☐ Chemical reactions of nitro alkane :

I] Reduction :

Nitro alkanes are reduced to corresponding 1^0 – amines in presence of tin (Sn) / Iron (Fe) and conc. HCl or $LiAlH_4$ or when catalytic hydrogenation is carried out

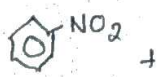
(A)

- $R - NO_2 + 6[H] \xrightarrow{Sn\ /\ conc.\ HCl} R - NH_2 + 2H_2O$

  1^0 — amine

$C_2H_5NO_2 + 6[H] \xrightarrow{Sn\ /\ conc.\ HCl} C_2H_5 - NH_2 + 2H_2O$

Nitro ethane — Ethyl amine

(*)  $+ 6[H] \xrightarrow{Sn/conc.\ HCl}$  $+ 2H_2O$

(aniline) / (phenyl amine)

(B)

- **Niro alkanes are converted into N—alkyl hydroxyl amine when the reduction is carried out in neutral medium with a metal.**

$R - NO_2 + 4[H] \xrightarrow[H_2O]{Zn\ /\ NH_4Cl} R - NH - OH + H_2O$

N – alkyl hydroxyl amine

$C_2H_5 - NO_2 + 4[H] \xrightarrow{Zn/NH_4Cl} C_2H_5 - NH - OH + H_2O$

N-ethyl hydroxyl amine.

(C)

- **Nitro alkanes are converted into N—alkyl hydroxyl amine and oxime when stannous chloride and HCl are used as reducing agent.**

$CH_3 - CH_2 - NO_2 \xrightarrow[HCl]{SnCl_2} CH_3CH_2 - NH - OH + CH_3 - CH = N - OH$

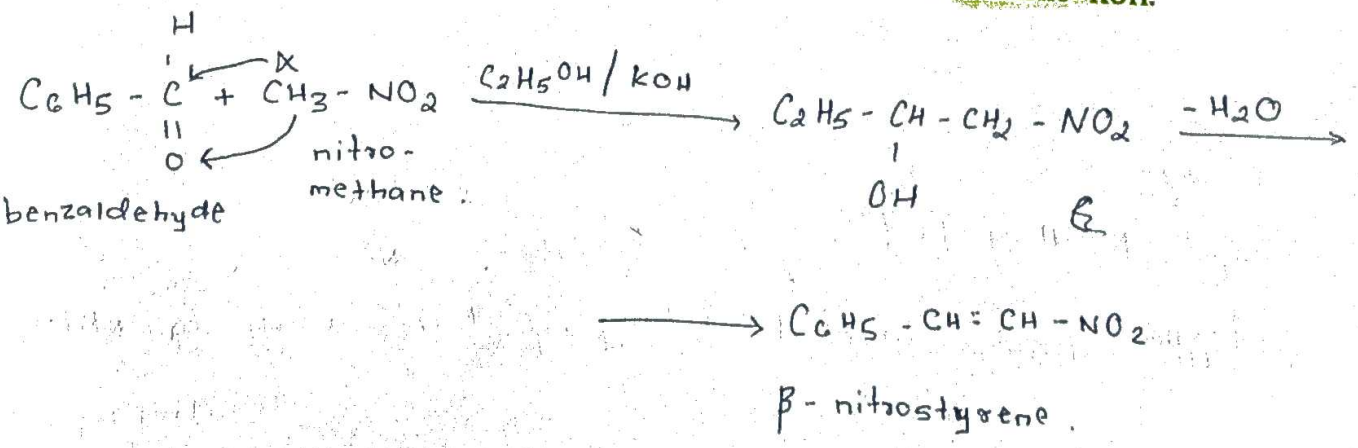
acetyldoxime

N-ethyl hydroxyl amine.

(*)

II] Condensation with aldehydes and ketones :

- It is similar to aldol condensation.
- 1^0 and 2^0 nitro alkanes contain ∝— hydrogen atom ∴ undergo condensation with aldehydes or ketones in presence of ethanolic KOH.



III] Hydrolysis :

- 1^0 nitro alkanes on boiling with HCl or H_2SO_4 undergo hydrolysis to form **carboxylic acid and hydroxyl amine.**

$$\underset{1^0\text{—nitro alkane}}{R-CH_2-NO_2} + H_2O \xrightarrow[H_2SO_4]{HCl \text{ or } \Delta} \underset{\text{acid}}{R-\overset{\overset{O}{\|}}{C}-OH} + \underset{\text{hydroxyl amine}}{H_2N-OH}$$

$$\underset{\text{nitro ethane}}{CH_3-CH_2-NO_2} + H_2O \xrightarrow[H_2SO_4]{\Delta} \underset{\text{acetic acid}}{CH_3-\overset{\overset{O}{\|}}{C}-OH} + \underset{\text{hydroxyl amine}}{H_2N-OH}$$

