text{C} - \text{C} - \text{N}^+ - \text{O}^- \\ \\ \text{H}_2 \end{array}$ Nitroethane
$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C} - \text{CH} - \text{C} - \text{NO}_2 \\ \\ \text{H}_2 \end{array}$ 2-Methyl-1-nitropropane	$\begin{array}{c} \text{NO}_2 \\ \\ \text{H}_3\text{C} - \text{CH} - \text{CH}_3 \end{array}$ 2-Nitropropane	$\begin{array}{c} \text{H}_3\text{C} - \text{C} - \text{O} - \text{N} = \text{O} \\ \\ \text{H}_2 \end{array}$ Nitrosooxyethane

- Tautomerism:**

Primary and secondary nitro compounds also exist in following tautomeric forms. The acidic character is due to tautomerism. Primary and secondary nitro alkanes are weakly acidic (k_a for nitromethane is 6×10^{-11} and for nitroethane it is 3.5×10^{-9}), but tertiary nitro alkanes are neutral.



Nitro form

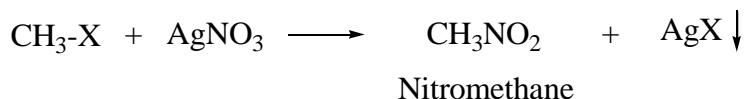


Aci-Nitro form

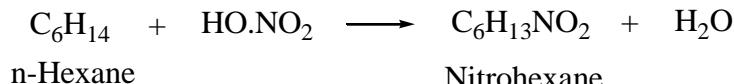
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- General methods of preparation of nitroalkanes:

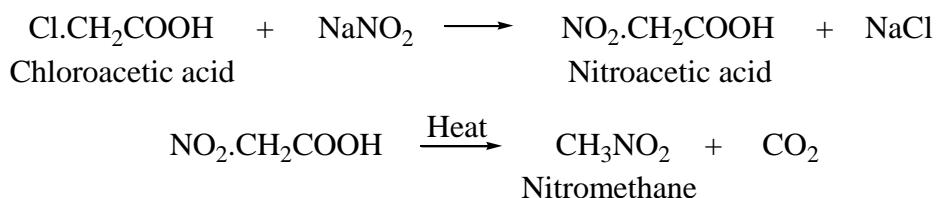
1. **From alkyl halides:**



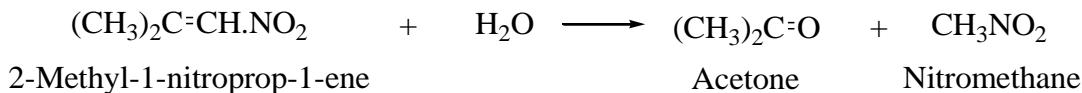
2. **By direct nitration of paraffins:**



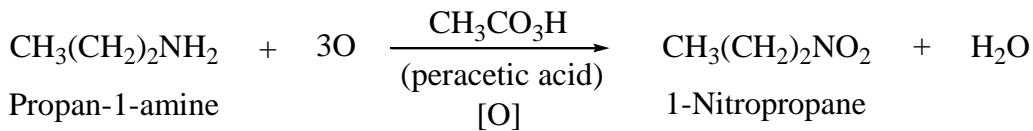
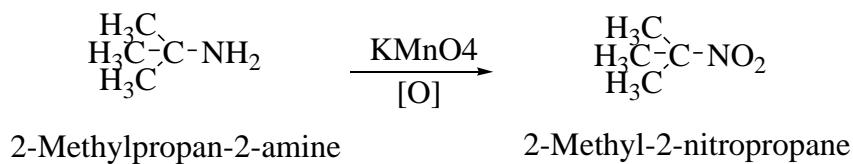
3. **From halo acids:**



4. **By hydrolysis of α -nitro olefins:**

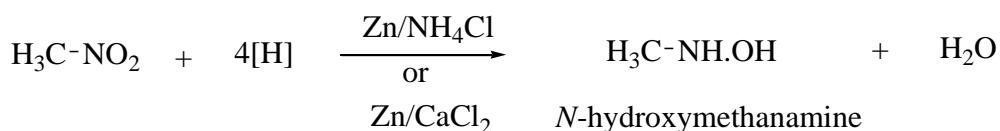
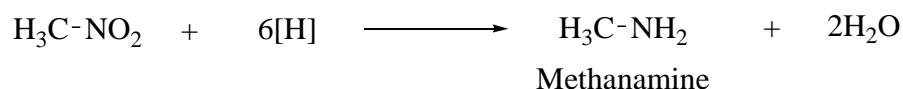


