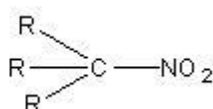
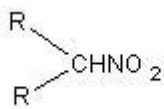
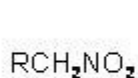


Nitro and Cyno Compounds

Nitro alkanes are derivatives of alkanes. They are isomeric to nitrites (esters) classified as primary, secondary and tertiary depending on the nature of carbon atom to which nitro group is linked.



Primary nitro alkane

Secondary Nitro alkane

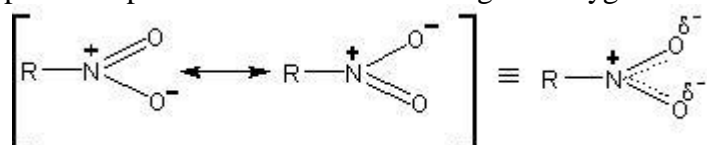
Tertiary nitro alkane

—NO₂ group is an ambident group. If it attacks through nitrogen. It is called nitro and if it attacks through oxygen atom, it is called nitrite. Hence nitrites and nitro compounds are isomers.

Ambident nucleophiles:

Nucleophiles which can attack from two sites such as CN⁻, NO₂⁻ are called ambident nucleophiles

Evidences show that nitrogen is attached to one of the oxygen atoms by a double bond and to the other by a dative bond. The resonance hybrid is shown as under which confirms the spectroscopic evidence that both nitrogen – oxygen bonds have same bond length.



Resonating forms

Hybrid structure

Out of three hybrid orbitals of nitrogen one overlaps with alkyl group and two with oxygens while the unhybridized p orbital of N – atom containing a pair of electrons and lying perpendicular to the plane of hybrid orbitals overlaps sideways with half filled 2p – orbitals of two oxygen atoms. This forms π-bond above and below the plane of molecule.

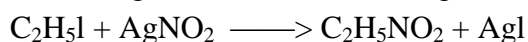
Preparation of Nitro Compounds

(i) From alkyl halides:

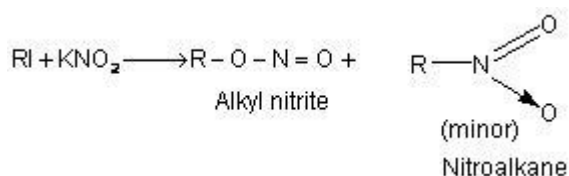
Alkyl halides react with silver nitrite in ethanolic solution to give nitro compounds. Alkyl nitrite is formed in minor quantity. This reaction is used to prepare 1° nitro compounds primarily while 2° and 3° halides give major proportion of alkenes due to β – elimination. Contrary to this alkali nitrites give alkyl nitrites as major product. This is due to ionic nature of alkali nitrite.

But if the reaction is carried out in solvents like DMF or DMSO, then even NaNO₂ or KNO₂ give good yield (about 60%) of nitro compound.

Reactions:

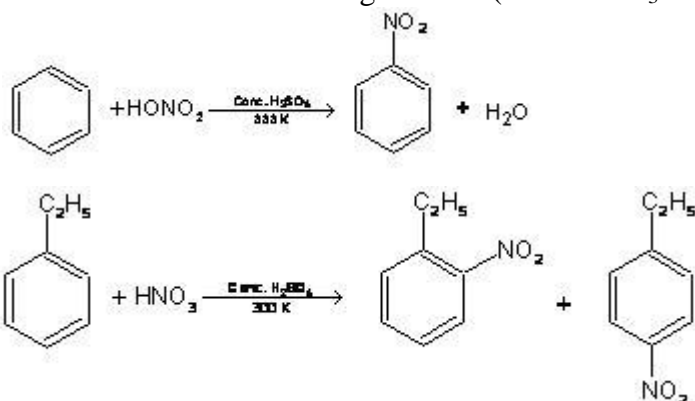


Nitroethane



(ii) Nitration:

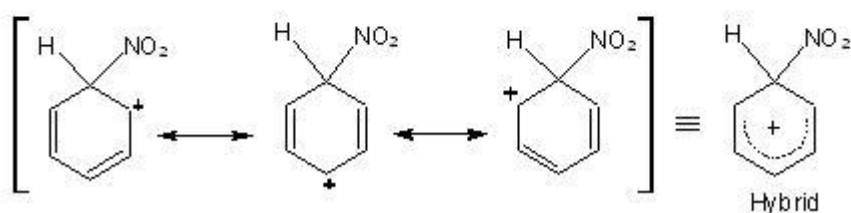
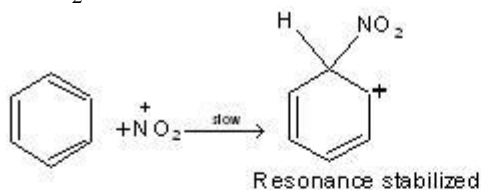
Nitro derivatives of aromatic compounds like nitrobenzene are produced when benzene is allowed to react with nitrating mixture. (conc. HNO_3 /conc. H_2SO_4).