- 2^0 **nitroalkanes on boiling with HCl form ketone and nitrous oxide.**

$$2\,R-\underset{\underset{R}{|}}{CH}-NO_2 \xrightarrow[\Delta]{HCl} 2\,R-\underset{\underset{R}{|}}{C}=O + N_2O + H_2O$$

2^0 – nitro alkane → ketone; nitrous Oxide

$$2\,CH_3-\underset{\underset{CH_3}{|}}{CH}-NO_2 \xrightarrow[\Delta]{HCl} 2\,CH_3-\underset{\underset{CH_3}{|}}{C}=O + N_2O + H_2O$$

- 3^0 – nitro alkane does not react with HCl.

☐ Nef carbonyl synthesis :

- 1^0 and 2^0 nitroalkanes containing α – hydrogen atom show tautomerism.
- These nitroalkanes dissolve in aqueous NaOH to form salts.
- When the solution of sodium salt of aciform is acidified with 50% H_2SO_4 at room temperature then an aldehyde or ketone is obtained.

1^0 nitro alkane ⟶ aldehyde

2^0 nitro alkane ⟶ ketone

- Sodium salt of 1^0 nitro alkane in aci form.

$$2\,R-\underset{\underset{H}{|}}{C}=\overset{\oplus}{N}\begin{matrix}\diagup\,ONa \\ \diagdown\,O^-\end{matrix} + 2\,H_2SO_4 \xrightarrow{50\%} 2\,R-\underset{\underset{H}{|}}{C}=O + N_2O + 2\,NaHSO_4 + H_2O$$

aldehyde

$$2\,CH_3-\underset{\underset{H}{|}}{C}=\overset{\oplus}{N}\begin{matrix}\diagup\,ONa \\ \diagdown\,O^-\end{matrix} + 2\,H_2SO_4 \longrightarrow 2\,CH_3-\overset{\overset{O}{\|}}{C}-H + N_2O + 2\,NaHSO_4 + H_2O$$

acetaldehyde

sodium salt of aciform of 1° - nitro ethene

II] Basic nature of amines :-

- It is due to the presence of lone pair of electrons on nitrogen atom of amine which can be donated for bonding.
- With acid it accepts a proton to form a salt indicating their basic nature.

$$R-\ddot{N}H_2 + H^+ \longrightarrow R-\overset{\oplus}{N}H_3$$

$$R-\ddot{N}H_2 + HCl \longrightarrow \underset{\text{Protonated amine}}{R-\overset{\oplus}{N}H_3\ \overset{\ominus}{Cl}}$$

Eg. (1) $CH_3-\ddot{N}H_2 + HCl \longrightarrow \underset{\text{Alkyl ammonium chloride}}{CH_3-\overset{\oplus}{N}H_3\ \overset{\ominus}{Cl}}$

Eg (2) $C_2H_5-\ddot{N}H_2 + HNO_3 \longrightarrow \underset{\text{Ethyl ammonium nitrate}}{\underset{\text{Methyl ammonium chloride}}{C_2H_5-\overset{\oplus}{N}H_3\ \overset{\ominus}{NO_3}}}$

$2\,C_2H_5-\ddot{N}H_2 + H_2SO_4 \longrightarrow \underset{\text{Ethylammonium sulphate}}{\left[C_2H_5-\overset{\oplus}{N}H_3\right]_2SO_4^{--}}$

$2\,C_2H_5-\ddot{N}H-C_2H_5 + H_2SO_4 \longrightarrow \underset{\text{Diethyl ammonium sulphate}}{\left[C_2H_5-\overset{\oplus}{N}H_2-C_2H_5\right]_2SO_4^{--}}$

$CH_3-\ddot{N}(CH_3)-CH_3 + HCl \longrightarrow \underset{\text{Dimethyl ammonium chloride}}{CH_3-\overset{\oplus}{N}H(CH_3)_2\ \overset{\ominus}{Cl}}$

- Amines are neucleophilic.
- Amines are lewis bases as well as they are lowry – bronsted base.

Aniline → anilinium chloride or phenyl ammonium chloride

Q. Aqueous solution of amine is weak base

$$R-\ddot{N}H_2 + H-OH \rightleftharpoons R-\overset{\oplus}{N}H_3 + OH^-$$

- In amines nitrogen atom contains a lone pair of e⁻s which can be donated for bonding.
- When amine is treated with water, above equilibrium is observed because of reversible reaction.
- This aqueous solution contains free OH^- ions.
- ∴ According to Arhenius theory, amines are basic in nature.
- As conc. of free OH^- ions is low (equilibrium shift to LHS), the aqueous solution of amine is weak base.