5. **From *tert.* carbinamines:**

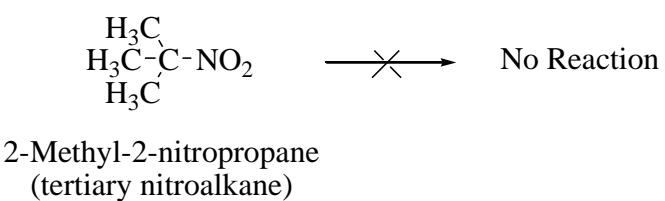
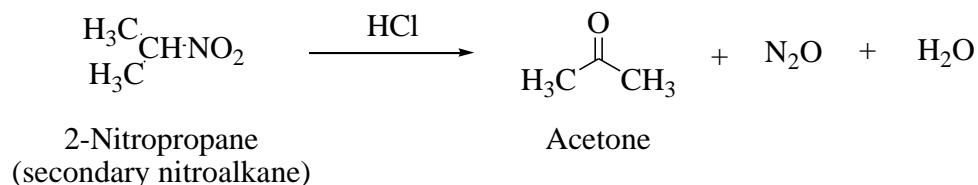
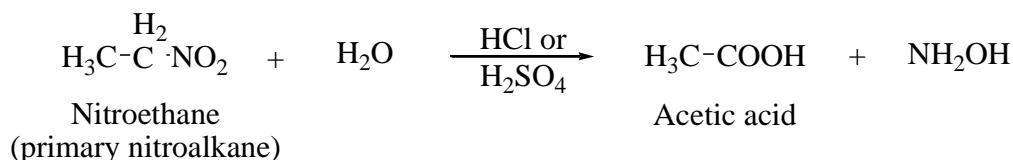


• Reaction of Nitro alkanes:

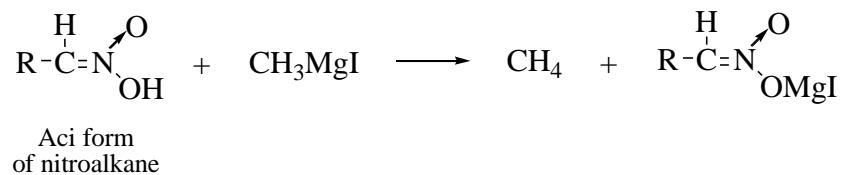
1. Reduction:



2. Hydrolysis:

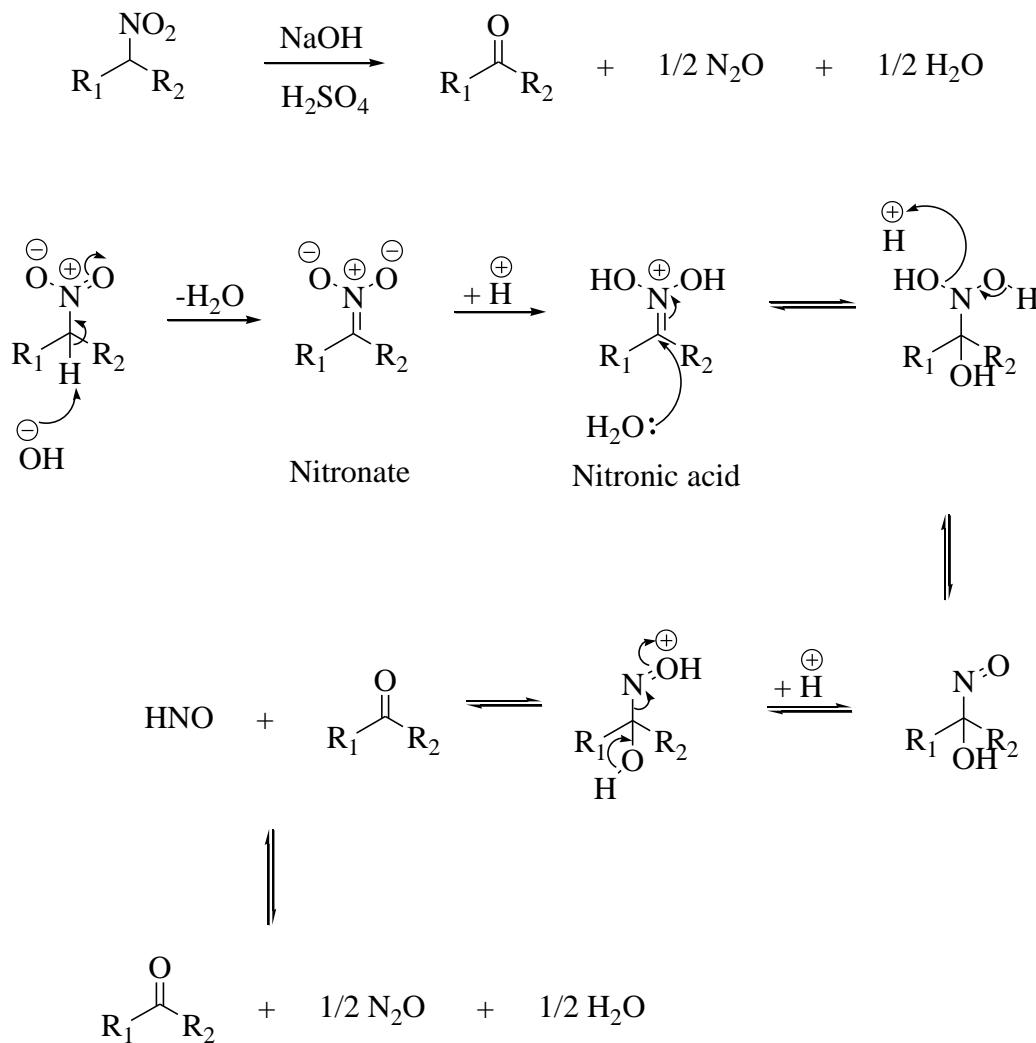


3. Reaction with Grignard Reagent:

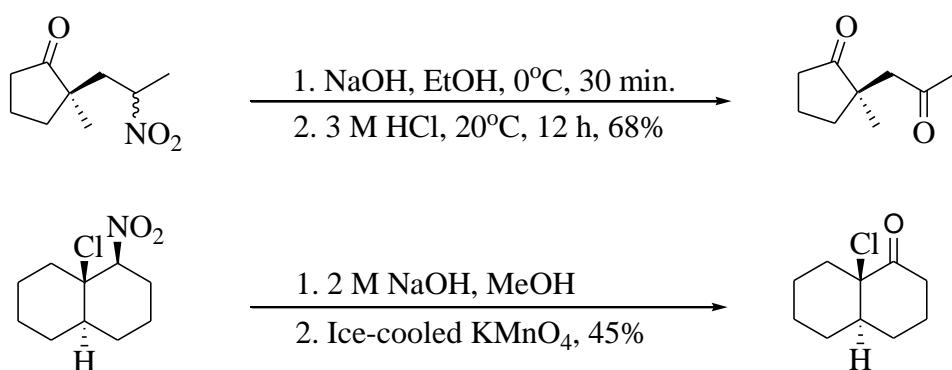


4. Nef Carbonyl Synthesis:

Conversion of a primary or secondary nitro alkane into corresponding carbonyl compound.