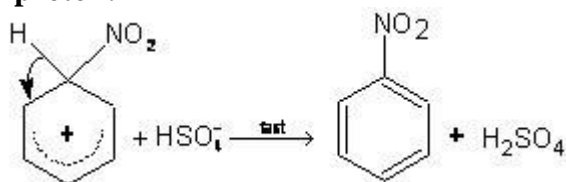
Mechanism:

Generation of nitronium ion

Attack of NO_2^+ on benzene molecule

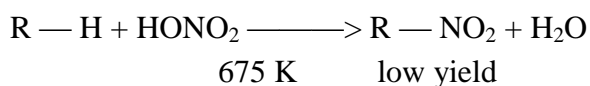


Loss of proton:



Nitrobenzene

Direct nitration of alkane involves vapour phase nitration at high temperature.

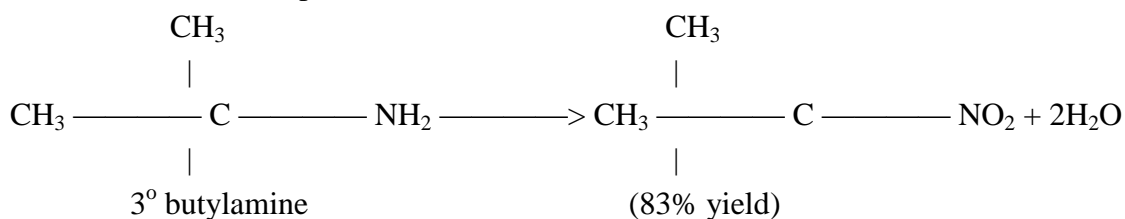


Problem faced in the method is that at such high temperature, a mixture of nitro alkanes is formed due to C – C cleavage.

e.g. $\text{CH}_3\text{CH}_2\text{CH}_3 + \text{HNO}_3 \longrightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{NO}_2 + \text{CH}_3\text{CH}_2\text{NO}_2 + \text{CH}_3\text{NH}_2 + \text{other products}$

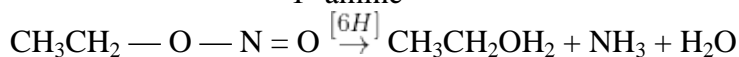
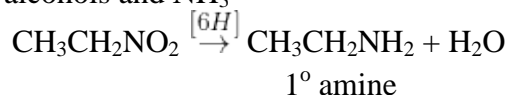
(iii) From amines:

3° nitroalkanes can be produced as follows:



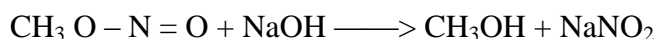
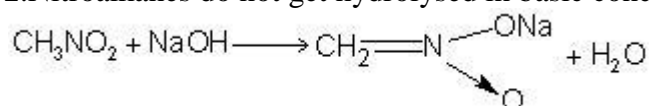
Distinguish test between nitroalkanes and alkyl nitrites

1. Nitroalkane on reduction with H_2/Ni produce 1° amines while alkyl nitrites produce alcohols and NH_3



Ethyl nitrite

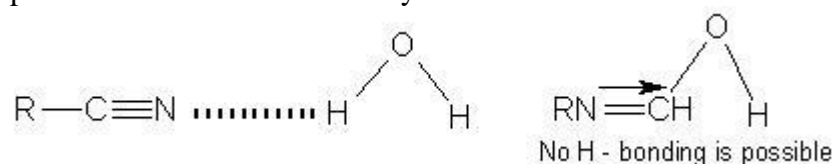
2. Nitroalkanes do not get hydrolysed in basic conditions while nitrites produce alcohols



Cyanides and Isocyanides

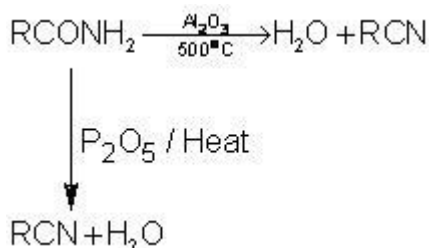
Both alkyl cyanides (RCN) and alkyl isocyanides (RNC) are organic derivatives of

hydrocyanic acid HCN. Alkali cyanides are ionic $\left(: \text{C} \equiv \text{N}^- : \right)$ and cyanide ion is ambident in nature (can form covalent bond either from carbon or nitrogen). $\text{AgC} \equiv \text{N}$ is covalent, hence lone pair on nitrogen is mainly available for covalent bond formation, resulting in predominant formation of isocyanides.

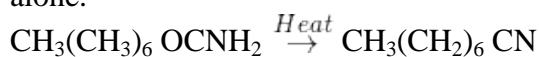


Methods of preparation of Cyanides

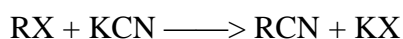
1. Dehydration of Amides:



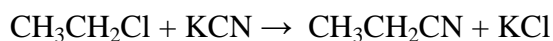
High molecular weight acid amides are dehydrated to the corresponding cyanide by heat alone.



2. From RX:



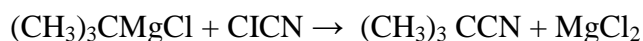
This method is satisfactory only if R is 1° or 2° group. If it is 3° group, then it is converted into alkene.



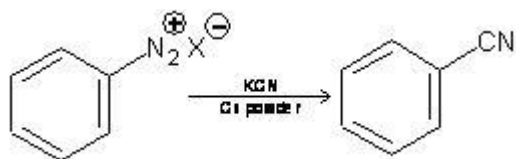
3. By Grignard's reagent and Cyanogen chloride reaction:



This is best method for preparing 3° alkyl cyanides.

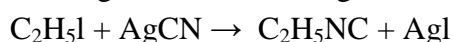
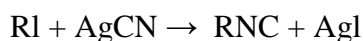


4. From Diazonium salt



Methods of Preparation of Isocyanides

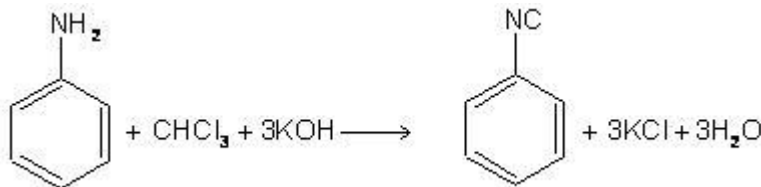
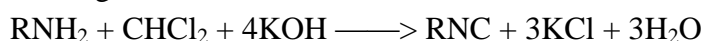
1. By heating an alkyl iodide with AgCN in aqueous ethanolic solution



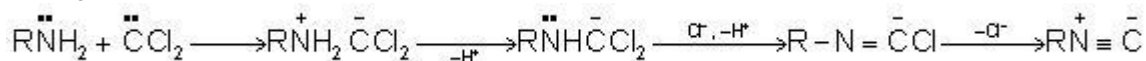
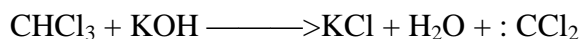
Ethylisocyanide

2. By carbylamine reaction

Heating a mixture of 1° amine and chloroform with ethanolic potassium hydroxide



Mechanism proceeds via intermediate formation of dichloromethylene or, dichloro carbene produced from chloroform in alkaline solution. (Via α-elimination)



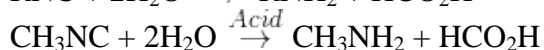
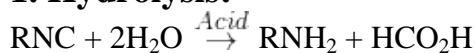
Properties of Isocyanides

1. Alkyl isocyanides are poisonous, unpleasant smelling, with lower boiling points than isomeric cyanides.

2. RNC are not very soluble in water, nitrogen atom not having a lone pair of electrons available for hydrogen bonding.

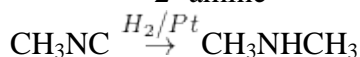
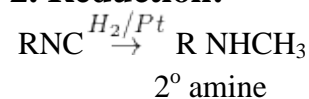
Reactions:

1. Hydrolysis:



RNC are not hydrolysed by alkalis.

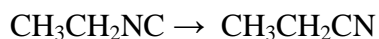
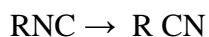
2. Reduction:



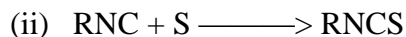
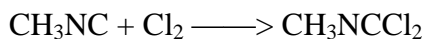
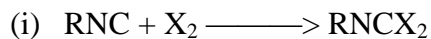
Methyl isocyanide Dimethyl amine

3. Rearrangement:

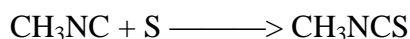
When alkyl isocyanides are heated for a long time, they arrange to form cyanide



4. Reaction with non metals:

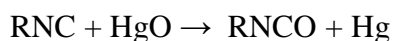


Alkyl isothiocyanates



5. Oxidation:

with HgO:



Alkyl isocyanates