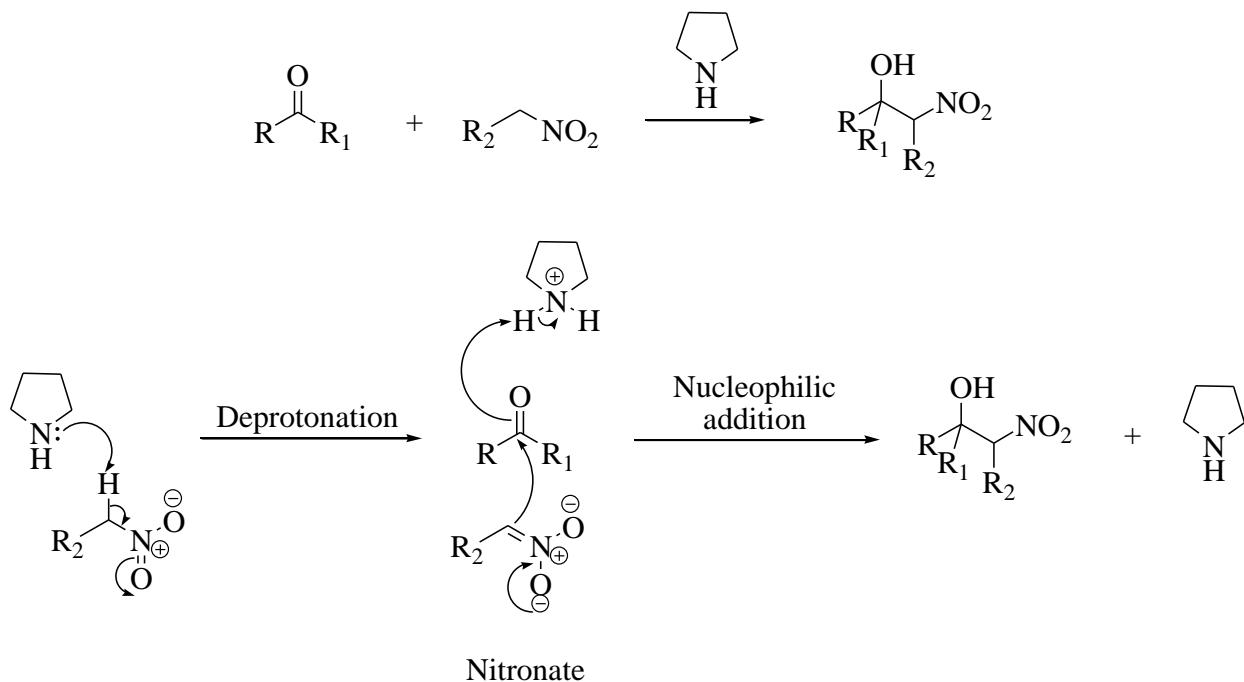


Examples:

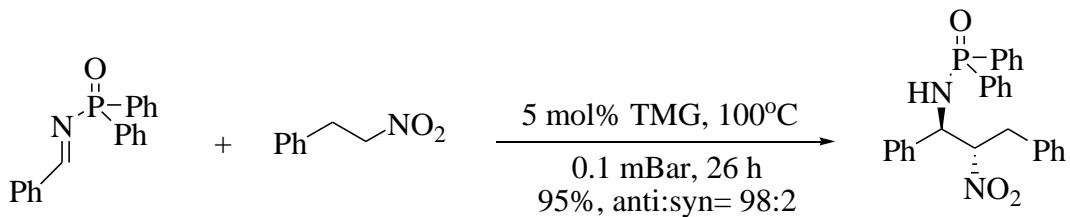
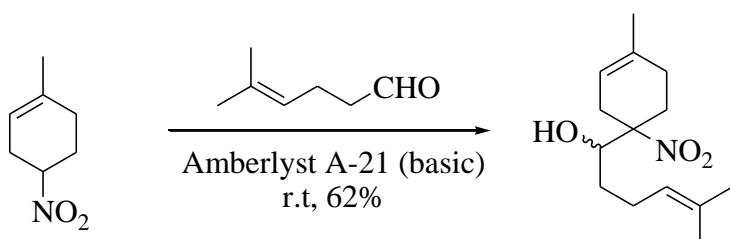


5. Henry nitroaldol reaction:

The nitroaldol condensation reaction involving aldehydes and nitronates, derived from deprotonation of nitro alkanes by bases.

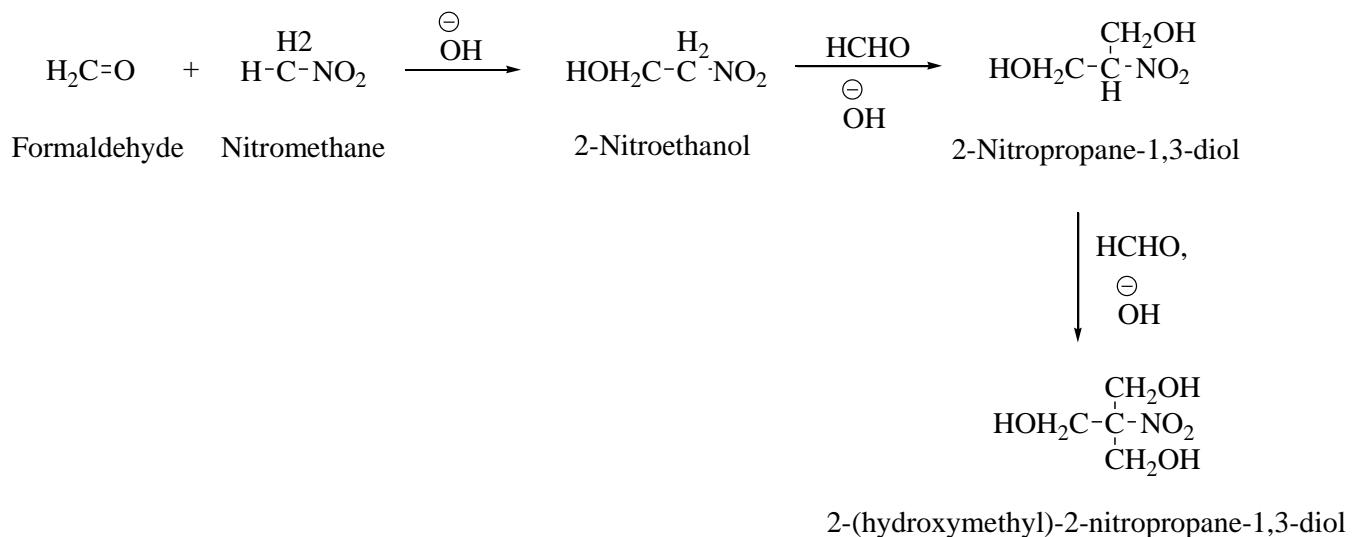


Examples:

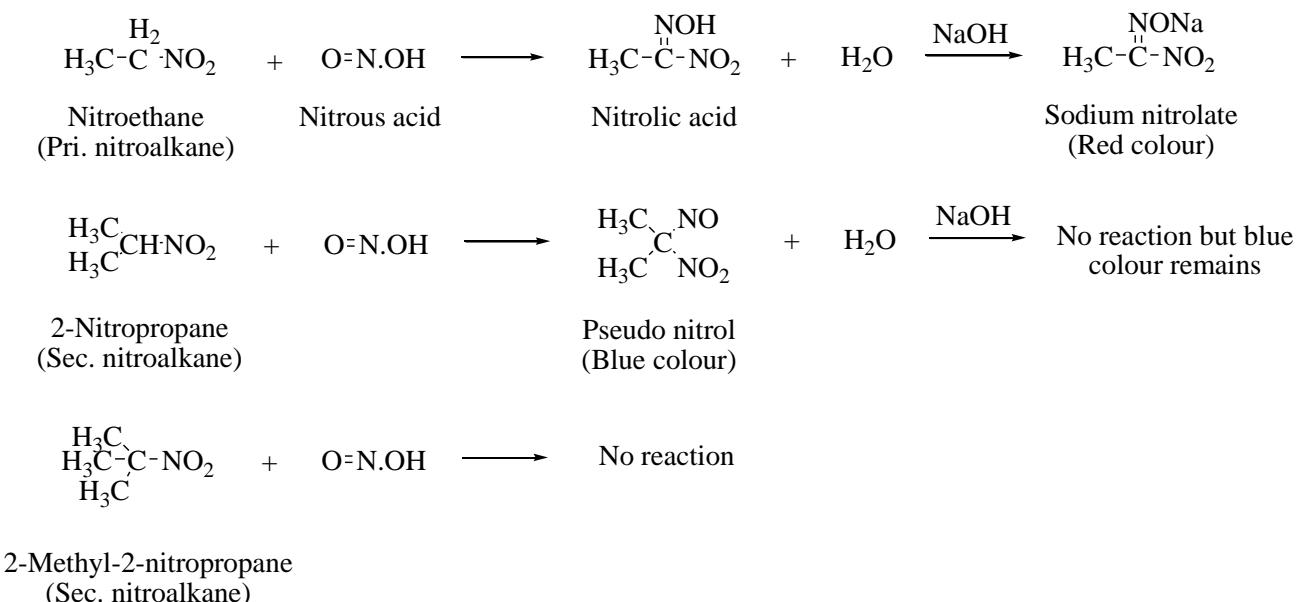


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6. Condensation with aldehyde:



7. Reaction with nitrous acid:



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8. Halogenation:

